

RAPRA
TECHNOLOGY LTD.

Rubber Basics

Edited by
R.B. Simpson

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Foreword

The Rubber Industry has a long history going back several hundred years and during its development the terminology used has not always been the most logical or descriptive. For example, Hancock described his masticator and mixing device as a 'Pickle' to avoid conveying any knowledge of what it did or how it worked.

As it carries the baggage of this considerable period of time, some new to the industry find it difficult to understand. With terms such as spew, mould dope, pig, drug room and cracking all having their own rubber-related meaning, it is little wonder that the industry is regarded by outsiders as a Black Art.

Consequently, this book has been compiled to be used as a quick reference. It includes a glossary of terms, tables of technical data, and, for those who require more detail, there are more comprehensive text sections covering the major rubber types, compounding ingredients and the equipment used in the most common processes.

It should prove useful to those coming into the Rubber Industry, those in other businesses who have to work with it, and as a reference document for the everyday practitioner.

R. B. Simpson

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Section 1

Glossary of Rubber Terms

1,1,3-Tributyl Thiourea
TBTU, accelerator.

1,3-Diethyl-2-Thiourea
DETU, accelerator.

1,3-Diphenyl-2-thiourea
DPTU, accelerator.

2,2'-Dihydroxy-5,5'-Dichloro-Diphenylmethane
DDM, latex auxiliary.

2-Mercaptobenzimidazole
MBI, antidegradant – non-staining.

2-(Morpholiniothio) benzothiazole
MBS, accelerator.

4,4'-Dithiodimorpholine
DTDM, vulcanising agent.

6-Ethoxy-2,2,4-Trimethyl-1,2-Dihydroquinoline
ETMQ, antidegradant – staining.

6PPD
N-1,3-Dimethylbutyl-*N'*-phenyl-*p*-phenylenediamine, antidegradant – staining.

77PD
N,N'-Bis(1,4-dimethylpentyl)-*p*-phenylenediamine, antidegradant – staining.

A

AAS
Atomic absorption spectroscopy.

Ablation
Literally 'removal', but applied particularly in space technology to the process of using up the frictional heat developed on re-entry of the vehicle into the Earth's atmosphere by degradation of the heat shield. Certain thermoplastics, thermosetting resins and polytetrafluoroethylene have been evaluated as ablative materials.

Abrasion Resistance
The ability of a rubber article to withstand wearing away in service. Standard BS 903: Part A9. Determination of abrasion resistance.

ABS
Abbreviation for acrylonitrile-butadiene-styrene, an amorphous thermoplastic.

Absolute Pressure
Pressure measured with respect to zero pressure. *See Gauge Pressure.*

Absolute Zero
Zero on the absolute or Kelvin scale of temperature; 0 K = -273 °C.

Absorption
The taking up of gases or liquids into solids. Absorption occurs throughout the whole mass of the absorbing medium, whereas adsorption is confined only to the surface.

Accumulator
A device for storing hydraulic pressure; in its simplest form it is a long vertical hydraulic cylinder, on top of the ram on which weights may be placed or suspended.

Acetylene
C₂H₂, a colourless poisonous flammable gas; the starting material for many organic compounds, e.g., chloroprene. *See Neoprene.*

ACM
An abbreviation for acrylic rubbers.

Accelerated Ageing (Air Oven)

This is carried out in a heated oven through which air is circulating; the temperature ranges from 70 °C to > 200 °C, depending on the base polymer and application. The temperature used should be the lowest that gives a measurable deterioration within a reasonable test period. Higher temperatures are likely to involve different ageing mechanisms and hence correlation with real ageing will be poor.

Accelerator

A compounding ingredient which speeds up the vulcanisation reaction, enabling it to take place in a shorter time or at a lower temperature or both; the physical properties of the vulcanisate and its resistance to ageing are also improved.

ACGIH

American Conference of Governmental Industrial Hygienists

ACN

Abbreviation for acrylonitrile.

ACOP

Approved Code of Practice (UK)

Acrylic Rubbers

Rubbers based on polymers of organic acrylates.

Acrylonitrile

CH₂CHCN (vinyl cyanide); raw material for the manufacture of nitrile rubber, synthetic fibres and plastics.

Acrylonitrile-Butadiene Rubber

See Nitrile Rubber.

Activator

A compounding ingredient that enables an accelerator to exercise its maximum effect. Inorganic activators are metallic oxides (such as zinc, lead and magnesium oxides) and organic activators are long-chain saturated fatty acids, e.g., stearic and oleic.

ADC

Azodicarbonamide, blowing agent.

ADCA

Abbreviation for azodicarbonamide.

Adhesives

Polymeric materials are commonly used for bonding materials. Impact or contact adhesives are mainly based on highly crystalline polychloroprene (Neoprene), NR latex is used as a flexible adhesive very suitable for use with fabrics. Rigid adhesives based on materials such as polystyrene cement, epoxy resin or cyanoacrylates are suitable for bonding of rigid materials. The bond is provided by intermolecular forces between the adhesive and the adherend.

Adiabatic

Taking place without gain or loss of heat.

ADPA

Acetone-diphenylamine condensation product, antidegradant – staining.

ADS

Abbreviation for air-dried sheets of rubber.

Adsorption

The taking up of molecules of a gas or of a dissolved substance by the surface of a solid; adsorption is a surface effect only. *See Absorption.*

AEM

Abbreviation for ethylene-acrylic terpolymer.

Aftercure

In the vulcanisation of rubber products, aftercure is the amount of cure received after the termination of the cure proper, e.g., the cure effect resulting from the heat remaining in the product after removal from the mould or autoclave. The term is also applied to the continuation of the curing effect that results from exposure of the article to heat in use, or from accelerated ageing. *See Post Cure.*

Ageing

The deterioration of the physical properties of rubber products when exposed to service conditions; also the controlled exposure of rubber samples to a variety of deteriorating influences in the evaluation of antioxidants and antiozonants. *See Accelerated Ageing.*

Air Oven Ageing

See Accelerated Ageing.

Air Spring

An inflatable bellows used in a pneumatic suspension system for motor transport; irrespective of load the centre of gravity of the vehicle can be maintained at a constant height above ground level with appropriate control systems.

Alcohols

A family of organic compounds obtained by removing one or more -H atoms from a paraffin and substituting the hydroxyl radical -OH. The best-known alcohols are ethyl alcohol (ethanol) and methyl alcohol (methanol). Glycerine is a trihydric alcohol.

Allotropy

Many elements including sulphur, carbon and oxygen can exist in two or more forms with different physical, and often chemical, properties; such elements are said to exhibit allotropy and the different forms are known as allotropes or allotropic forms.

Alumina

Aluminium hydroxide, inorganic filler.

Aluminium Hydroxide

Alumina, inorganic filler.

Ammonium Polyphosphate

AP, flame retardant.

Amorphous

Having no definite shape; non-crystalline.

Anatase

One of the crystalline forms of titanium dioxide.

Anisotropic

Describes a material that has different physical properties in different directions. *See Calender Grain.*

Anticoagulant

Any substance used to prevent premature coagulation of rubber latex; the commonest are ammonia, sodium sulphite and formaldehyde.

Antidegradant

A term applied to compounding ingredients, mainly antioxidants, which inhibit premature degradation of elastomers.

Antimony Trioxide

Flame retardant.

Antioxidant

An ingredient added to a rubber compound to protect the product against deterioration by

oxygen. Antioxidants belong to the class of compounding ingredients known as protective agents, and their mode of action is considered to be removal of free radicals which are generated by the interaction of oxygen and the polymer at elevated temperatures. Failure to remove these free radicals will result in an ongoing deterioration of the polymer.

Antiozonant

An ingredient added to rubber compounds to protect the product against the deteriorating influence of ozone. The function of antiozonants is not limited to protection against ozone attack, they also give a high level of protection against oxidative and thermal degradation, and against fatigue failure (flex cracking).

Antirad

A compounding ingredient added to elastomers to increase their resistance to ionising radiation.

Antistatic Rubber

Rubber so compounded as to produce a vulcanisate having an electrical resistivity of about 10^7 to 10^9 ohm-cm. *See Conductive Rubber.*

AP

Abbreviation for ammonium polyphosphate.

ASTM

Abbreviation for American Society for Testing and Materials.

Atactic

A term applied to high polymers which are irregular in their stereo configuration, i.e., which do not show stereoregularity.

Atomic Absorption Spectroscopy

This technique is used to detect metals in rubber analysis.

AU

Abbreviation for polyester type polyurethane rubbers.

Autoclave

A pressure vessel constructed of steel, used for the vulcanisation of rubber products by the 'open steam' method. The autoclave may be horizontal (vulcanisation of footwear, cables, hose), or vertical and fitted with a hydraulic ram (e.g., moulding pneumatic tyres).

AZDN

Azobis-isobutyronitrile, blowing agent.

Azobis-Isobutyronitrile

AZDN, blowing agent.

Azodicarbonamide

ADC, blowing agent.

B

BAA

Butyraldehyde-aniline condensation product, accelerator.

Back Rinding

Tearing or distortion of a moulded rubber product at the line of separation of the two mould halves (the spew line) due to the sudden release, on opening the mould, of the high pressures developed by the thermal expansion of the heated rubber; other names are suck back, flash back and retracted spew.

Band

- (1) A strip of rubber from a previous batch left running round the front roll of an open mill to facilitate loading of the next batch.
- (2) An assembly of plies of rubberised cord fabric used in 'building' or making; the casing of a pneumatic tyre.

Bank

- (1) On an open mill, the proportion of the mill load which runs in the space immediately adjacent to the nip between the rolls.
- (2) The amount of rubber compound running at the nip or nips of a calender during the operations of frictioning, sheeting, coating or profiling.

Balata

The hard thermoplastic hydrocarbon obtained from the latex of *Mimusops globosa*. Balata has the same molecular formula as natural rubber (C_5H_8)_n but has the *trans* polyisoprene structure whereas natural rubber has *cis*-structure.

Ball Mill

A cylindrical container half to two-thirds filled with a grinding charge consisting of unglazed porcelain, glass balls, pebbles or flint gravel; it is used in the preparation of aqueous dispersions of ingredients for use in the manufacture of products direct from latex.

Ballotini

A material used in fluid bed vulcanisation. It consists of very small spherical particles of glass of a narrow size distribution, approximately 0.1 to 0.2 mm.

Banbury Mixer

The type of internal mixer designed by F.H. Banbury; the name 'Banbury' is often erroneously applied to any type of internal mixer.

Barium Sulphate

See Barytes and Blanc Fixe.

Barrel

That part of an extruder in which the screw rotates.

Barwell Preformer/Ram Extruder

An apparatus for preparing moulding blanks. It is a development of the Barwell ram extruder which feeds through interchangeable dies to give the correct profile of blank, while an electronically operated cutter, working across the face of the die, cuts the blanks. Oil is admitted to the ram of the extruder in controlled quantities, set by a metering device, so that the compound is forced from the die in the correct amount to form each blank.

Barytes

Naturally occurring barium sulphate, BaSO₄; it has the high specific gravity of approximately 4.45 and is used as a filler, especially when a high specific gravity rubber compound is desired or is not a disadvantage. Is also used as an acid resistant white filler.

BCMA

British Colour Makers' Association

BCUP

Tert.-Butyl cumylperoxide, organic peroxide.

BDMC

Bismuth dimethyl dithiocarbamate, accelerator.

Bead

- (1) In a pneumatic tyre, that portion of the structure which holds the tyre on the wheel; it consists of a circular assembly of steel wires insulated with rubber, suitably wrapped and covered with rubberised fabric to enable the bead assembly to be built into the uncured casing.
- (2) In dipped goods, a reinforcing edge made by rolling back for a short distance the film of rubber deposited on the former.

Bead to Bead Remoulding

A tyre retreading process in which new rubber is applied as tread, on the tyre shoulders and on the tyre sidewalls.

Bentonite

A colloidal clay used as a thickener in latex compounding and as a filler in dry rubber compounding; the reaction of bentonite with amines has produced several useful rubber reinforcing fillers.

Benzene

C₆H₆, the simplest member of the aromatic series of hydrocarbons; it is a colourless liquid with b.p. of 80 °C and is used in the manufacture of many organic compounds.

Benzoyl Peroxide

A vulcanising agent particularly for silicone rubber and fluoroelastomers; it has been used as a non-sulphur vulcanising agent for natural rubber. It is also a catalyst in emulsion polymerisation.

Beta Rays

Streams of swiftly moving electrons given off by some radioactive substances; they are used in beta ray gauges which give continuous measurement of the thickness of films of rubber or plastics.

BgVV

Bundesinstituts für gesundheitlichen Verbraucherschutz und Veterinärmedizin, German body which sets legislation on compounding ingredients and migration testing for rubbers which come into contact with food.

BHT

Butylated hydroxytoluene, (2,6-Di-*tert.*-butyl-*p.*-cresol), antidegradant – non-staining.

Bias

In the manufacture of pneumatic tyres and some types of hose, the angle at which the textile material is cut with respect to the running edge of the fabric.

BIBRA

British Industrial Biological Research Association

BiDD

Bismuth dimethyl dithiocarbamate, accelerator.

BIIR

Abbreviation for bromobutyl rubber.

Biodeterioration

Deterioration of rubbers, fibres or plastics resulting from attack by living organisms.

Birefringence

The existence in a high polymer (elastomer, fibre or plastic) of two refractive indices. The ratio of the two indices is a measure of the crystallinity of the polymer.

Bismuth Dimethyl Dithiocarbamate

BDMC and BiDD, accelerator.

Bisphenol AF

2,2'-Bis(4-hydroxyphenyl)perfluoropropane, vulcanising agent.

Black

Abbreviation of carbon black.

Bladder

Another name for the inflatable diaphragm which takes the place of the curing bag in the automatic curing of pneumatic tyres in a diaphragm press.

Blanc Fixe

Precipitated barium sulphate.

Blank

A piece of uncured rubber compound of suitable shape and volume to fill the cavity of the mould in which it is to be vulcanised; also termed a 'slug'.

Blanket - Compressible

A printing blanket with a specially manufactured layer designed to 'give' or compress, under pressure from the printing plate and impression cylinder. Compressible blankets resist smashing and usually print a sharper halftone dot.

Blanket Crepe

A grade of natural rubber inferior to estate brown crepe and formerly known as thick remilled brown crepe; cuttings removed in the inspection of smoked sheet rubber are washed, creped and designated 'smoked blanket crepe'.

Bleaching Agent

A substance added to latex in the preparation of pale crepe rubber; sodium bisulphate prevents darkening of the crepe due to the presence of oxidising enzymes, xylyl mercaptan is an effective bleaching agent proper.

BLIC

Bureau de Liaison des Industries du Caoutchouc de L'Union Européenne.

Block Copolymer

A copolymer in which blocks of one polymer are inserted in a primary chain of the other or where the arrangement of the different monomers is not random but in distinct multiple monomer blocks.

Blocking

The tendency of sheets of rubber to stick together, dusting and anti-tack agents are used to overcome this problem.

Blooming

The formation on the surface of uncured or cured rubber of a thin coating of a compounding ingredient, often, but not necessarily, sulphur, which is present in excess of the amount which the rubber can dissolve.

Blowing Agent

Used in the manufacture of sponge rubber.

- (1) Chemical blowing agents undergo decomposition at the vulcanisation temperature to form a gaseous species such as nitrogen or carbon dioxide, e.g., azo compounds, nitroso compounds, sulphonyl hydrazide compounds, ammonium carbonate, ammonium bicarbonate and sodium bicarbonate.
- (2) Physical blowing agents are low boiling point organic compounds (e.g., dichloromethane or

pentane), which volatilise at the processing temperature.

Blow Moulding

A manufacturing method predominately used by the thermoplastic industry for the manufacture of hollow components, also used for thermosetting rubber. The polymer is forced against the inside of the mould surface by gas pressure applied either by a hollow needle or by the decomposition of a blowing agent.

BNPD

2-Bromo-2-nitropropane-1,3-diol, latex auxiliary.

Bound Rubber

The rubber in unvulcanised filler-rubber mixes which is insoluble in a usual rubber solvent.

Bonding Agent

A material used to promote the bonding of rubber to other materials, principally metal and textiles.

Bowl

Another name for a calender roll.

BPH

2,2'-Methylene-bis(4-methyl-6-*tert*-butylphenol), antidegradant – non-staining.

BPO

Dibenzoyl peroxide, organic peroxide.

BR

Abbreviation for rubber based on butadiene.

Brabender Plasti-Corder and Plastograph

An apparatus for the determination of the processibility of polymers. It measures cure rate, scorch characteristics, extrusion rate and similar properties. BRABENDER® single screw measuring extruders and Extrusiograph® are interchangeable measuring heads which, in connection with a Plasti-Corder® Lab-Station or Plastograph®, serve for testing the extrudability of polymers and for studying problems occurring in research and development as well as in practical application. The BRABENDER® modular system allows the complete instrumentation of the extruders for raw material checks and development. Manifold screws, die heads, and downstream equipment fulfil many kinds of extrusion tasks.

Braid Angle

Angle between the braid and the axis of the hose in fabric- or wire-braided hose.

Braided Fabric

A structure produced by interlacing several ends or yarns in a manner such that the paths of the yarns are not parallel to the fabric axis.

Braided Hose

Hose in which the textile or steel wire reinforcement is applied by a braiding method. The braiding may be applied to the hose, supported either horizontally or vertically.

Breakdown

The plasticising of raw rubber prior to the incorporation of compounding ingredients or the plasticising (warming or warming-up) of mixed compound prior to subsequent processing.

Breaker

- (1) In a pneumatic tyre, a strip or strips of textile or metallic fabric of more open construction than the casing fabric, placed circumferentially around the tyre underneath

the tread; in belting a similar fabric fitted as an outer ply.

(2) The term is also applied to a cracker mill.

British Standards Institution

The recognised body in the United Kingdom for the preparation of specifications for quality, performance or dimensions, methods of test, definitions and symbols, codes of practice, etc. British Standards are prepared under the guidance of representative committees and are widely circulated before they are authorised for publication. BSI co-operates in preparing international standards for rubber and plastics through ISO/TC45 and ISO/TC61 respectively. *See ISO.*

British Thermal Unit

The amount of heat required to raise the temperature of 1 lb of water by 1 degree Fahrenheit.

Brittle Point

When an elastomer sample is subjected to low temperatures, the brittle point is the highest temperature at which the sample breaks when subjected to a sharp blow. The brittle point is one indication of low temperature flexibility and is usually somewhat higher than the glass transition temperature.

BRMA

British Rubber Manufacturers' Association

Brown Crepe

Crepe rubber of lower quality than pale crepe; it is made from the pre-coagulated lumps which form in the latex before the coagulation process is carried out.

Brownian Movement

The rapid motion in all directions of the particles in a colloidal solution; it results from the irregular bombardment of the suspended particles by the molecules of the liquid.

BS

Abbreviation for British Standard.

BSI

Abbreviation for British Standards Institution.

Bud Grafting

A means of reproducing high yielding or other desirable characteristics in the rubber tree; a bud taken from a seedling bred from a tree known to yield large quantities of good quality latex is grafted onto the stem of a young rubber plant.

Buffing

Worn tyres are prepared for retreading by a buffing/grinding process to provide a fresh rubber surface.

Bulk Density

The ratio of the apparent volume of a material in powder form to the volume of the material in solid form, i.e., after removal of the air entrapped between the particles. In moulding (plastics or rubber) using powdered material, the bulk factor is thus the ratio of the volume of the powder to the volume of the moulding made from it.

Bumping

In the moulding of rubber products, the operation of opening and closing the press rapidly in the early stages of the cure to drive out any trapped air.

Buna

The name originally applied to all synthetic rubbers produced by the sodium polymerisation of butadiene; it is derived from Bu for butadiene and Na for sodium. The name was subsequently used in various forms, e.g., Buna N for nitrile rubber or NBR, and Buna S for SBR. The tradename Perbunan (Bayer) is also derived from Buna.

Butadiene

A gas, $\text{CH}_2\text{CHCHCH}_2$ (buta-1,3-diene), used in the manufacture of polybutadiene rubber and as one of the copolymers in the manufacture of styrene-butadiene and nitrile rubbers.

Tert-Butyl Cumylperoxide

BCUP, organic peroxide.

Butyl Rubber (Isobutylene Isoprene Rubber – IIR)

A synthetic rubber made by copolymerising isobutylene with 1% to 3% of isoprene, depending on the degree of unsaturation required. The percentage of isoprene determines the cure rate of the compound, the higher the isoprene content the faster the cure.

Butyl has high gum strength, high resistance to ozone attack, low permeability to gases, good flex and tear resistance and good electrical properties. A characteristics of butyl is its low resilience compared to natural rubber at room temperature, but at higher temperatures, about 100 °C, its resilience matches that of natural rubber. Butyl has poor resistance to mineral oils and organic solvents.

Butyl rubber is not compatible with natural rubber, SBR, nitrile rubber or with any other elastomer having an appreciable degree of unsaturation; modified butyls (chlorobutyl and bromobutyl) are compatible with such elastomers and used as liners in tubeless tyres to improve air retention.

Butyl can be processed without great difficulty on standard rubber machinery, but equipment should be well cleaned before and after processing butyl, since contamination can result in local undercure and delamination.

In the early days of development in the 1940s, butyl was largely used for tyre inner tubes because of its excellent air-retention properties, but it is now finding wide application in mechanicals and cables.

Butylated Hydroxytoluene

BHT, 2,6-di-*tert.*-butyl-*p*-cresol, antidegradant – non-staining.

C

CAD

Abbreviation for computer-aided design.

Calcium Carbonate

CaCO_3 , a white solid which occurs in nature as chalk, limestone and marble; the ground product, often termed whiting, is used as an extending filler in rubber compounding.

Calcium Nitrate

Ca(NO₃)₂, used in an alcoholic solution in coagulant dipping for the manufacture of latex dipped goods.

Calcium Silicate

CaSiO₃, a reinforcing filler in rubber compounding.

Calender

A machine having two, three or four heavy rolls, used in the rubber manufacturing techniques of coating, doubling, embossing, frictioning, profiling and sheeting.

Calender Bowl Deflection

The distortion suffered by calender rolls resulting from the pressure of the rubber running between them. If uncorrected the deflection produces a rubber sheet thicker in the middle than at the edges. *See Camber, Crossed Axes and Roll Bending*, all techniques to compensate for calender bowl deflection.

Calender Grain

The name given to the differences in properties lengthwise and crosswise in calendered sheet. In the direction of calendering tensile strength is high and extensibility low; at right angles to the direction in which it leaves the calender rolls, strength is relatively low and extensibility high. In some non-moulded articles the heat of vulcanisation may cause distortion, the grain effect causing the sheet to contract in length and become wider and thicker. This distortion may be minimised by plying up two thin sheets at right angles or by subjecting the sheet to the process of shrinking.

Calendering

The various processes carried out on a calender. *See Coating, Doubling, Embossing, Frictioning, Profiling and Sheeting*.

CAM

Abbreviation for computer-aided manufacture.

Camber

The slight curvature given to calender bowls to counteract the deflection produced when the calender is running, thus enabling a rubber sheet of uniform thickness across its width to be obtained.

Camelback

Tread-type rubber compound extruded in a variety of thicknesses and widths for use in tyre retreading. The standard section is in the shape of a regular trapezium, but variations are made to suit particular types of tyre and different makes of moulding equipment.

Caoutchouc

The French word for rubber, formerly used to denote highly purified natural rubber, also termed rubber hydrocarbon.

Caprolactam

1,6-hexanolactam, the monomer from which nylon 6 is prepared; nylon 6 is polycaprolactam.

Carbon Black

The name given to a variety of forms of fine particle carbon which have the property of conferring reinforcement on rubber compounds, the degree of reinforcement increasing with decreasing particle size.

Carbon Black Structure

When electron microscope studies first showed clearly the anisotropy of carbon black particles the appearance was of a chain of particles fused together, to which the term 'reticulate chain structure' was given, later abbreviated simply to 'structure'. The degree of structure has an influence on the level of reinforcement conferred by the carbon black.

Carbon Gel

Bound rubber in an unvulcanised carbon black-rubber mix. It results from the production of free radicals in the mastication of rubber; these radicals attach themselves chemically to the particles of carbon black and form a proportion of carbon gel which is insoluble in the usual rubber solvents.

Carcinogenicity

The capacity of some agent or chemical substance to induce cancer in man or other animal species.

Casein

A pale yellow solid, the main protein in milk. It is used as a stabilising agent in latex compounding.

Casting

A method of manufacturing rubber articles by pouring a compounded latex into an absorbent hollow mould; the skin of rubber thus formed is removed, dried and vulcanised. The term is also applied to the pouring into moulds of liquid polymer systems based on silicone or polyurethane elastomers.

Catalyst

A substance which alters the rate of a chemical reaction, but which exists chemically unchanged at the end of the reaction.

Cavity Transfer Mixer

The cavity transfer mixer (CTM) is a distributive mixing device used as an add-on unit to extruders; the barrel and screw have hemispheres cut out of their surfaces to give an overlap of half a pitch.

CBS

Abbreviation for cyclohexylbenzothiazole sulphenamide, the first of the sulphenamide range of delayed action accelerators.

CEFIC

European Council of Chemical Manufacturers Federations.

Celsius

A scale of temperature in which the interval between freezing point and boiling point of water is divided into one hundred degrees. This scale therefore came to be known as the centigrade scale, although the official designation is Celsius.

Centrifuge

An apparatus which rotates at very high speed, used for separating solids from liquids, or liquids from other liquids; there must be a difference in specific gravity between the two substances.

Centrifuging

A process for separating particles from a suspension by using centrifugal force. It is the most popular method for concentrating natural rubber latex before shipment from plantation to country of use.

Cetyltrimethylammonium Bromide

See CTAB.

Chafer

The reinforcing rubber and fabric around the bead in the rim area of a tyre to prevent chafing of the tyre by the rim.

Chalk

Natural calcium carbonate, CaCO₃, formed from the shells of tiny marine organisms, used as an extending filler in rubber compounding and as a release agent. The term is often loosely applied to any dusting agent. See *Whiting*.

Chalking

The release of filler particles at the surface of a product due to oxidation of the rubber. The term is also used in the sense of 'dusting' an uncured rubber surface to prevent adhesion.

Chelating Agent

A substance which results in the chemical inactivation of a metal. The catalytic effect of heavy metals, mainly copper and manganese, on the oxidation of unsaturated compounds such as rubber, results in very rapid deterioration. Chelating agents convert the metal into a chelate co-ordination compound and thus render the metal inactive. The term 'sequestering agents' has been applied to chelating agents but this infers that the metal has been removed and not merely inactivated.

CHIP

Chemicals (Hazard Information and Packaging for Supply) Regulations (UK).

Chlorinated Rubber

A white fibrous product obtained when chlorine is passed into a solution of rubber. It was used mainly in corrosion-resistant paints and varnishes but has been superseded by tailored synthetic polymers systems.

Chlorobutadiene

2-chloro-1,3-butadiene (chloroprene), a volatile colourless liquid, the monomer for the preparation of polychloroprene rubbers.

Chlorobutyl

Chlorinated butyl rubber. Chlorination or bromination of butyl rubber overcomes the difficulty of vulcanising butyl rubber in mixtures with more highly unsaturated substances due to the preferential absorption of the sulphur by the more highly unsaturated component.

Chlorohydrin Rubbers

A class of synthetic elastomers based on epichlorohydrin.

Chloroprene Rubber (CR)

This is the preferred designation for all chloroprene polymers and copolymers. Chloroprene rubber was first introduced commercially in 1931 by DuPont and their trade name, originally DuPrene, later Neoprene, has almost become a generic term for all such rubber. See *Chlorobutadiene*.

Chlorosulphonated Polyethylene (CSPE)

An elastomer made by substituting chlorine and sulphonyl chloride groups into polyethylene. The material is best known by the trade name Hypalon, which is the DuPont trade mark for their brand of chlorosulphonated polyethylene.

Chromatography

A technique of chemical analysis in which the components of a liquid mixture are adsorbed in separate layers in a column of adsorbing material. Variations of the technique are paper chromatography and gas chromatography.

CI

Abbreviation for Colour Index.

CIIR

Abbreviation for chlorobutyl rubber.

CIPG

Abbreviation for cured-in-place gasket.

Cis-trans Isomerism

A form of isomerism associated with compounds containing a double bond; similar groups of atoms may be either on the same side of the plane of the double bond (*cis*-form), or on opposite sides (*trans*-form). The terms are from the Latin, *cis*, on this side and *trans*, across. The important properties of a polymer are determined by the geometrical arrangement of its building units. Natural rubber (polyisoprene) has the *cis*-form giving a highly elastic material, while gutta-percha has the *trans*-form and is relatively non-elastic and more crystalline.

Clay

This term is applied to a wide variety of materials known chemically as hydrated aluminium silicates, used as inorganic fillers. China clay (kaolin) shows a slight reinforcing effect; 'treated' clays show considerably greater reinforcement.

Clone

A group of trees (of, for example, Hevea Brasiliensis) derived by bud grafting from a single mother tree.

Cloth Count

The number of warp ends and the number of weft picks per unit length in a woven fabric; written, e.g., 23 x 23, the unit length being 1 inch on the imperial system of measurement.

CM

Abbreviation for chlorinated polyethylene.

CNR

Abbreviation for Cameroon Natural Rubber.

CO

Epichlorohydrin homopolymer.

Coacervation

Any process which brings about destabilisation of a latex to such an extent that the particles coalesce. Depending on the form resulting from the agglomeration, the coacervation may be described as either coagulation, flocculation or gelation.

Coagulant

Any substance which will bring about coagulation. In the preparation of natural rubber the usual coagulants are acetic or formic acids. In the manufacture of dipped goods from latex, the coagulant used depends on the method of dipping employed.

Coagulation

In rubber latex, the process whereby the dispersed rubber globules separate out from the watery serum; the globules clot together to form a jelly-like mass, the coagulum. In the preparation of natural rubber, coagulation of the latex is

brought about by the addition of either acetic or formic acid but it may occur spontaneously through the action of microorganisms in the latex.

Coagulum

In the preparation of natural rubber, the coagulum is the soft clot or mass of rubber particles which separates out from the serum after addition of the coagulant.

Coacervant

A coacervant is a material, solid or liquid, which destabilises a latex so that the particles coalesce in large numbers. May also be described as coagulant or flocculant.

Coating

Coating, skim-coating or topping is a calendaring process in which a thin sheet of rubber formed at one nip is applied to the surface of a textile material as it passes through a second nip. The term 'coating' may also be used in the wider sense of applying rubber to a textile by any non-calendaring method such as spreading, dipping or spraying.

Coefficient of Friction

Static friction is the force which must be overcome in order to start the motion of a body over a surface. Kinetic friction is the force which must be continuously overcome in order to maintain uniform motion of the body over the surface. The coefficient of friction (static or kinetic respectively) is the frictional force divided by the perpendicular or normal force between the surfaces in contact.

Coefficient of Thermal Expansion (Volume)

Increase in volume per unit volume resulting from a temperature rise of 1 °C. The coefficient of thermal expansion of rubber compounds varies from 0.00066 for a pure gum mix down to approximately 0.00048 depending on the amount of the loading. This high expansion relative to steel (about 10 to 20 times greater) can result in moulding defects. *See Back Rinding, Shrinkage.*

Cold Cure

A now obsolete process for vulcanising coated, usually spread fabrics. No sulphur was added to the mix from which the spreading dough was made, the curing effect being obtained by exposing the fabric to the action of sulphur monochloride diluted with a petroleum solvent. The cloth was passed over a roller which ran in a trough containing the curing solvent. Combinations of ultra accelerators are now used.

Cold End

A section at each end of the platens of a hydraulic press used for curing belting, where the temperature is lower than that of the remainder of the platens. The object is to reduce overcure at the overlapped areas, which would otherwise receive a double cure.

Cold Mastication

Mastication of rubber which is carried out at temperatures below 90 °C is termed 'cold'. The masticating effect is at a minimum at temperatures around 105 °C, breakdown occurring much more rapidly at higher or lower temperatures.

Cold Rubber

This is styrene-butadiene rubber polymerised at a temperature of 5 °C (41 °F) in contrast to the original polymerisation temperature of 50 °C (122 °F). It is also known as Low Temperature Polymer (LTP). Nitrile rubber can also be made by a low temperature process. Such polymers are characterised by improved processibility.

Colloid

A colloid is a suspension of particles with diameters between 1 nm and 100 nm. The particles are charged and can be subjected to cataphoresis (electrophoresis). They are subject to Brownian movement and have a large amount of surface activity. Their properties lie between those of true solutions and coarse suspensions.

Colloidal State

A state of subdivision of matter with a particle size between 10^{-7} and 10^{-5} cm (1 nm to 100 nm). The properties of colloids lie between those of true solutions and coarse suspensions.

Colour Index (CI)

Pigments are classified by an internationally recognised convention, published in the International Colour Index by the Society of Dyers and Colourists in Bradford, in association with the American Association of Textile Chemists and Colorists. The Index issues a generic name to chemically identical products (e.g., titanium dioxide is classified as C.I. Pigment White 6). Where structures are known, pigments are also given a constitution number (e.g., titanium dioxide has the constitution number CI 77891). This number is reserved for the essential colorant, other ingredients, such as the carriers used in a masterbatch, do not affect this classification.

Compound

In chemistry a compound is defined as a substance consisting of two or more elements chemically united in definite proportions by weight. However, many technologists use the term 'compound' in the sense of a mixture. In rubber technology, a compound is a composition obtained by adding to an elastomer substances known as compounding ingredients and blending to produce a homogeneous mixture or mix. Other terms for this unvulcanised mix are mixing, stock, blend or quality. The term may also be used in the sense of the mix formulation, i.e., the kinds and amounts of the elastomers and compounding ingredients used to give the requisite properties in the end product.

Compounding

The development of rubber compounds which will effectively withstand the conditions under which the products made from them are to be used; the mixes so developed must be capable of being processed in the factory without undue difficulty. The term is also applied to the assembling of elastomer and compounding ingredients ready for the mixing proper.

Compounding Ingredient

Any substance added to an elastomer to produce a rubber compound.

Compression Moulding

The method of manufacture of solid rubber products by simultaneous shaping and vulcanising. An uncured blank of rubber compound is placed in the bottom half of a mould, the top half of the mould placed in position and the mould placed in a heated hydraulic press. The press performs the dual function of both closing and heating the mould. *See Transfer Moulding and Injection Moulding.*

Compression Set

The residual decrease in thickness of a rubber test piece, expressed as a percentage of the original thickness, after the test piece has been subjected to a compression stress under specified conditions of time of loading, time of recovery and temperature. BS 903: Part A6. Determination of compression set.

Concentrated Latex

Natural rubber latex as obtained from the tree contains only about 30% by weight of rubber. Concentration of the latex is done by either centrifuging, creaming, electro-decantation or evaporation.

Condensate

Water formed in a steam supply system when the steam has given up its heat and returned to the liquid state. Since condensate still contains useful heat it is returned to the boiler as make-up water.

Condensation

A chemical reaction in which two or more molecules react, with the elimination of water or of some other simple substance.

Condensation Polymerisation

Polymerisation resulting from a chemical reaction involving condensation. The synthetic elastomers produced by condensation polymerisation include polysulphide rubbers, silicone rubbers and the ester and isocyanate rubbers.

Conductive Rubber

Rubber which is deliberately rendered electrically conductive by the inclusion in the unvulcanised mix of certain types of carbon black. Conductive rubber for use in, e.g., aircraft tyres has a resistivity below about 10^5 to 10^7 ohm-cm. The changeover from the use of channel blacks to oil-based furnace blacks has conferred a degree of conductivity (sometimes unwanted) on many black rubber products, and it should no longer be assumed that any black rubber is a good electrical insulator. *See Antistatic Rubber.*

Conductivity

The ability of a substance to permit the passage of heat (thermal conductivity) or of electricity (electrical conductivity).

Conjugated Double Bonds

An arrangement of alternate single and double bonds between the carbon atoms in diolefinic compounds.

Continuous Filament

In the manufacture of man-made and synthetic textiles the base materials are extruded through tiny orifices producing continuous lengths of very fine fibres or filaments. The textiles are mostly used in this 'continuous filament' form, but for some purposes the filaments may be cut up into short fibres and spun into a yarn.

Continuous Vulcanisation

Any method of vulcanising rubber products which proceeds without interruption from start to finish as compared to the method of vulcanising separate batches of products or sections of a product. Continuous vulcanisation processes include the cold curing of proofed cloth, the vulcanisation of belting and flooring, of cables and certain extruded products by either the Liquid Curing Medium, Fluid Bed, Microwave, or Hot Air techniques.

Conveyor Belting

Belting used mainly in the transmission of materials, although increasing use is being made of conveyor belting in the transportation of passengers.

Co-ordination Polymerisation

A process related to ionic polymerisation where the catalyst system complexes of aluminium alkyls and titanium halides governs the way in which a monomer and a growing chain approach each other.

Copolymer

A 'high polymer' resulting from the polymerisation of a mixture of two different monomers; styrene-butadiene rubber, butyl (isoprene-isobutylene) rubber and nitrile (acrylonitrile-butadiene) rubber are typical copolymers.

Copolymerisation

The chemical reaction which brings about the formation of a copolymer.

Copper Dimethyl Dithiocarbamate

A fast accelerator for SBR compounds. It is used as either a primary or as a secondary accelerator along with a thiazole type.

Copper Inhibitor

Certain antioxidants also offer protection against the deleterious effects of copper and manganese, and are thus termed copper inhibitors.

Cord

- (1) A solid circular extruded section of rubber compound generally of small diameter used as blanks in moulding O-rings and similar products.
- (2) The twisted fibre of polyester, rayon, nylon or steel, which imparts strength to the tyre carcass and belt. *See Tyre Cord.*

Corona

A luminous discharge resulting from air breakdown in the vicinity of high voltage cables. Corona produces ozone (from the oxygen in the air) and may result in rapid deterioration of the cable insulation and other unsaturated rubber in the vicinity.

COSHH

Control of Substances Hazardous to Health Regulations (UK).

Cotton

A natural fibre which has been superseded by the various synthetic fibres for use as reinforcement in rubber articles.

Coumarone-Indene Resins

Resins resulting from the polymerisation of one of the fractions of coal tar. Used as processing aids, tackifiers and as non-black organic reinforcing agents in rubber compounding.

Count

The count of a rubber thread is the number of threads which measure exactly one inch across when placed side by side. *See Cloth Count and Yarn Count.*

Covalency

A valency bond created by the sharing of a pair of electrons; also termed a 'non-polar' bond.

CPE

Abbreviation for chlorinated polyethylene.

CR

Abbreviation for chloroprene rubbers.

Cracker

A heavy type of open mill with deeply corrugated rolls, used for the preliminary breakdown of rubber compound prior to the processes of extrusion and calendering.

Cracking

- (1) The tearing apart or breaking down of rubber compound on a cracker.
- (2) The appearance on the surface of rubber products of cracks or fissures as a result of exposure to the atmosphere (atmospheric cracking) or to repeated bending or stretching (flex cracking).
- (3) Decomposition of a chemical substance by heat; particularly the decomposition of heavier petroleum distillates to produce a larger supply of lighter fractions.

Crazing

The name given to the surface appearance of a vulcanised elastomer which has suffered oxidation catalysed by light. The inelastic skin first formed gradually thickens and cracks in random directions.

Creamed Latex

Latex which has been concentrated by creaming.

Creaming

One of the methods of concentrating normal rubber latex; the rubber globules rise to the surface of the heavier serum, the process usually being hastened by the addition of creaming agents such as ammonium alginate.

Creep

That characteristic of vulcanised elastomers or thermoplastics in showing a gradual increase in deformation under constant load with passage of time; also known as strain relaxation or drift.

Crepe Rubber

Any form of natural rubber which is marketed with the rough surface produced by passing the rubber through a series of mills with grooved rolls travelling at differential speeds. The main types are pale crepe, sole crepe, brown crepe and flat bark crepe.

Crimp

The difference in length between the ends of a yarn as it lies in the woven cloth and its length when removed from the cloth and straightened out, expressed as a percentage of the length in the cloth.

Crocking

The staining of a surface by light rubbing contact with a pigmented rubber.

Crossed Axes

A method of producing the effect of a variable camber on a calender. By skewing or crossing the

axis of one roll in relation to the other the nip is thus opened more at the ends of the roll than in the middle.

Crosslink Density

The number of moles of physically effective crosslinks per gram of vulcanisate.

Crosslinking

The joining of polymer molecules to each other by valency bonds. In very long chain-like elastomer molecules crosslinking introduces lateral links between either two separate molecules or different parts of the same molecule. *See Vulcanisation.*

Crown

With reference to a calender, another term for camber.

Crows' Feet

Arrow-shaped markings on the surface of calendered sheet rubber due either to the use of insufficiently warmed stock or to too low temperature of the calender rolls.

Crumb Rubber

Vulcanised waste rubber which has been ground down to a desired mesh size (18, 20, 24, 30 or 40) for addition to new compound as a filler; a better term is vulcanised rubber crumb. *See Powdered Rubber.*

Crystallinity

Degree of crystallisation. Although no polymer is completely crystalline, the term 'crystalline polymer' is applied to one with an appreciable degree of crystallinity.

Crystallisation

In high polymers crystallisation means the formation of areas of regularity in chain aggregation rather than the formation of discrete crystals, as in simple chemical compounds.

Crystallite

A crystalline region in a polymer matrix. *See Crystallisation.*

CSM

Abbreviation for chlorosulphonated polyethylene.

CSPE

Abbreviation for chlorosulphonated polyethylene.

CTAB

Cetyltrimethylammonium bromide, latex auxiliary. Also used as an adsorbent to measure the total surface area of carbon black.

CTM

Abbreviation for cavity transfer mixer.

CTP

N-(Cyclohexylthio)phthalimide, retarder.

Cup Lump

A blanket crepe rubber produced from the dried films and lumps of rubber found in the tapping cups at the beginning of the next tapping. Cup lump results from the spontaneous coagulation of the latex which has dripped from the tree after the cup has been emptied of the main flow.

Curing

This term is synonymous with vulcanisation but is generally applied to the factory methods of vulcanising rubber products, e.g., press curing, open steam curing, cold curing.

Curing Bag

In pneumatic tyre manufacture, the heavy rubber tube to which is admitted the inflation medium

which provides the pressure for moulding. Air, steam or hot water have all been used for inflation and curing bags may therefore be termed air bag, steam bag or water bag. *See Bladder.*

Curometer

An apparatus for determining the curing characteristics of rubber compounds.

Cut Edge

Term applied to belting made without a moulded edge.

Cut Thread

Rubber in the form of fine 'threads' produced by vulcanising a thin sheet of rubber compound, winding it on a drum and slitting it to the required size by revolving the drum against a number of sharp, wetted knives which revolve at high speed.

Cyclised Rubber

An isomeric derivative of natural rubber produced by a variety of chemical treatments. The products are resinous and find application as reinforcing agents in natural rubber compounds (particularly in shoe soles) and as rubber-to-metal adhesives.

D

Damping

Decrease in the amplitude of an oscillation or wave motion with time. Damping in rubber testing results from hysteresis.

Daylight Press

An apparatus, usually operated by hydraulic pressure, in which the vulcanisation of moulded rubber products is carried out. The 'daylight' is the space between the heated platens on which the moulds are placed. A press is specified by the platen area, the number of daylights and the press tonnage.

DBP

Abbreviation for dibutyl phthalate, a plasticiser for natural and synthetic rubbers.

DBTU

N,N'-Dibutylthiourea, accelerator.

DCBS

N,N-Dicyclohexyl-2-benzothiazole sulphenamide, accelerator.

DDM

2,2'-Dihydroxy-5,5'-dichloro-diphenylmethane, latex auxiliary.

De Mattia Flex Test

A test method for comparing the resistance of rubbers to the formation and growth of cracks. Moulded samples with a central groove are repeatedly bent from a straight to a doubled position. The degree of cracking is estimated by comparison with photographs of standard samples. BS ISO 132 Determination of flex cracking and crack growth (De Mattia).

Dead Milled

Applied to rubber which has been subjected to prolonged mastication, often carried out with periods of rest between mastication stages; such rubber shows little or no elastic recovery.

Deflashing

The removal of flash or spew from moulded rubber products. This may be done by hand, by

trimming machine or by 'tumbling' the products in a barrel held at a temperature low enough to harden the flash and permit it to be rubbed off by the motion of the products in the barrel.

Defo Plastometer

A type of parallel plate plastometer developed in Germany; it differs from the conventional parallel plate instrument in that it measures the load required to deform the test sample by a specified amount in a fixed time.

Degradation

Deterioration usually by chemical or physical means rather than by a mechanical process.

Degraded Modulus

After a test specimen of an elastomer has been subjected to repeated deformation, the modulus at some lesser deformation is lower than the initial value. The modulus after such stress softening has been termed the degraded modulus. *See Mullins Effect.*

DEHP

Di-2-ethylhexyl phthalate, ester plasticiser.

Dehydration

Simply removal of water, but the term is usually applied to the removal of chemically-combined water.

Delamination

Splitting into layers; usually applied to the separation of the plies from which a composite rubber article has been built up.

Delayed Action Accelerator

An accelerator which permits processing of rubber compounds to be carried out with less risk of scorching but which does not slow down the rate of cure at normal vulcanisation temperatures.

Demoulding

The operation of removing a vulcanised product from the mould in which it has been cured.

Denier

A system of numbering yarns and filaments, generally of man-made and synthetic fibres. Denier is the weight in grams of 9000 m of the filament or yarn.

Density

The weight of unit volume of a substance. *See Specific Gravity.*

Deodorant

Compounding ingredient used to neutralise unpleasant odours in rubber.

Depolymerisation

Breaking down of a long chain molecule into relatively short chain molecules of the same empirical composition as the original substance or in some cases to the original monomer.

Depolymerised Rubber (DPR)

Natural rubber which has been reduced to an easy flowing consistency by prolonged mastication in the presence of peptising agents. Suitably compounded, DPR may be cast into moulds and vulcanised; ebonite products from DPR are also possible.

Desiccant

A substance added to rubber compounds to absorb and retain (even at curing temperatures) moisture which would otherwise be a factor in producing porosity.

DETU

Abbreviation for 1,3-diethyl-2-thiourea, accelerator.

Dew Point

That temperature at which the water vapour present in the air saturates the air and therefore begins to condense as 'dew'.

DHBP

2,5-Dimethylhexane-2,5-di-*tert.*-butyl peroxide, organic peroxide.

Di-2-Ethylhexyl Adipate

DOA, ester plasticiser.

Di-2-Ethylhexyl Phthalate

DEHP, ester plasticiser.

Di-2-Ethylhexyl Sebacate

DOS, ester plasticiser.

Di-*o*-tolyl guanidine

DOTG, accelerator.

Di-*tert.*-Butyl Peroxide

DTBP, organic peroxide.

Diaphragm

- (1) A sheet of rubber or of rubber-textile composite moulded, if desired, to a particular shape and used in a wide variety of applications in industry, e.g., diaphragm packings, diaphragm-operated valves for steam, air or liquids.
- (2) The flexible membrane or 'bladder' which supplies internal pressure in the curing of pneumatic tyres in diaphragm presses of the Bag-o-matic or Autoform type.

Diaphragm Press

In tyre manufacture, a press which uses a flexible diaphragm to supply to the inside of the tyre the internal inflation medium for both shaping and vulcanising. The diaphragm replaces the heavy curing bag used in the now obsolete autoclave moulding of tyres. Diaphragm presses are generally automated.

Dibenzoyl Peroxide

BPO, organic peroxide.

Dibenzthiazyl Disulphide

MBTS, an organic accelerator of the thiazole class.

Dibutyl Phthalate (DBP)

An organic (ester) compound used as a plasticiser in nitrile rubbers and in polyvinyl chloride.

***N,N*-Dibutylthiourea**

DBTU, accelerator.

Dicumyl Peroxide

A non-sulphur vulcanising agent for natural rubber and some types of synthetic rubber. One trade name is Dicap.

***N,N*-Dicyclohexyl-2-benzothiazole sulphenamide**

DCBS, accelerator.

DIDP

Abbreviation for diisodecyl phthalate, plasticiser.

Die

- (1) In extrusion of solid rubber sections, the shaped metal plate fitted in the head of the extruder to produce the desired contour; in extrusion of hollow tubing the outer circular part which fits over the pin, pencil or nozzle to give the hollow section.
- (2) A sharp tool used in punching out special shapes of rubber or rubbered fabric or used in

preparing test-pieces of vulcanised rubber, e.g., dumbbell strips for tensile testing.

Dielectric Heating

Also termed electronic or high frequency (HF) heating. Heating is carried out by placing the object between plates connected to a source of high-frequency current. Vulcanising of rubber products may be done by HF heating but the method finds its greatest application in the preheating of blanks prior to moulding. It has also been used for thawing out frozen rubber.

Dielectric Strength

The electrical stress required to puncture a sample of a material of known thickness; usually expressed in kilovolts per mm of thickness. The standard BS EN 60243-1 gives details of the test procedure.

Diene

Another name for diolefin.

Die Swell

The increase in dimensions of an extruded section as it leaves the die; the swell is mainly due to elastic recovery.

Diethylene Glycol

A plasticiser of particular use in compounds containing silica or silicate fillers.

Differential Scanning Calorimetry

This technique is used to generate thermograms, which can be used in quality control and to identify additives in rubber.

Diffusion

The migration of the molecules of a fluid (liquid or gas) into another medium. Diffusion results from the kinetic energy of the molecules and is therefore speedy in gases, slower in liquids and almost negligible in solids.

Dimethyl Butadiene

$\text{CH}_2\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)\text{CH}_2$, a diolefin from which was manufactured 'methyl rubber' in Germany during World War I.

DIN

Abbreviation for Deutsche Industrie Normen - German Industrial Standard. The organisation issuing these standards is the Deutscher Normenausschuss (DNA), the German equivalent of the BSI.

Dinitroso-Pentamethylenetetramine

DNPT, blowing agent.

DINP

Abbreviation for diisononyl phthalate, plasticiser.

Diocetyl Phthalate

An organic (ester) compound used as a plasticiser in nitrile rubbers and in polyvinyl chloride.

Diolefin

A hydrocarbon of the ethylene series, containing two double bonds in the molecule.

Dipentamethylene Thiuram Tetrasulphide

DPTT, accelerator.

***N,N*-Diphenyl Guanidine**

DPG, accelerator.

***N,N*-Diphenyl-*p*-Phenylenediamine**

DPPD, antidegradant - staining.

Dipping

A method of manufacturing rubber articles by dipping a former of the shape required into a rubber 'solution' or into compounded,

concentrated latex which may be either unvulcanised or vulcanised.

Direct Moulding of Footwear

A method of manufacturing footwear by simultaneously forming and vulcanising the rubber sole and heel direct to a leather upper, as compared to moulding the unit separately and sticking it to the upper.

Dispersion

The uniform distribution of particles throughout a medium, e.g., particles of compounding ingredients in rubber.

Dithiocarbamates

A class of very fast accelerators for rubber, particularly useful in latex work. The principal member of the class is zinc diethyl dithiocarbamate.

DMC

Abbreviation for dough moulding compound.

DMS

Abbreviation for direct moulded soling. *See Direct Moulding of Footwear.*

DMTA

Abbreviation for dynamic mechanical thermal analysis.

DNPT

Dinitroso-pentamethylenetetramine, blowing agent.

DOA

Di-2-ethylhexyl adipate, ester plasticiser.

Doctor Knife or Doctor Blade

- (1) The blunt-edged blade which spreads rubber dough on to fabrics in the spreading process.
- (2) A blade fitted to a refiner mill to enable the thin sheet of rubber to be removed.
- (3) An elastomeric (usually polyurethane) blade used to clean the rollers in laser printers and copiers.

Dolly

A roll of masticated rubber cut from an open mill, also known as a pig.

Dolomite

Calcium magnesium carbonate, inorganic filler.

DOP

Abbreviation for dioctylphthalate, a plasticiser for natural and synthetic rubbers.

DOPD

N,N'-Bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine, antidegradant – staining.

DOS

Di-2-ethylhexyl sebacate, ester plasticiser.

DOTG

Abbreviation for diorthotolylguanidine, an organic accelerator.

Double Bond

Also termed bivalent gap and ethylenic linkage. The type of bond in which two valency bonds link two atoms in a molecule. It is typical of compounds showing unsaturation, such as ethylene. A double bond does not indicate extra strength of the bond but rather chemical instability and reactivity.

Doubling

Sticking two layers of uncured rubber or rubbered fabric together and consolidating them by applying pressure in a doubling machine or doubling calender. In textile technology doubling

is the twisting together of two or more threads to make yarn for weaving of fabrics, and also the operation of combining and twisting yarns to make cord for use in pneumatic tyre casings.

Dough

Rubber compounded and swollen in solvent and worked on a 'wet' mill until it reaches the consistency of dough. It is then applied behind the doctor blade of a spreading machine through which the fabric to be coated is passing. Self-curing doughs are used in the repair of rubber products (tyre tread cut-filling) and the splicing of belting.

Dough Moulding Compound

A plastics material of particular application in electrical components. It consists of a thermosetting polyester resin, mineral fillers, fibrous reinforcement and a liquid crosslinking medium such as diallyl phthalate.

Down-Stroking Press

In a conventional rubber moulding press the main ram travels upwards. In a down-stroking press the main ram is situated above the movable top platen to which pressure is applied by a downward movement of the ram.

DPG

Abbreviation for diphenylguanidine, an organic accelerator.

DPPD

N,N'-Diphenyl-*p*-phenylenediamine, antidegradant – staining.

DPR

Abbreviation for depolymerised rubber.

DPTT

Dipentamethylene thiuram tetrasulphide/hexasulphide, accelerator.

DPTU

1,3-Diphenyl-2-thiourea, accelerator.

DRC

Abbreviation for dry rubber content, generally of latices and similar dispersions.

Drafting Apron

A driven, fabric reinforced, beltlike component over which loosely formed textile fibres (slub) are drafted (orientated and drawn) to improve yarn formation and consolidation. Two aprons work face to face, between which the yarn being formed is drawn. The aprons separate two sets of cots and fluted steel rollers, revolving at different speeds to create the stretching required.

Drop

In curing thick articles in open steam it is sometimes necessary to reduce the temperature of cure at the end of the 'hold' period at a slow yet uniform rate. This part of the cure schedule is the 'drop'.

Drug Room

An obsolescent term for compound room - the area where the elastomers and compounding ingredients are weighed out in the proportions called for by the compound formula, prior to the mixing process.

Dry

Said of uncured rubber surfaces which have lost their natural tack.

Dry Heat Cure

Also called hot air cure. A method of curing, mainly used for footwear. The articles are placed in a double-walled vulcaniser, the heat for curing being obtained from steam circulating between the double walls. Steam does not therefore come in contact with the articles in the vulcaniser itself.

Dry Rubber Compound

The use of compounds based on solid elastomers (natural or synthetic) as opposed to their use in the latex or 'wet' form.

Dry Saturated Steam

Steam at the same temperature as the water from which it was formed, but not containing any particles of entrained water.

DSC

Abbreviation for differential scanning calorimetry.

DTBP

Di-*tert.*-butyl peroxide, organic peroxide.

DTDMD

4,4'-Dithiodimorpholine, vulcanising agent.

Duck

A strong, firm, tightly woven, durable fabric usually of cotton but sometimes of linen, hemp or other fibres. It is produced in a variety of weights.

Dunlop Process

A method of manufacturing latex foam. Compounded latex is foamed and gelling agent added; the mould is filled and the gelled foam vulcanised by steam at 100 °C; the product is stripped from the mould, washed and dried. *See Talalay Process.*

Durometer

An instrument for the determination of the hardness of vulcanised rubber. The name is usually, but not necessarily, applied to a pocket-type instrument made by the Shore Instrument and Manufacturing Co. Inc. The use of the term in the sense of hardness (a durometer of 60°) is not recommended.

Dusting

The operation of applying a dusting agent to rubber.

Dusting Agent

Any powder or liquid used for reducing the surface tack of unvulcanised rubber. Dry dusting agents are traditionally applied to rubber by the very uneconomical and unhealthy procedure of shaking a cloth bag containing the powder over the rubber surface. Extrudates may be coated by passing them through a chalk 'tank' between rotating brushes.

Dynamic Mechanical Thermal Analysis

This is very useful for generating modulus versus temperature data on rubber compounds. The effects of temperature on this important material property can be obtained over a wide temperature range (typically -150 to +200 °C), along with the glass transition temperature and information on thermal stability.

Dynamic Properties

The study of the response of elastomers to forces which produce changes of motion in them. *See Heat Build-up, Hysteresis and Resilience.*

Dynamometer

Any apparatus used for the measurement of power. Various types of dynamometer are used in the testing of pneumatic tyres and belting.

E

EACM

Abbreviation for ethylene-acrylic terpolymer.

EAM

Abbreviation for ethylene-vinyl acetate.

EBC

Abbreviation for estate brown crepe.

Ebonite

Also known as vulcanite and (mainly in the USA) 'hard rubber'. The hard, horn-like product obtained when natural rubber and some synthetic rubbers such as nitrile (NBR) are vulcanised with a high proportion of sulphur or organic non-sulphur vulcanising agent. Butyl rubber and polysulphide rubber do not form ebonites.

Ebullioscopy

A technique for determining the boiling point of liquids, especially for determining the alcoholic strength of a mixture by the temperature at which it boils. The method has been used to give an indication of the molecular weight of a substance by observing the elevation of the boiling point of a dilute solution of the substance in a suitable solvent.

Eccentricity

Displacement with reference to a centre; an off-centre condition of, say, a cable conductor in relation to its rubber covering, a section of tubing thicker on one side than the other, or a lateral displacement of the two halves of a circular mould. *See Off Centre.*

ECETOC

European Centre for Ecotoxicology and Toxicology of Chemicals.

ECO

Epichlorohydrin copolymer with ethylene oxide.

EDAX

Energy dispersive analysis combines SEM and XRF and is used to analyse small samples, sample surfaces or contaminants in samples.

EFA

Formaldehyde-ammonia-ethyl chloride condensation product, accelerator.

Efficient Vulcanisation

A term applied to vulcanisation systems in which sulphur or a sulphur donor is used very efficiently for crosslinking the rubber. EV systems produce vulcanisates with crosslinks that are mainly monosulphidic, which are thermally and mechanically stable.

Elasticity

The ability of a material to regain its original shape, on removal of the force which has caused the change of shape.

Elastomer

A collective term for rubber and rubber-like substances. Tree rubber is a natural elastomer and man-made rubbers are synthetic elastomers.

Electric Strength

An alternative term for dielectric strength.

Electrode

A conductor whereby an electric current is led into a liquid or a gas. The positive electrode is the anode, the negative one is the cathode.

Electrodecantation

A method of concentrating latex by passing an electric current through the latex contained in a rectangular tank. The rubber particles move toward the anode and also tend to rise because of their lower specific gravity. The separation is facilitated by a large number of semi-permeable membranes fitted between the electrodes.

Electrodeposition

A process, now obsolescent, of forming rubber articles on an anode by the migration of coagulating ions resulting from the passage of an electric current.

Electrolysis

Chemical decomposition of certain substances by the passage of an electric current through a solution of the substance or of the substance in a molten condition.

Electrolyte

A substance which, in the molten state or dissolved in a suitable solvent, conducts electricity and is simultaneously decomposed by it.

Electronic Theory of Valency

An explanation of valency on the basis of modern views of atomic structure. It is assumed that certain arrangements of outer electrons in atoms ('octets' or outer shells of eight electrons) are stable and tend to be formed by the transfer or sharing of electrons between atoms. *See Covalency and Electrovalency.*

Electron Microscope

The ordinary microscope uses a beam of light to illuminate the object; the electron microscope uses a beam of electrons which pass through the object (in the form of a very thin film of the material). Differential scattering of the beam produces an image of the object which is seen on a fluorescent screen and recorded, if required, by a camera. When the beam passes through the object this is known as a Transmission Electron Microscope (TEM). Alternatively the electrons can be used to 'illuminate' the surface of the object and in this case it is termed a Scanning Electron Microscope (SEM). The TEM is used on thin sections, the SEM can be used with 3 dimensional objects.

Electron Spin Resonance

A type of spectroscopy used in the study of molecules which contain one or more unpaired electrons.

Electrostatic Spraying

A method of (1) dusting uncured rubber surfaces or (2) painting a metal surface, by giving the dusting agent or powder paint a charge. The charged powder, driven by a low air pressure, is attracted to the oppositely-charged surface, thus coating it completely and evenly.

Electrovalency

A valency bond formed by the transfer of electrons from one atom to another.

Element

A substance which cannot be decomposed by chemical means into simpler substances; a substance consisting entirely of atoms of the same atomic number.

Elongation

In tensile testing of rubber, elongation is the increase in the distance between bench marks on a dumbbell strip or the distance apart of the grips holding a ring test piece, on the application of a load to the test sample. It is expressed as a percentage of the original distance between the marks.

Elongation at Break

See Ultimate Elongation.

ELS

Evaporative light scattering.

Embossing

The impressing of a design on an uncured rubber surface by passing it through a calender fitted with an auxiliary roll engraved in the negative with the desired pattern.

Empirical Formula

The formula for a chemical compound which gives only the proportions of the different elements in the molecule and not their actual number, which may be calculated only from the molecular weight of the compound.

Emulsifying Agent

A substance added to an emulsion to increase its stability and reduce the risk of separation of the two components. In latex work soaps are widely used as emulsifying agents.

Emulsion

A two-phase system consisting of minute droplets of one liquid dispersed in a second liquid with which it is incompletely miscible.

Emulsion Polymerisation

Polymerisation of a monomer or mixture of monomers which have been emulsified with soap in water. SBR, neoprene and nitrile rubbers are manufactured by the emulsion polymerisation process.

Endothermic

Accompanied by the absorption of heat.

Ends

The warp threads of a woven fabric.

EPA

Environmental Protection Agency (USA)

EPDM

The preferred systematic abbreviation for ethylene-propylene terpolymer, also designated EPT. The use of the term EPR for a copolymer of ethylene and propylene, and the use of EPT for a terpolymer of these monomers with a small amount of a diene to provide double bonds is common but is not recommended.

Epichlorohydrin

1-chloro-2,3-epoxypropane, the basis of epoxy resin and chlorohydrin elastomers.

Epichlorohydrin Elastomers

See Chlorohydrin Rubbers.

EPM

Abbreviation for ethylene-propylene rubber.

Epoxy Resins

Another term for Epoxy Resins.

Epoxy Resins

These are thermosetting viscous liquids or brittle solids, the most widely used being those based on the condensation reaction between epichlorohydrin and bisphenol A. The name is derived from the Greek prefix 'epi' meaning 'over' or 'between', an epoxy material being an 'oxygen between' compound. They are used mainly as adhesives and as surface coatings on metals, wood, other plastics and glass.

EPR

Abbreviation for ethylene-propylene rubber.

EPSOM

Syndicat des Fabricants d'Emaux, Pigments, Sels et Oxydes Métalliques

EPT

Abbreviation for ethylene-propylene terpolymer.

Ergonomics

The engineering aspects of the study of the relation between human workers and their working environment.

Escalator

A slatted conveyor fitted above an open mixing mill and used to increase the efficiency of mastication by cooling the rubber before returning it to the mill nip.

Estate Brown Crepe

Grades of crepe rubber made from lump and other high quality scrap made on rubber estates. Both Thin Brown Crepe and Thick Brown Crepe are produced, in no. 1, no. 2 and no. 3 qualities.

Esters

Organic compounds derived by replacing the hydrogen of an acid by an organic radical or group. Examples of ester plasticisers are tritolyl phosphate, dioctyl phthalate and dioctyl sebacate.

ETAD

Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers

ETER

ASTM designation for epichlorohydrin terpolymers.

Ethane

The second member of the paraffin series of hydrocarbons. It is a constituent of the natural gas found in association with oil fields.

Ethanol

Another term for ethyl alcohol.

Ethanolamines

Organic compounds derived from ethanol and amino groups ($-\text{NH}_2$). See *Triethanolamine*.

Ethenoid Plastics

Those plastics made from substances containing an ethylenic linkage or double bond; the acrylic, vinyl and styrene groups of plastics.

Ethers

A group of organic compounds derived from two molecules of an alcohol by elimination of one molecule of water. The compound commonly called 'ether' is diethyl ether.

Ethyl Alcohol

The commonest alcohol (see *Alcohols*) and therefore often called simply 'alcohol'. It is used as a solvent, as a fuel and in the manufacture of many other organic compounds.

Ethylene

C_2H_4 , a colourless flammable gas; first stable member of the olefin series of hydrocarbons.

Ethylene-Acrylic Terpolymer

This terpolymer is formed from methyl acrylate, ethylene and a carboxylic monomer. It has properties comparable to those of an acrylic.

Ethylene Dichloride

A liquid produced by the addition of chlorine to the ethylene double bond. It is reacted with sodium polysulphide to produce polysulphide polymers, trade name Thiokol.

Ethylene Glycol

A colourless, syrupy, sweet-tasting liquid; the synthetic fibre Terylene is made by condensation polymerisation of terephthalic acid and ethylene glycol.

Ethylene-Propylene Rubber

A stereospecific polymer produced by the copolymerisation of ethylene and propylene with Ziegler-type catalysts.

Ethylene-Propylene Terpolymer

An elastomer consisting of a terpolymer of ethylene, propylene and a diene, e.g., dicyclopentadiene.

Ethylene Thiourea

ETU, accelerator.

Ethylene-Vinyl Acetate

A copolymer of ethylene and vinyl acetate which processes like a plastic and performs like a rubber. The copolymer, of which there are various grades, is similar to rubber in softness and flexibility but can be injection moulded without vulcanisation.

ETMQ

6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, antidegradant – staining.

ETU

Abbreviation for ethylene thiourea, an accelerator.

EU

Abbreviation for polyether urethane.

EV

Abbreviation for efficient vulcanisation.

EVA

Abbreviation for ethylene-vinyl acetate.

Evaporation

Conversion of a liquid into vapour, without necessarily raising the temperature to the boiling point of the liquid; solutions are concentrated by evaporating off the solvent. One method of concentrating natural rubber latex is by the controlled evaporation of the liquid in which the rubber particles are dispersed.

Evaporative Light Scattering

This is used in polymer analysis, it involves the removal of solvent from a solvated polymer as it elutes down a drift tube and the isolated polymer particles then scatter light from the light source allowing molecular weight to be calculated.

Even Speed

When the rolls of a mixing mill or calender are travelling at the same surface speed they are said to be running at even speed. See *Friction Ratio*.

Exothermic

Accompanied by the giving off of heat.

Expanded Rubber

A form of cellular rubber in which the cells are non-intercommunicating, self-contained units. It has low thermal conductivity. Expanded rubber is buoyant and does not absorb water and was therefore initially used in both the soft rubber and ebonite forms in the construction of lifebuoys and other marine buoyancy equipment. The most commonly used polymer is now polyurethane for both flexible and rigid systems.

These products are most usually formed by moulding or extrusion processes and have a solid outer skin around the cell structure. Organic blowing agents are used for this type of process.

Extender

In the broadest sense, any compounding ingredient added to rubber to reduce the cost of the compound. The use of the term is now usually limited to certain cheap petroleum rubber processing oils.

Extending Filler

A filler which is added to a rubber with the sole object of cheapening the compound. *See Reinforcing Fillers.*

Extensibility

A term descriptive of the extent to which an elastomer can be deformed by the application of a tensile stress.

Extension

- (1) In tensile testing of rubber, another term for elongation.
- (2) In rubber compounding, the addition of a high proportion (40-50 phr) of a rubber processing oil to an elastomer with the object of improving the processibility of a tough polymer and/or cheapening the compound.

Extensivity Factor

The surface area of a filler per cubic centimetre coming into interfacial contact with the rubber.

Extraction

A process for removing certain constituents of a mixture by treating it with a solvent which dissolves only the desired constituents.

Extrudate

A term descriptive of the product of extrusion especially where no particular shape is specified.

Extruder

A machine for carrying out the processing operation of extrusion; also historically termed tubing machine and forcing machine. The majority of extruders use an electrically-driven screw to force the rubber to the head of the machine, but a piston-operated type has recently been introduced. *See Barwell Preformer/Ram Extruder.*

Extrusion

The process in which unvulcanised elastomer or thermoplastic compound is forced through a die to give long lengths of a definite cross-section. The compound is normally warmed by working on a mill but in some modern machines this is unnecessary and cold stock may be used. The feed strip is led into a hopper situated over a screw which compacts the stock and forces it up to the head of the machine and through the die. In the production of tubing a core-bridge is fitted in the head. The extrusion principle is used in hose

and cable covering and in the operation of straining.

F

Fabric

A structure of interwoven or interlaced textile fibres, yarns or threads.

Factice

A compounding ingredient with the main functions of a processing aid or extender. Dark factice (sulphur factice) is produced by heating certain unsaturated oils (principally rape seed oil) with sulphur. White factice (sulphur chloride factice) is prepared by treating rape seed oil with sulphur monochloride at normal temperatures. Factice is still sometimes referred to as rubber substitute or simply 'sub', but these terms are not recommended.

In appearance factices are friable, slightly elastic materials, the colour ranging from white to dark brown depending on the method of manufacture. Factice has been popular for many years as a low-gravity resilient filler, finding particular application in spread sheeting compounds vulcanised by the cold cure method, and in erasers where the factice content may be as high as 300 phr. In recent years work has been done on the use of factice in quite small amounts, since it has been found to have accelerating powers. Factices are available for use with most synthetic rubbers: SBR, polychloroprene, butyl, nitrile and chlorosulphonated polyethylene.

Factories Acts

The legislation which sets out, for the United Kingdom, the regulations governing industrial health, safety, welfare, hours of work, reporting of accidents, etc.

Fahrenheit

A temperature scale widely used in the US industry. On this scale 32° is the freezing point of water and 212° the boiling point. *See Celsius.* To convert x °F to y °C:

$$\frac{5(x \text{ °F} - 32)}{9} = y \text{ °C}$$

Farina

Potato starch used as a finishing agent on proofed cloths.

Fatigue

The weakening of an elastomer or rubber article due to subjecting it to a continually repeated series of distortions stretching, compression, bending, or any combination of these.

Fatty Acids

A term applied to the whole group of saturated and unsaturated monobasic aliphatic carboxylic acids. *See Oleic Acid and Stearic Acid.*

FDA

Food and Drug Administration (USA); sets regulations for materials that come into contact with food.

FEA

Abbreviation for Finite Element Analysis.

FEF

Fast extrusion furnace grade of carbon black. *See Furnace Black.*

Festoon

An assembly of weighted or tensioned rollers for suspending long lengths of rubber or fabric in a limited space. It may be arranged to store a limited amount of fabric during temporary stoppage of a following process and may then be termed an 'accumulator'.

Fibre

Often used nowadays in the sense of textile material, e.g., natural fibre, man-made fibre, but correctly it refers to the comparatively short thread (staple fibre) of natural textiles. A fibre is fine, flexible, and very long in relation to its thickness.

Ficus

A genus of trees yielding a good type of natural rubber, of little commercial importance nowadays. The *Ficus elastica* is the well-known ornamental rubber plant.

FID

Flame ionisation detector.

Field Latex

Natural rubber latex, freshly tapped, before the addition of preservatives or before concentration.

FIFO

The first-in, first-out principle of injection moulding; the material first plasticised is the first material to be injected.

Filament

A fine wire or thread. In textile technology the fine thread formed at the spinnerettes in the manufacture of synthetic and man-made fibres. See *Continuous Filament*.

Filastic Process

A method of impregnating textile fibres with latex. There is no natural affinity between the textile fibre and the latex particle; this is overcome by making the latex slightly acid and the surface of the textile strongly alkaline.

Filler

A compounding ingredient added to rubber for the purpose of either reinforcing or cheapening the compound. See *Reinforcing Filler and Extending Filler*.

Fine Hard Para

The best grade of wild rubber formerly obtained from Hevea trees indigenous to the Amazon Valley, and originally exported from the town of Para.

Finite Element Analysis

A mathematical technique developed originally for predicting the stress-strain behaviour of complex shaped objects which do not lend themselves to simple analysis. The object is broken down into a large number of simple units or elements whose behaviour can be more simply calculated. The net behaviour of all the elements is then added together to give the gross behaviour of the component. The range of applications is now very wide and includes thermal behaviour, high speed impact and fatigue. Developments in the capabilities of modern computers have opened this techniques up to a much larger spectrum of the industry and its potential has allowed designers much greater freedom and shortened the time to market of new products.

FIPG

Abbreviation for formed-in-place gasket. See *Flowed-In Gasket*.

Fire Retardant

An additive used in rubber compounding to reduce the fire hazard.

Firing Up

Another name for burning.

Fischer-Tropsch Process

A process for the manufacture of hydrocarbon oils, alcohols, fatty acids, etc., from coal.

FKM

Abbreviation for fluorocarbon rubber.

Flammability

The preferred term for what is generally called 'inflammability'; it reduces the possibility of confusion between 'non-flammable' and 'inflammable'.

Flap

A shaped strip of rubber fitted between the beads of certain pneumatic tyre assemblies to protect the inner tube from damage by the beads and the wheel rim.

Flash

Another term for spew.

Flash Point

The temperature at which a liquid heated in a special test apparatus gives off sufficient vapour to flash momentarily on the application of a small flame.

Flat Bark Crepe

The lowest grade of plantation crepe rubber. It is made from earth scrap (rubber from latex which has fallen on the ground) and any other plantation salvage scrap. It was formerly called Rolled Brown Crepe.

Flat Curing

When the curve of a particular property (usually tensile strength) of vulcanised rubber plotted against time of vulcanisation shows a levelling off or only a slow fall after the maximum has been reached, the compound or compounding ingredient under test is said to be flat curing, to have flat curing characteristics or to show a plateau effect.

Flex Cracking

Repeated bending or flexing of a rubber causes cracks to develop in that part of the surface where tension stress is set up during flexing or, if this part of the surface contains a crack, causes this crack to extend in a direction perpendicular to the stress. Certain soft vulcanisates, for instance those prepared from styrene-butadiene rubber, show marked resistance to crack initiation, but it is possible for these vulcanisates to have a low resistance to growth (propagation) of cracks. It is important, therefore, to measure both the resistance to crack initiation by flexing and the resistance to crack propagation.

There are various test methods, one being the De Mattia Flex Test method which is suitable for rubbers that have reasonably stable stress-strain properties, at least after a period of cycling, and do not show undue stress softening or set, or highly viscous behaviour. The results obtained for some thermoplastic rubber should be treated with caution if the elongation at break is below,

or close to, the maximum strain imposed during the test. BS ISO 132, Determination of resistance to flex cracking.

Fleximers

Compounds of plastic resins or rubbers used for flooring and ships' decking.

Flexometer

An instrument for the measurement of heat build-up in vulcanised rubber by a forced vibration method.

Flocculation

That type of coacervation in which are formed large numbers of very small agglomerates of polymer particles, termed floccs.

Flooring

The use of rubber as a floor covering (continuous sheets, tiles or mats) was one of its earliest applications but is now being challenged by a variety of plastics, mainly PVC.

Flowed-In Gasket

A gasket made *in situ* by extruding the sealing compound on to a rotating component thereby forming a layer of compound which, after curing, becomes a gasket, solid or cellular as desired. Also known as 'formed in place gasket'.

Flowers of Sulphur

A form of sulphur mainly of the rhombic variety but containing a proportion (up to 30%) of insoluble sulphur.

Fluid Bed Vulcanisation

A continuous process for the vulcanisation of extruded sections. The heating medium is a bed of tiny glass spheres fluidised by steam or hot air.

Fluidisation

The technique of passing a gas into a solid which is in the form of tiny granules and thus making the solid behave as if it were a dense, viscous liquid. Fluidised materials may be easily piped from place to place, but a particular application in the rubber industry is the vulcanisation of extruded sections. *See Fluid Bed Vulcanisation.*

Fluorinated Elastomers

Elastomers containing fluorine, also called fluorelastomers. These combine the good physical properties of organic elastomers with the thermal stability of inorganic materials. Trade names are Viton, Fluorel, Kel-F and Technoflon.

FMQ

Abbreviation for fluoro methyl silicone.

Foam Rubber

A product produced exclusively from a liquid base, e.g., latex. Latex foam has an interconnecting cell structure and is most commonly used for cushioning applications.

Foamback

A thin layer of rubber or plastic foam applied to knitted or woven fabrics, used mainly in the garment trade and in carpet backing.

Foaming Agent

A substance which assists in holding the foam structure produced by whipping or frothing in the manufacture of latex foam rubber.

Footwear

Rubber, thermoplastic elastomers and PVC are employed in the manufacture of a wide range of footwear: trainers, shoe soles and Wellington

boots for both industrial and sports uses. *See Direct Moulding of Footwear.*

Forced Vibration

The motion resulting from the application to a rubber specimen of an oscillating force.

Forcing

Another name for extrusion.

Formaldehyde

HCHO, a gas with an irritating smell. It is made industrially by the oxidation of methyl alcohol, and is used in the manufacture of phenol-formaldehyde and urea-formaldehyde resins and plastics.

Former

Any specially shaped device on which a rubber product may be assembled, on which a product may be fitted to bring it nearer the cured shape or on which an article may be produced by dipping

Formic Acid

HCOOH, an organic acid which may be used in diluted form as the latex coagulant in the production of natural rubber.

Formula

- (1) (Mathematics) A rule expressed in algebraic symbols;
- (2) (Chemistry) The representation of the kind and number of the atoms in a molecule of a compound, by means of letters and figures;
- (3) (Rubber Technology) The statement of the kinds and amounts of elastomers and compounding ingredients which comprise a rubber compound.

FPM

Abbreviation for fluorocarbon rubber.

Fractional Coagulation

Coagulation of natural rubber latex by stages with the object of removing the yellow colouring matter in the first fraction. The latex in the second fraction produces a white crepe rubber. *See Bleaching Agent.*

Frasch Process

A method of obtaining sulphur from underground deposits where normal mining is not possible. In Louisiana and Texas the sulphur lies beneath a layer of quicksand through which is driven a pipe carrying hot water to melt the sulphur and compressed air to drive it up to the surface.

Free Radical

A radical which can exist in the free or uncombined state. Such radicals are extremely reactive with themselves and with other neighbouring molecules. Free radicals are considered to take part in many reactions of importance to the rubber industry - vulcanisation, oxidation, ageing, polymerisation, etc.

Free Sulphur

The amount of sulphur which has not combined with the rubber during the vulcanisation reaction. The determination of the free sulphur content is widely used in assessing the state of cure of a rubber product. The addition of the free sulphur curve to the modulus and tensile/time curves of the particular compound enables the state of cure of the vulcanised product to be estimated.

French Chalk

A hydrated magnesium silicate in the form of a soft white powder. It is used as a dusting agent,

as an embedding agent in open steam vulcanisation and as an extending filler. Also called talc or soapstone and often referred to simply as 'chalk'.

Freshening

- (1) Generally, the restoration of the tack of an uncured rubber surface by washing with solvent.
- (2) Used in the sense of warming up rubber compound prior to calendaring or extrusion.

Friction

See Coefficient of Friction.

Frictioning

A calendaring process in which hot soft unvulcanised rubber compound is applied to a fabric. The cloth passes between the bottom and middle bowls of a three-bowl calender; it travels at the speed of the bottom bowl and the faster middle bowl shears the rubber into the pores of the fabric.

Friction Ratio

The ratio of the relative surface speeds of adjacent mill or calender rolls; usually given in the form 1.25:1, where the 1 represents the speed of the slower roll.

Frosting

A dulling of the surface of vulcanised rubber articles considered to result from the action of atmospheric ozone, particularly in conditions of high humidity. It is quite different from blooming.

Frozen Rubber

Raw natural rubber which has been kept at temperatures lower than about 10 °C (50 °F) becomes extremely hard or 'frozen' and must be softened by heating before it can be processed satisfactorily.

FSA

Food Standards Agency (UK).

FT

Abbreviation for Fine Thermal Carbon Black. The only form of thermal black now in common use is Medium Thermal (MT) black. *See Thermal Black.*

Furnace Black

A type of carbon black produced by burning natural gas or oil in a large furnace with a supply of air much lower than that required for complete combustion. The main types are super abrasion (SAF), intermediate super abrasion (ISAF), high abrasion (HAF), fast extrusion (FEF), general purpose (GPF), conductive (CF) and semi-reinforcing (SRF).

FVMQ

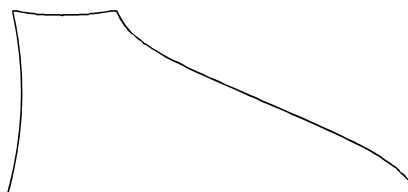
Abbreviation for fluoro vinyl methyl silicone.

G

Garvey Die

A small die of base of approximate dimensions 9/16 in by 1/4 in, having a shape approximately that of a vertical section through a shoe last as per the figure below. It is used in a laboratory extruder to evaluate the extrudability or processibility of a rubber compound. ASTM

D2230 gives full details of the die and procedures used.



Gas Chromatography

GC is used in rubber analysis to obtain polymer type information by use of a pyrolysis approach, also to identify some additives.

Gasket

A flat sheet or shaped section of rubber compound or rubber textile composite fitted between two metal faces to make a fluid-tight joint.

Gauge

- (1) Any instrument for measuring, e.g., pressure gauge, thickness gauge, strain gauge.
- (2) Sometimes used to mean 'thickness', e.g., a 'gauge' of 3 mm.
- (3) Also used as a verb, to measure thickness.

Gauge Pressure

Pressure shown by a gauge; pressure above the pressure of the atmosphere. *See Absolute Pressure.*

Gauze

- (1) A light-weight fabric of open texture.
- (2) A similarly constructed arrangement using wire instead of textile threads.

GC-MS

Gas chromatography-mass spectroscopy is used to obtain extensive compositional information on rubbers. It can identify minor components of the sample such as the breakdown products of the cure system and the antidegradants.

Geer Oven

An electrically heated oven supplied with circulating kit, originally used in accelerated ageing tests.

Gehman Test

A method of determining the stiffening of vulcanised rubber at low temperatures by submitting the rubber to torsion, as in BS 903-A13.

Gel

Chemically, a colloidal solution which has set to a jelly. The term has a special significance in rubber technology. *See Bound Rubber, Carbon Gel.*

Gelation

Setting to a jelly: in latex processing it is a type of coagulation in which very little separation of the aqueous phase takes place during the gel formation.

Gel Permeation Chromatography

The molecular weights of high polymers are normally measured by gel permeation chromatography (GPC) where both an average molecular weight and a molecular weight distribution are determined. A solution of the polymer is prepared which is then passed through a chromatographic column. The speed at which

the solution passes through is determined by the molecular weight of the polymer. At the end of the column there is a detector which establishes the concentration of the polymer in the solvent. Detectors can be based on viscosity, infrared absorption spectra or light scattering.

Gland

A device for preventing leakage at the point where a reciprocating or rotating shaft emerges from a cylinder or vessel containing a fluid under pressure.

Glass Hardening

See Glass Transition.

Glass Temperature

Another name for glass transition temperature.

Glass Transition

On lowering the temperature to which an elastomer is exposed the resulting changes are simple stiffening, crystallisation and glass transition (second order transition) shown by a rapid change in physical properties within a narrow temperature range. It is convenient to characterise a particular vulcanisate by the temperatures at which the stiffness is double or ten times that at room temperature, T_2 and T_{10} , and also by the temperature (T_g) at which the stiffness changes most rapidly.

Glass Transition Temperature

Also termed 'glass temperature' or T_g . The temperature at which the stiffness of an elastomer subjected to low temperatures changes most rapidly. If the glass temperature is close to the operational temperature the material will be 'leathery' in its behaviour rather than rubber-like. Approximate glass transition temperatures for different polymers are NR -70 °C; SBR -52 °C; IIR -75 °C; PCP -40 °C and silicone rubber -85 °C.

Glycerine

Glycerin, glycerol. A thick, syrupy, sweetish liquid used as a plasticiser, a mould lubricant and as a raw material for the manufacture of glyptal resins.

Glyptal Resins

Resins used as surface coatings prepared from glycerol and phthalic acid, now termed alkyd resins.

Goodyear

Charles Goodyear (1800-1860) is acknowledged by some as the discoverer of vulcanisation by the heating of a rubber-sulphur mixture. Many others including Ludersdorf and Hancock were also researching means to impart long term stability to rubber at around the same time. Goodyear did not patent his discovery until 1844, whereas Hancock obtained a British Patent for a process of vulcanisation in 1843.

Gooseneck Press

A type of daylight press in which the frame holding the platens is in the shape of a gooseneck or swan-neck thus permitting full access to three sides of the platen area.

Gough-Joule Effect

When rubber is stretched adiabatically (without heat entering or leaving the system) heat is evolved. The effect was originally discovered by

Gough in 1805 and re-discovered by Joule in 1859. *See Wiegand Pendulum.*

GPC

Abbreviation for gel permeation chromatography.

GPF

Abbreviation for general purpose furnace carbon black. *See Furnace Black.*

GPO

Abbreviation for copolymer of propylene oxide and allyl glycidyl ether.

Graft Copolymer

A copolymer in which chains or branches of one polymer are grafted on to the main chain of the other polymer. *See Block Copolymer and Heveaplus.*

Grain

Difference in physical properties along and across a section of rubber compound resulting from the passage of the rubber through a mill nip, a calender nip or through an extruder die. *See Calender Grain.*

Green

'Raw' or 'uncured'.

Green Budding

An improved technique of bud grafting which may reduce by up to twelve months the non-productive period in the life of the rubber trees, i.e., between planting and first tapping. Green seedlings of 1/4 in to 1/2 in diameter, perhaps only three months old, are used as the rootstock in place of 12-month-old woody seedlings. Instead of using budwood as the grafts, dormant buds derived from green cuttings are used.

Grinding

Passing rubber compound through a tight nip of either a mill, a calender, or more usually a refiner to break down any agglomerates of compounding ingredients. Vulcanised scrap rubber may be reduced to crumb rubber by a grinding process.

Ground Rubber

Another term for crumb rubber.

Guanidine

Guanidine itself is imido-urea, but the term 'guanidines' usually refers to the accelerators of vulcanisation, diphenylguanidine and diorthotolylguanidine.

Guayule

Rubber obtained from the shrub, *Parthenium argentatum*, native to north central Mexico and the adjacent part of Texas. The rubber is not obtained by tapping but by harvesting the shrubs and crushing the woody tissue to separate it from the rubber. Intensive research, started in 1942, has not succeeded in making guayule competitive with Hevea rubber, and since 1962 there has been no commercial production.

Gum

Jargon for any rubber compound during processing. *See High Gum and Pure Gum.*

Gutta Percha

A hard resinous thermoplastic substance of the same chemical composition as rubber hydrocarbon but having the *trans*-structure. *See Cis-trans Isomerism.* Formerly extensively used for the insulation of submarine cables (now superseded by polyethylene) and in the early manufacture of golf balls (now superseded by

ionomers), but has now all but disappeared from the world market.

H

HAF

Abbreviation for high abrasion furnace carbon black. *See Furnace Black.*

Hancock

Thomas Hancock (1785-1865) is designated the 'father of the rubber industry' and to him Great Britain is indebted for the honour of being the first country to manufacture rubber successfully as a large-scale project. His first major discovery, in 1819, was the process of masticating and mixing raw rubber. His subsequent claim, in his Personal Narrative published in 1857, that this 'was unquestionably the origin and commencement of the India-rubber manufacture, properly so called', has been amply verified since.

Hank

A length of yarn which has been wound on a reel; also the standard length of yarn (which varies with different textiles) used in calculating yarn counts.

Hardness

Since all practical methods of measuring the hardness of rubber involve measuring the resistance to indentation, hardness may be defined simply as 'resistance to indentation'. Hardness is an expression of the elastic modulus of the rubber. More specifically, the load required to press a ball of given diameter to a given depth into the rubber is proportional to its elastic modulus. *See Hardness Testing, Pusey and Jones Plastometer, Microhardness Testing.*

Hardness Testing

The determination of the hardness of rubber. Instruments are either dead-load (non-portable) or spring-loaded (pocket) type (BS 903-A26). *See Durometer, IRHD.*

Hard Rubber

Another term for ebonite.

HBS

Abbreviation for the organic accelerator cyclohexylbenzothiazole sulphenamide, also abbreviated to CBS.

HCR

Abbreviation for high consistency rubber, e.g., a type of so-called solid silicone rubber.

HDI

Hexamethylene diisocyanate. *See Isocyanate.*

Heat

(1) Energy possessed by a substance in the form of kinetic energy of its molecules. Gain or loss of heat may result in a rise or fall in temperature of the substance, or in a change of state (solid to liquid to gas). The term 'heat' is sometimes used in industry where temperature is meant. *See Latent Heat and Sensible Heat.*

(2) In the rubber industry a 'heat' is a number of products comprising a press or autoclave load vulcanised at the same time.

Heat Build-Up

The rise in temperature which occurs when rubber is deformed. The energy used in deformation is not fully returned when the rubber recovers its original shape and the 'lost' energy shows as a rise in temperature of the rubber. *See Flexometer, Hysteresis and Resilience.*

Heat Capacity

Heat or thermal capacity is the ratio of the change in heat energy of a unit mass of a substance to the change in temperature of the substance; like its melting point or boiling point, the heat capacity is a characteristic of a substance. The measurement of heat and heat capacity is called calorimetry. In the metric system, heat capacity is often expressed in units of calories per gram per degree Celsius (cal/g/°C); in the imperial system, British thermal units per pound per degree Fahrenheit (Btu/lb/°F) are often used. Because of the definitions of the calorie and Btu, these two heat capacity units are equivalent; the heat capacity of pure water is 1 cal/g/°C and 1 Btu/lb/°F.

Heat Distortion Temperature

The temperature at which polymers cannot maintain structure or sag, it is close to the glass transition.

Heater

A term applied to a variety of vessels used in vulcanising rubber articles. *See Autoclave and Dry Heat Cure.* Also refers to heater bands used on extruder barrels and similar machines.

Heat History

In the processing of rubber compounds (mixing, rewarmings, calendaring, extrusion) heat history is a term used to indicate the total heat which has been received by the compound, particularly the temperatures reached by the rubber and the time it has been held at these temperatures. *See Scorching.*

Heat-Sensitive Latex

Latex used in the manufacture of dipped goods using a heated former. The latex is heat-sensitised by addition of polyvinylmethyl ether (PVME) or certain polyglycols and the action of the hot former causes a layer of coagulated rubber to be deposited.

Hevea Brasiliensis

The most important species of the Hevea genus of the order Euphorbiaceae. All but a tiny proportion of the world supply of natural rubber is obtained from the Hevea tree originally native to the Amazon valley but now cultivated on a plantation scale in Indonesia, Thailand, Malaysia and a number of other equatorial countries.

Heveacrumb

Natural rubber prepared to technical specifications by a process which converts the coagulum into finely divided granules which are subsequently dried and compacted into bales. The agent which brings about the crumbling is castor oil.

Heveaplus

The generic name of a series of raw materials made by intimate mixture or chemical combination of natural rubber and other polymeric or resinous substances.

Hexamethylene Tetramine

Also known as hexamine, hexa or HMT, a once-popular aldehyde-amine type of accelerator for natural rubber, now used as a vulcanising agent for polyacrylate rubbers.

Hexane

A solvent for natural and most synthetic rubbers except nitrile. It is a petroleum spirit existing in five isomeric forms; normal hexane has a boiling point of 69 °C.

HF or High Frequency Heating

Another term for dielectric heating.

HFA

Abbreviation for higher fatty acids.

HFP

Abbreviation for hexafluoropropylene.

High Gum Compound

A rubber compound containing elastomer, curatives and the minimum of fillers. Also called a pure gum compound.

High-Level Tapping

Another term for ladder tapping.

High Polymer

A chemical compound consisting of groups of atoms which are repeated almost indefinitely until very high molecular weights are achieved.

High Styrene Resins

Copolymers of styrene and butadiene with styrene content of 75-90%. They are organic non-black reinforcing materials and find their greatest application in leather-type shoe soles. They facilitate the easy processing of relatively hard compounds due to a high degree of thermoplastic behaviour.

High Yielding

A term applied to clones of Hevea trees which give a much higher yield of latex than ordinary rubber trees. The average yield in the 1950s was under 500 kg of rubber per hectare per annum. It is now more common to achieve a two- to three-fold increase on these figures from modern planting material.

HMT

Abbreviation for hexamethylene tetramine.

HNBR

Abbreviation for hydrogenated nitrile rubber.

Hold

The part of a cure schedule during which the temperature is held at a specified figure.

Holland Cloth

A plain weave cotton fabric filled with a starchy substance to give it a glossy, non-adherent surface. It was formerly much used to preserve a fresh tacky surface on unvulcanised rubber (tyre, tube and belt repair patches) but has been almost completely superseded by polyethylene film.

Holofol

A process for making hollow rubber articles from a single sheet of calendered unvulcanised rubber. The surface of the sheet is semi-vulcanised and the application of a swelling agent causes the sheet to split thus forming the hollow article, the vulcanisation of which is completed thereafter.

Homopolymer

Polymer resulting from the polymerisation of a single monomer.

Hooke's Law

Within the limits of elasticity of a material, tension is proportional to extension, or strain is proportional to the stress producing it.

Hose

Flexible tubing for the conveyance of fluids (fluidised solids, liquids or gases); the construction, which includes textile and/or wire reinforcement, varies according to the pressure and the type of fluid.

Hose is of two main types, delivery hose for handling fluids under pressure, and suction hose where the fluids are conveyed at pressures lower than that of the atmosphere. Hoses may convey water, steam, compressed air, chemical liquids and gases, crude oil, organic solvents, edible fluids, etc. Some types of hose are required to withstand internal pressures as high as 170 MPa at temperatures as low as ~60 °C or as high as 150 °C. One development is a floating hose whereby tankers can lie offshore and discharge to the land terminal through the hose, without the need for a deep-water jetty.

The three basic parts of a hose are the rubber lining, the reinforcing element and the rubber cover. Reinforcement includes fabric, braided yarns and wire braids together with wire helices; the rubber lining is made from an elastomer chosen to suit the fluid being conveyed, while the cover compounds are designed to give maximum abrasion resistance, to resist external heat and the swelling effect of oils and solvents. *See Lead Moulded Hose.*

Hot Air Curing

Another term for dry heat cure.

Hot Mastication

Mastication which is carried out at temperatures exceeding 115 °C. In hot mastication, the plasticising effect results from oxidative reactions. *See Cold Mastication.*

HPLC

High performance liquid chromatography, used in analysis to identify and quantify additives.

HSE

Health and Safety Executive (UK).

H-Test

A method of measuring the adhesion between tyre cord and rubber. The test takes its name from the shape of the test specimen, two end strips of rubber with the interconnecting cord forming an H-shape.

HTV

Abbreviation for high temperature vulcanising.

Humidity

See Relative Humidity.

Hydraulic Accumulator

See Accumulator.

Hydraulic Pressure

Pressure resulting from the application of a force to a liquid medium, usually water or oil. Since liquids are virtually incompressible, applied forces are transmitted equally in all directions. In the rubber industry hydraulic pressure is supplied at various pressures (e.g., 2, 7, 14 MPa) depending on the requirements of the operation.

Hydraulic Ram

The solid metal cylinder or plunger which is moved by hydraulic pressure to operate the apparatus, e.g., daylight press, autoclave press, bale splitter, etc. The ram diameter and hydraulic pressure determine the press tonnage.

Hydrocarbon

A chemical compound consisting solely of the elements hydrogen and carbon.

Hydrogen Ion Concentration

The number of grams of hydrogen ions per litre of solution; it is a measure of the acidity or alkalinity of a solution. The pH of a solution is $-\log(\text{hydrogen ion concentration})$ and ranges from 0 (highly acid) through 7 (neutral) to 14 (highly alkaline).

Hydrometer

An instrument for measuring the specific gravity of liquids. It consists of a weighted bulb with a thin graduated stem; it floats vertically in the liquid to be tested and the specific gravity is read off at the point where the liquid level meets the stem.

Hydrophilic

A substance which readily forms a solution in water or is readily wetted.

Hydrophobic

A substance which forms a solution in water only with difficulty. A hydrophobic surface will not be wetted, the water tending to form large droplets.

Hygrometer

An instrument for measuring the relative humidity of the air.

Hysteresis

When rubber is deformed the difference between the energy input and output is known as hysteresis. The loss of energy is consumed in internal friction and results in heat build-up. *See Hysteresis Loop and Resilience.*

Hysteresis Loop

A graphical representation of the energy loss due to hysteresis.

IARC

International Agency for Research on Cancer. The World Health Organization (WHO) funds the IARC and carries out an ongoing program to evaluate the carcinogenic hazard of many different materials. The IARC classification is: Group 1 Carcinogenic to humans; Group 2A Probably carcinogenic to humans; Group 2B Possibly carcinogenic to humans; Group 3 Not classifiable for carcinogenicity to humans; Group 4 Probably not carcinogenic to humans.

ICP

Inductively coupled plasma spectroscopy, used to detect metals in rubber analysis.

ICR

Abbreviation for Initial Concentration Rubber, a form of natural rubber made by the Decan process.

ICR-NAT

Former trade name for initial concentration rubber. *See ICR.*

ICT

Imaging chemiluminescence technique. Chemiluminescence analysis is suitable for studying the early stages of the thermal oxidation of rubbers. A weak emission of light formed by chemical reactions appears during the oxidative degradation of hydrocarbons. This technique can be used to depth profile the oxidation of rubbers.

IIR

Abbreviation for isobutylene-isoprene rubbers, popularly known as butyl rubbers.

Impact Resilience

See Rebound Resilience.

Impregnation

The saturation of the individual fibres of a textile with rubber. The rubber may be in the form of a rubber solution, a natural or synthetic latex.

India Rubber

An obsolete term for natural rubber. The 'India' is not the present-day India but derives from the West Indies since some of the first commercial rubber was obtained from there in the eighteenth century.

Industrial Processing Cloth

Fabrics used during the processing of rubber, e.g., liners (linings) and wrapping cloths, which do not become part of the finished product.

Inflating Agent

Similar to blowing agent but generally applied only to those gas producing substances used, in pellet form, in moulding hollow balls and toys.

Infrared Radiation

Radiant heat or invisible heat radiation. Infrared rays have wavelengths from approximately 7500 Angstrom units to 1 mm.

Infrared Spectroscopy

This is used to identify the polymer and additive types in rubber analysis.

Injection Moulding

A method of moulding rubber articles by injecting the warm stock into mould cavities. The injection head is similar to an extruder; the mould is fitted in a press of tonnage to suit the size of the product and the number of cavities. There are two preferred arrangements: (1) Extruder and separate injection ram, and (2) Reciprocating screw machines where the screw initially conveys and warms the material and in doing so pushes itself backwards to build up a charge of material in front of it. The screw then moves forward to inject the warm material into the mould. The end of the screw will have a non-return or check valve to prevent material flowing back along the screw under the high injection pressures.

Inner Tube

The part of the pneumatic tyre assembly which holds the inflation air under pressure. It is protected by the outer cover or tyre and, in giant sizes, protected from rim damage by the 'flap'. Inner tubes are primarily made of butyl rubber. Some cycle tubes still use NR. *See Tubeless.*

Inorganic

Of mineral origin; inorganic chemistry is the study of all chemical elements and compounds, except carbon and its compounds; certain simple carbon compounds, e.g., oxides and sulphides,

are included in inorganic chemistry. *See Organic Chemistry.*

Insoluble Sulphur

An amorphous form of sulphur which is insoluble in rubber. It is used in rubber compounds which have to be stored for some considerable time in the uncured state without loss of tack, e.g., repair materials for tyres and belting. Since this form of sulphur is insoluble in the rubber it cannot bloom to the surface. The use of insoluble sulphur also gives some degree of scorch control since it is inactive until it reverts to the soluble form.

Insulation

Prevention of the passage of electricity or heat; also applied to the material which prevents such passage.

Insulator

A material which is a poor conductor of heat or electricity.

Intensity Factor

The specific activity of a filler at its interface with a rubber.

Internal Mixer

A machine for the incorporation of compounding ingredients into rubber or similar materials. Two rotors revolve in an enclosed chamber (*see Open Mill*). It is provided with a hopper for feeding the materials and a sliding or drop-door for discharge of the batch.

Intrusion

A method of injection moulding thermoplastics, which makes large-part moulding possible on injection equipment normally capable of moulding only small parts. The injection moulding machine fills the mould at relatively low pressures. *See Injection Moulding.*

Ion

An electrically charged atom or group of atoms. An atom which loses an electron becomes a positive ion (cation) and one which gains an electron becomes a negative ion (anion). In electrolysis anions are attracted to the anode and cations to the cathode.

Ionomer

A family of plastics, their main constituent is ethylene, the polymer chains being interlinked by metal ions such as sodium, potassium, magnesium or zinc.

IPPD

n-Isopropyl-*n*'-phenyl-*p*-phenylenediamine, antidegradant – staining.

IR

- (1) Abbreviation for isoprene rubbers, synthetic.
- (2) Abbreviation for infrared.

IRHD

Abbreviation for International Rubber Hardness Degrees as measured according to BS 903-A26

Iron

- (1) The unit (1/48 in) formerly used for measuring the thickness of leather and rubber soling.
- (2) A strip of metal used to confine the edges of moulded products, e.g., belting, during press vulcanisation.

ISAF

Abbreviation for intermediate super abrasion furnace carbon black.

ISNR

Abbreviation for Indian Standard Natural Rubber.

ISO

Abbreviation for International Organisation for Standardization. ISO/TC45 is the Rubber Committee of the ISO and ISO/TC61 the Plastics Committee.

Isobutylene

(2-methyl-1-propene). The chief monomer in the manufacture of butyl rubber. It is prepared by thermal cracking of petroleum. *See Polyisobutylene.*

Isocyanates

- (1) Organic substances containing nitrogen and oxygen used in bonding rubber to textiles. They are prepared in the form of a solution of mixed polyisocyanates in an organic solvent, and added to the dip solution for impregnation or to the dough for spreading. It will also cause the polymer to crosslink.
- (2) A reactant used in the production of polyurethane.

Isoelectric Point

The hydrogen ion concentration at which a colloidal system is electrically neutral; the addition of acidic substances to, for example, rubber latex causes the pH value to move towards the isoelectric point, which is the region of minimum stability, and coagulation may take place.

Isomerism

The existence of two (or more) chemical compounds with the same molecular formula but having different properties owing to a different arrangement of atoms within the molecule.

Isomers

Chemical compounds having the same molecular formula. *See Isomerism.*

iso-PBDT

Abbreviation for isopropylthiobenzthiazole, a prevulcanisation inhibitor.

iso-PCBS

Abbreviation for *N*-isopropylthio-*N*-cyclohexylbenzothiazyl-2-sulphenamide, a prevulcanisation inhibitor.

Isoprene

2-Methyl-1,3-butadiene $\text{CH}_2\text{C}(\text{CH}_3)\text{CHCH}_2$. A liquid hydrocarbon of boiling point 34 °C. It is regarded as the unit molecule of natural rubber, which is polyisoprene. Synthetic polyisoprene is marketed under a variety of trade names.

Isotactic

One of the terms coined by G. Natta to describe different arrangements of atoms in long-chain molecules. *See Stereoregular Polymers.*

Isotactic Polymer

Molecules that are polymerised in parallel arrangements of radicals on one side of the polymer chain.

Isotopes

Atoms of the same element (having the same atomic number) but differing in atomic weight. The isotopes of an element all have the same chemical properties. *See Radioactive Isotopes.*

IUPAC

International Union of Pure and Applied Chemistry.

J

Jacket

- (1) The hollow outer wall of a hot-air vulcaniser.
- (2) A removable layer of heat-insulating material applied to any process vessel to reduce heat loss.
- (3) A braided or woven fabric covering for certain types of hose.

Joule Effect

See *Gough-Joule Effect*.

K

Kaolin

See *Clay*.

Katathermometer

A thermometer type of instrument used to measure the cooling power of air on the human body.

Kaysam Process

A process for making hollow articles from latex. A heat-sensitised compounded latex is poured into a hollow non-porous mould which is then rotated about several axes until the latex has gelled on the surface of the mould. See *Rotational Moulding*. Similar to slip casting of ceramics.

Ketones

The series of organic compounds with the general formula $RR'CO$, where R and R' are univalent hydrocarbon radicals, e.g., methyl ethyl ketone; acetone is dimethyl ketone.

Kevlar

Trade name of aromatic polyamide materials produced by DuPont with high strength and impact resistance, hence used as reinforcement.

Kieselguhr

Diatomaceous earth, a fairly pure silica, formed from the skeletons of minute organisms, known as diatoms. In rubber compounding it is used as an inert filler.

Kok-Saghyz

The Russian dandelion, which may contain up to 10% of good quality rubber. The plants are harvested and the rubber obtained in the manner of sugar from sugar beet. It is claimed that the yield per acre approaches that of plantation rubber.

L

Ladder Polymer

A high polymer made by linking the individual molecules in double chains as in a ladder, with consequent improvement in the properties of the polymer.

Ladder Tapping

The opening of a second tapping panel on rubber trees at a height of about 2.5 m above the ground, access to which requires the use of a ladder or long-handled tapping knife.

Lagging

The process of covering surfaces with a material of low thermal conductivity to prevent loss or

ingress of heat. The name is also applied to the material itself.

Lake

A shallow depression on the otherwise smooth surface of a moulded product, generally due to air trapping.

LALLS

Low angle laser light scattering.

Lampblack

An early form of carbon black produced by the burning of oils in a simple type of furnace. It was used in the compounding of rubber mainly as a black pigment; it has little or no reinforcing effect.

Lanolin

A wax-like material obtained from wool grease. It is readily absorbed by the skin and may be used to prevent dermatitis.

Laser Induced Mass Analysis

This is a surface analysis technique, used, for example, in examining causes of bonding failure.

Latent Heat

The quantity of heat required to change the state of 1 g of a substance from solid to liquid (latent heat of fusion) or from liquid to vapour (latent heat of vaporisation) without change of temperature.

Latex

An aqueous colloid/emulsion of rubber particles; can be up to 65% solids content; generally low viscosity compared to polymer solutions. Only rubbers produced by emulsion polymerisation or natural rubber can be found in this form.

The rubber may be natural, in which case the latex is produced by the rubber tree. Latex of the main synthetic rubbers is produced by the technique of emulsion polymerisation. The term 'latex' has been broadened in recent years and a general definition is now 'a stable dispersion of a polymeric substance in an aqueous medium'.

Latices may be classified as natural (from trees and plants), synthetic (by emulsion polymerisation) and artificial (by dispersion of the solid polymer in an aqueous medium). They may also be classified according to the chemical nature of the polymer, e.g., SBR, nitrile, polychloroprene, etc.

Natural latex was used locally in the districts in which it was found for the manufacture of crude articles such as footwear, bottles, balls, ponchos, etc. It coagulates very quickly after leaving the tree (spontaneous coagulation) and large scale use had to await the discovery of methods and materials for overcoming this disadvantage. Further, latex contains only about 30% of rubber and the transport of the 70% of water from the country of origin to the manufacturer is obviously uneconomical; methods of preservation and concentration had therefore to be developed. Once these methods were adopted it was thought that latex processes would supersede many of the conventional dry rubber processes, because technologists have long considered it illogical that the fine fluid dispersion called latex should be converted into an intractable solid which requires further costly treatment before it can be processed. The wholesale adoption of latex

processes in rubber manufacture did not prove feasible, and the direct use of latex is mainly in cellular rubber (latex foam), in dipped goods and in adhesives.

The treatment of latex which is to be shipped as latex differs somewhat from that which is to be made immediately into dry rubber. For short-term preservation it is customary to add a small amount of an anti-coagulant to the tapping cups. Where the latex is to be concentrated and shipped as such, much greater preservation is necessary and additional ammonia is added, up to about 0.7%. For latex foam manufacture most of this ammonia must be removed, and to eliminate the de-ammoniation operation several low ammonia latices have been developed.

Natural latex is concentrated by three main methods centrifuging, evaporation and creaming; electrodecantation once showed promise, but the output of latex concentrated by this method is now negligible.

The principal branches of the latex manufacturing industry are latex foam and dipped goods. *See Dipping, Casting, Adhesives and Rubberised Hair.*

Latex Resorcinol Formaldehyde

A mixture of rubber latex and resorcinol-formaldehyde resin used to treat man-made and synthetic textiles to improve rubber/textile adhesion.

Latex Thread

Rubber thread of circular section (*see Cut Thread*) made by extruding compounded latex through glass nozzles into a coagulating bath of acid.

LATU

Mixed ethyl butyl thiourea, accelerator.

LC-MS

Liquid chromatography–mass spectroscopy.

LCM

Abbreviation for liquid curing medium.

L/D

Abbreviation for length/diameter ratio, commonly used to describe machine barrels and screws.

Leader

A length of woven fabric attached to both ends of a roll of textile which is to be spread or calendered, the purpose being to 'lead in' and wind up the textile without damage.

Lead Moulded Hose

Hose which has been vulcanised by covering it with an extruded lead sheath which acts as a mould. The lead is stripped off after cure. Now superseded by modern continuous curing techniques.

Leaker

Any rubber product, usually rubber/textile composite, which permits the escape of air or other fluids, or permits the passage of fluids to sections of the product where it is undesirable.

Leno Weave

A type of weave in which the weft threads are kept apart, passing through loops formed by double-warp threads. Leno gauze fabrics were used as breakers in early tyres and belting.

LEV

Local Exhaust Ventilation.

Light

A term applied to a moulded product which has failed to fill out the pattern details, showing rounded edges and porosity, either surface and/or internal. It does not necessarily mean that insufficient weight of compound has been used.

Light Ageing

Oxidation of vulcanised rubber catalysed by light, resulting in the production of an inelastic skin and discoloration on the surface.

Lignin

An organic material which occurs in the woody tissues of plants. It is a by-product in the preparation of cellulose for the manufacture of paper, rayon and the cellulose plastics, and its use has been proposed as a reinforcing filler for rubber.

LIM

Abbreviation for liquid injection moulding.

LIMA

Laser induced mass analysis.

Lime

Hydrated or slaked lime Ca(OH)_2 is an inorganic accelerator used in the curing of fluoroelastomers. In conventional sulphur cured polymers it counteracts the retardation of cure due to the presence of acidic substances in a rubber compound. Quicklime (CaO) dispersed in mineral oil or in wax/oil is used as a desiccant to reduce porosity in vulcanisates, particularly in fluid bed curing.

Limestone

A sedimentary rock comprising > 50% calcium carbonate.

Line Pressure

The hydraulic pressure in the pipeline feeding the press, bale-cutter or other hydraulically-operated apparatus.

Liner

A textile material used to prevent the tacky surfaces of unvulcanised rubber from adhering. The liner is often 'treated' to permit easy release from the rubber.

Lining

Another name for liner. Also used with the normal meaning as in chemical plant lining, hose lining, etc.

Linkage

See Valency and Double Bond.

Lip Seal

A gasket which effects a seal by means of a protruding lip.

Liquid Chromatography–Mass Spectroscopy

This is used in rubber analysis. HPLC combined with a mass selective detector enables unknown samples to be analysed.

Liquid Curing Medium

A heated mixture of low melting point alloys or of chemical salts used to provide the heat for curing extrudates in one method of continuous vulcanisation.

Litharge

Lead monoxide, PbO , formerly used as an inorganic accelerator but now mainly used as a vulcanising agent in some polychloroprene

mixes. It has a stiffening effect on uncured rubber mixes and helps in reducing distortion in open steam curing.

Lithium Catalyst

A catalyst made from the metal lithium and used in the preparation of stereospecific polymers.

Lithopone

A co-precipitated mixture of approximately 28% zinc sulphide, 71% barium sulphate and 1% zinc oxide. It is used as an extending filler and white pigment.

Loading

A term used to describe the addition of fillers to a base compound; a heavily loaded mix is one containing a large proportion of fillers. *See High Gum Compound.*

Long-Length Hose

Machine-made hose with braided reinforcement, vulcanised in a lead sheath. It is available in lengths up to 500 ft, compared to the comparatively short lengths of hand-made hose. *See Braided Hose and Lead Moulded Hose.*

Loop Selvedge

A selvedge made by looping the weft thread round a wire (later withdrawn) parallel to the warp, thus leaving a series of small loops along the cloth edge, so that the thickness of the selvedge is the same as that of the body of the cloth.

Low Ammonia Latices

Natural rubber latices in which the customary 0.7% ammonia content has been reduced to 0.2% in conjunction with the addition of a secondary preservative, either sodium pentachlorophenate, zinc diethyl dithiocarbamate or boric acid; such latices have the advantage that the deammoniation process before manufacture is unnecessary.

Low Angle Laser Light Scattering

This analytical technique is used to determine polymer molecular weights.

Low-Temperature Polymer

See Cold Rubber.

Low-Temperature Testing

When testing the effect of low temperatures on elastomers it is rarely sufficient merely to enclose the standard apparatus in a refrigerated chamber; special procedures are necessary. The relevant standard is BS 903: Part A13. Method for determination of stiffness at low temperatures (Gehman test).

LR

Abbreviation for liquid rubber.

LRF

Abbreviation for latex resorcinol formaldehyde.

LSR

Abbreviation for liquid silicone rubber.

LTP

Abbreviation for low-temperature polymer.

Lubricant

Any substance used to prevent rubber sticking to itself or to the surface of a mould. The lubricant may be a dry powder such as soapstone or a liquid such as silicone emulsion. *See Dusting Agent and Mould Release Agent.*

Lupke Pendulum

An apparatus for the determination of resilience by a rebound method. Also called Lupke Impact Resiliometer. *See Resilience.* The relevant standard is BS 903-A 8, Method B, Method for determination of rebound resilience.

Lutoids

Easily deformable gelatinous particles which comprise part of the yellow fraction of fresh natural rubber latex. Lutoids break down on the addition of ammonia and pass into the latex serum.

Linear Polymer

A polymer in which the repeat units are joined end to end with no branches or crosslinks.

M

Macro

A prefix meaning large as in 'macromolecular', applied to the molecule of a high polymer. *See Micro.*

Magnesia

Magnesium oxide, MgO. Heavy calcined magnesia is used as an inorganic accelerator in ebonite; light calcined magnesia is the vulcanising agent (along with zinc oxide) for neoprene compounds.

Magnesite

Magnesium carbonate, inorganic reinforcing filler.

Magnesium Carbonate

MgCO₃ is used as a reinforcing filler for white and light-coloured rubber stocks. Certain types have almost the same refractive index as rubber and are therefore useful in making transparent and translucent vulcanisates.

Magnetic Rubber

This is made by incorporating barium ferrite powder into rubber. The material is suitable for use where a large but thin magnet is required or where a magnet must be flexible to follow a curved surface. In sheet form, magnetic rubber is used for holding small iron or steel objects in place for handling or spraying.

MALLS

Multi-angle laser light scattering.

Mandrel

A solid or hollow metal pole used in the assembly or vulcanising of rubber products, e.g., the assembly of hand-built hose.

Man-Made

Applied to polymers, i.e., rubbers, fibres or plastics, manufactured by a process which reforms a naturally-occurring substance, e.g., rayon from regenerated cellulose. *See Synthetic.*

Manometer

An instrument, generally in the form of a liquid-filled U-tube, for measuring pressures of gases.

Masterbatch

A mix consisting of elastomer and generally only one other ingredient, the proportion of which is much higher than will be present in the final production mix. Masterbatches are used for cleanliness, convenience, accuracy of weighing small quantities of accelerators, etc. Although it

is simpler to write compound formulations initially on the basis of parts per hundred of polymer (phr), masterbatches are usually expressed on a percentage basis. The calculation of the weight of masterbatch required (or of the dispersions used in latex work) is:

$$\text{Weight of masterbatch} = \frac{\text{Weight of ingredient required} \times 100}{\text{Percentage concentration of masterbatch}}$$

Mastication

The softening of rubber by milling to enable the addition of compounding ingredients to be made. Mastication may be done on an open mill, an internal mixer or in a plasticator. *See Cold Mastication and Hot Mastication.*

Matrix

- (1) A mould or removable section of a mould used in the repair or retreading of pneumatic tyres. Derived from the printing industry where it refers to the mould used for casting type.
- (2) Also used with its normal meaning of 'that in which anything is embedded', e.g., in a rubber mix the rubber is the matrix in which the compounding ingredients are dispersed.

Maturation

The process, now obsolescent, of permitting the coagulum of natural rubber to mature in the wet state before washing or smoking. Due to bacterial activity various natural accelerators are produced and the resulting rubber has a faster rate of cure than that prepared by the conventional method.

MBI

2-Mercaptobenzimidazole, antidegradant – non-staining.

MbOCA

Methylene bis-ortho-chloroaniline, crosslinking agent for polyurethane.

MBS

2-(Morpholinio) benzothiazole, accelerator.

MBT

Abbreviation for mercaptobenzothiazole, an organic accelerator.

MBTS

Abbreviation for dibenzthiazyl disulphide, an organic accelerator of the thiazole class.

MDHS

Methods for the Determination of Hazardous Substances (HSE documents, UK)

MDI

Diphenylmethane diisocyanate. *See Isocyanate.*

MDR

Abbreviation for moving die rheometer.

Mechanicals

Originally this term was applied to all rubber products used in association with machinery but its application has been widened in some respects and narrowed in others.

Mechano-Chemical

A term describing certain combinations of mechanical action and chemical reactions exemplified by, but not confined to, the mastication of elastomers. In this process it is considered that the deforming forces break the molecular chains into two pieces, with formation of free radicals at the chain ends. Such radicals may recombine, or combine with oxygen or other

radical acceptor to form stable substances, giving a permanent reduction in the molecular weight of the polymer.

MEK

Abbreviation for methyl ethyl ketone.

MEL

Maximum Exposure Limit. *See Occupational Exposure Limits.*

Mercaptobenzothiazole

An organic accelerator sold under a variety of trade names. It was first introduced in about 1920 and gained wide acceptance especially in tyre compounds due to its flat curing characteristics and the good age resistance it imparts to its vulcanisates.

Mesh

The opening between the wires of a screen, commonly used to describe particle size, e.g., of crumb rubber. The finer the mesh the more openings it will have per unit of width, i.e., 30 mesh describes 30 holes/inch.

Metal Poisoning

The action of certain metals (e.g., copper) on unsaturated rubbers, primarily natural rubber, is to catalyse the oxidative degradation of the polymer. The metal must be in an ionic form, i.e., straightforward contact with the metal such as a seal with a copper pipe will not promote such degradation.

Methane

CH₄, marsh gas, fire damp. It is the first hydrocarbon of the paraffin series.

Methanol

Methyl alcohol, CH₂OH, also called wood alcohol or wood spirit, since it was formerly obtained from the destructive distillation of wood. It has also been synthesised from carbon monoxide and hydrogen or by fermentation of various sugar containing crops. Used as a part replacement for petrol in Gasohol to deliver a more environmentally friendly fuel, i.e., from renewable resources.

Methyl Cellulose

A thickening agent for latex.

Methyl Ethyl Ketone

An organic solvent, used particularly for making nitrile rubber cements.

Methyl Group

The organic radical CH₂.

Methyl Rubber

A synthetic elastomer produced by the polymerisation of dimethylbutadiene. It was manufactured in Germany during World War I to overcome the shortage of natural rubber.

Methylene Bis-Orthochloroaniline

MbOCA, crosslinking agent for polyurethane.

Metrolac

A hydrometer with a special scale, used for the determination of the approximate dry rubber content of latex.

Mica

The mineral muscovite, mainly an orthosilicate of aluminium and potassium, finely ground and used as a lubricant in rubber moulding and as an extended filler in latex compounds.

Micelle

In latex technology, a submicroscopic aggregation of oriented molecules; in polymer technology it is synonymous with crystallite. The term is also applied to the aggregates of soap molecules formed in emulsion polymerisation.

Micro

A prefix meaning very small or on a small scale; in metric units, a prefix denoting one-millionth. *See Macro.*

Microanalysis

Techniques of chemical analysis, qualitative and quantitative, employing only very tiny quantities of substances.

Microbiological Deterioration

See Biodeterioration.

Microcellular Rubber

Rubber of a cellular structure, the individual pores being so small as to be seen conveniently only with the aid of a lens. Microcellular rubber finds its greatest application at present in shoe soles.

Microgel

Gel present in natural rubber; when the crosslinked particles are at or below the limits of microscopic vision (0.1 μm) the gel is known as microgel. The term is also applied to similar structures in synthetic rubber.

Microhardness Testing

A procedure to enable hardness measurements to be made on specimens much thinner and smaller than those needed for the standard test. Normally the whole test equipment is scaled down to 1/6th of its original dimensions.

Micrometer

An instrument for the very accurate measurement of thickness, length, depth or angles.

Micrometre

The preferred term for micron (μm).

Micromill

A device which enables very small quantities of elastomers to be mixed with compounding ingredients. The prototype is a single-roll machine, the mixing being carried out between the roll (1½ in diameter by 3 in wide (3.8 cm x 7.6 cm)) and a steel plate (9 in long by 3 in wide (22.9 cm x 7.6 cm)). Enables batches of 0.5 g to 2.5 g to be handled.

Micron

A unit in the measurement of microscopic particles. It is one-millionth of a metre or one-thousandth of a millimetre and is denoted by the Greek letter mu (μ). The particles of rubber in natural rubber latex vary in diameter from about 0.05 μm to 3 μm .

Microscope

An instrument used for obtaining magnified images of small objects. For illumination of the object microscopes may use ordinary light, ultraviolet light or a beam of electrons. *See Electron Microscope.*

Microscopy

The study of materials by the use of any type of microscope. The structure of latex, dispersion of compounding ingredients in elastomers and identification of blooms are typical uses in rubber technology.

Microtome

An instrument used in preparing very thin slices of rubber for studying under a microscope, dispersion of compounding ingredients, migration and blooming of sulphur, etc.

Microwave Curing

Vulcanisation of elastomers by heat produced by high frequency radiation, approximately 12.5 cm wavelength, 2450 MHz.

Migration

The motion of particles, ions or molecules in a given direction under the influence of a force. In rubber compounding it denotes the movement of any compounding ingredient from an area of high concentration to one of low concentration.

Mil

A unit of measurement equal to 0.001 in; the term is occasionally used incorrectly to denote a millimetre.

Mill

A machine for masticating rubber, mixing rubber compounds and for warming up rubber compounds prior to calendaring, extrusion, etc. *See Open Mill.*

Millimicron

One thousandth of a micron, denoted by the symbol $\text{m}\mu$. The mean particle diameter of HAF black is about 40 $\text{m}\mu$. The correct metric term is nanometre (nm).

Mill Room

That part of a factory which contains the rubber processing machinery known as mills. *See Internal Mixer, Mill, Open Mill.*

Mineral Oils

Petroleum and other hydrocarbons oils obtained from mineral sources. In rubber compounds they act as softeners and extenders. *See Oil Extended Polymer.*

Mineral Rubber

Originally bituminous materials such as natural asphalt but now a by-product of petroleum refining - an air-blown petroleum asphalt. In rubber compounding it is a tack-producing softener; in larger proportions it is classed as an extender.

Misalignment

Any mismatching or out-of-true condition of components of a product, parts of a mould, wheels of a vehicle, etc., which should bear a specified relationship to each other.

Mix

Another name for a rubber compound.

Mixer

Any apparatus for making homogeneous mixtures of materials used in rubber manufacture, e.g., blends of dry powders, rubber cements of solutions and rubber compounds themselves. *See Internal Mixer, Open Mill.*

Mixing

The operations carried out in a mixer.

MMBI

4- and 5-methyl-2-mercaptobenzimidazole, antidegradant - non-staining.

M_n

Number average molecular weight.

MOCA

Abbreviation for 4,4-methylene bis orthochloroaniline, crosslinking agent for polyurethane.

Modulus

Except at very low strains, up to about 15%, the ratio of stress to strain in vulcanised rubber is not a constant. Modulus is the tensile stress (measured in MPa, lb/in² or kg/cm²) required to stretch the rubber to a given strain (or elongation); the elongation must always be stated, otherwise the expression is meaningless. A more precise expression is 'stress per square unit (in² or cm²) at the given strain'.

Modulus of Elasticity

The ratio of stress to strain in a given material. The strain may be a change in length, a twist or shear, or a change in volume. Modulus of elasticity in this scientific sense must not be confused with the term modulus which has a particular significance in rubber technology.

Moisture Regain

The percentage moisture taken up by moisture-free textiles when exposed to a standard atmosphere, e.g., a temperature of 21 °C (70 °F) at a relative humidity of 65%.

Molecular Formula

Another term for Formula (Chemistry).

Molecular Sieves

Synthetic aluminosilicate materials having a structure with regularly spaced channels of molecular dimensions. Accelerators may be adsorbed on this structure and remain inactive at processing temperatures but are released at curing temperatures, thus preventing any possibility of scorching.

Molecular Weight

The weight of a molecule of a substance referred to that of an atom of oxygen as 16.000; the sum of the atomic weights of the atoms in a molecule. The molecular weight of a monomer is a definite figure calculated from its composition; in polymers the number of units making up the molecule varies considerably in one sample hence molecular weights are stated as averages and usually with reference to a polystyrene standard. The molecular weights of high polymers are normally measured by GPC (Gel Permeation Chromatography), where both an average molecular weight and a molecular weight distribution is determined. Molecular weights of cured polymers cannot be measured or even stated with any meaning as due to crosslinking, the whole article is in effect one molecule.

Molecule

The smallest portion of a substance capable of independent existence and retaining the properties of the original substance.

Monomer

A chemical compound consisting of single molecules; the term is generally applied to substances, the molecules of which may unite to form polymers.

Mooney

Melvin M. Mooney is best known for the development of an instrument for determining the plasticity (viscosity) of unvulcanised elastomers.

The name 'Mooney' is often used in referring to the value obtained on the Mooney viscometer.

Mooney Scorch Test

A development of plasticity determination by means of the Mooney viscometer. The same instrument is used but the temperature of operation is higher and the test is continued until the sample vulcanises. A curve of Mooney reading against time is drawn, from which the scorch and cure characteristics are estimated (BS 903-A58).

Mooney Viscometer

An instrument which determines the viscosity of unvulcanised elastomers by measuring the resistance of the rubber to the shearing action resulting from the motion of a rotor in the centre of the test piece (BS 903-A58).

Mother Stock

Another term for masterbatch.

Mould

- (1) Any cavity of a form suitable for producing a desired shape in an elastomer; the mould may be of any material (plaster, ebonite, aluminium, cast iron, steel) of strength suitable to the means employed in moulding the product.
- (2) A defect in raw rubber, generally the result of fungoid growth; it was formerly common in unsmoked sheet rubber.

Mould Dope

Jargon term for mould lubricant or mould release agent.

Moulding

The process of making rubber products by shaping in a mould; vulcanisation is generally effected at the same time. *See Compression Moulding, Injection Moulding and Transfer Moulding.*

Moulding Pressure

The pressure which must be exerted on each square unit of the surface of the product for satisfactory moulding, i.e., proper consolidation and freedom from porosity. It is usually expressed in lb/in² or kg/cm². Moulding pressure is not critical for rubber (700 lb/in², 5 MPa minimum) but is very critical for efficient moulding of the various types of plastics. Moulding pressures are calculated on the projected area of the product and should include the area of the spew groove.

Mould Loading

In sponge rubber moulding, the mould loading is the percentage of the mould volume which is occupied by the unblown blank of unvulcanised compound, e.g., the thickness of the blank to give a blowing ratio of 2:1 will be 1/3 of the height of the mould cavity, equivalent to a mould loading of 33.3%. The use of mould loading avoids possible ambiguity in blowing ratio, expansion, etc.

Mould Lubricant

Any substance used to prevent sticking of rubber to a mould surface, thus facilitating removal of the product without risk of tearing or splitting. The lubricant may be painted or sprayed on the mould surface or applied to the surface of the

uncured product, depending on circumstances.
See Mould Release Agent.

Mould Release Agent

Another term for mould lubricant but generally applied only to liquids particularly those based on silicones.

Moving Die Rheometer (MDR)

A particular type of rheometer developed by Monsanto, now known as Alpha Technologies. The mechanical portion of the rheometer consists of two dies forming a biconical cavity which contains the elastomeric specimen to be tested. The dies are heated and closely controlled and the torque required to oscillate one of the dies is accurately monitored. A graph of the torque against time is a clear indication of the progression of the curing reaction. As the material cures it gets stiffer and the torque increases. It has distinct advantages over the oscillating die rheometer (ODR) in that the rotor in the ODR is not heated and this mitigates against isothermal conditions. The MDR operates at much closer to isothermal conditions.

MQ

Abbreviation for polydimethyl siloxane.

MRPRA

Malaysian Rubber Producers' Research Association

MRX

Abbreviation for mineral rubber.

MT

Abbreviation for medium thermal carbon black.
See Thermal Black.

Mu (μ)

The symbol for micron (μm), for refractive index and for coefficient of friction. A high mu rubber (formerly termed high hysteresis, high energy-loss or 'cling' rubber) is one specially developed for the wearing surface of pneumatic tyre treads to improve road holding.

Mullins Effect

Work done by L. Mullins on the prestressing of filler-loaded vulcanisates showed that such prestressing gives a stress-strain curve approaching that of an unfilled rubber. This work has thrown much light on so called permanent set and the theory of filler reinforcement. *See Stress Softening.*

Multi-Angle Laser Light Scattering

MALLS detectors can provide information on the branching ratio of a polymer and molecular weight.

Mutagenicity

The capacity of some agent or chemical substance to induce genetic changes resulting from chromosomal alterations, which changes may be transmitted from parent to offspring.

M_w

Weight average molecular weight.

M_z

Z average molecular weight.

N

Naphtha

General name for mixtures of liquid hydrocarbons obtained from petroleum, coal tar or shale, used as solvents for unvulcanised rubber.

Naphthylamines

Amines resulting from the reaction of an amino group (-NH₂), with naphthalene; they are used as rubber antioxidants. *See PAN, PBN.*

Natta

See Stereospecific Catalysts.

Natural Gas

A mixture of gaseous hydrocarbons, principally methane, which issues from the earth in certain areas, particularly near petroleum wells. Natural gas was the main source of carbon black until some 50 years ago when it was found more economic to use the gas for heating and produce carbon black from petroleum residues by the more efficient furnace process.

Natural Rubber

Rubber obtained from botanical sources. The bulk of natural rubber is obtained from the Hevea Brasiliensis tree with small amounts from other vines, shrubs and plants mainly the Guayule shrub and the Kok-Saghyz plant. *See Isoprene.*

NBC

Nickel dibutyl dithiocarbamate, accelerator.

NBR

Abbreviation for nitrile-butadiene rubber. *See Nitrile Rubber.*

NCI

National Cancer Institute (USA).

NDI

Naphthalene 1,5-diisocyanate. *See Isocyanate.*

NDPA

N-Nitrosodiphenylamine, retarder.

Neoprene

This name has been widely adopted for the elastomer obtained by polymerising chloroprene, i.e., polychloroprene. It is however the trade name of those types of polychloroprene produced by the Du Pont Co. which were originally called 'Duprene'. Chloroprene rubber (CR) is the preferred term, but polychloroprene (PCP) is also popular.

The original route to chloroprene (2-chloro-1,3-butadiene) was acetylene-mono vinyl acetylene-chloroprene. Many properties of neoprene are similar to those of natural rubber, but neoprene has better oil resistance, a higher maximum operating temperature and resistance to the effects of sunlight and weathering. Neoprene also has high flame resistance due to the presence of the chlorine. It is a strain crystallising material (as is NR). The chlorine also lowers the reactivity of the double bond giving its improved environmental resistance.

Nerve

A term used to describe the toughness and elasticity of unvulcanised, unmasticated elastomers. Mastication reduces nerve, and, if the process is continued long enough, may destroy it altogether. *See Dead Milled.*

Neuberg Siliceous Earth

Natural mixture of quartz and kaolinite, inorganic filler.

Newtonian

In a Newtonian material the rate of shear deformation is proportional to the shear stress; except at very low stresses this is not true of elastomers which are accordingly termed non-Newtonian.

***n*-Isopropyl-*n*'-Phenyl-*p*-Phenylenediamine**

IPPD, antidegradant – staining.

Nickel Dibutyl Dithiocarbamate

NBC, accelerator.

Nickel Dimethyl Dithiocarbamate

NiDD, accelerator.

NiDD

Nickel dimethyl dithiocarbamate, accelerator.

NIOSH

National Institute for Occupational Safety and Health (USA).

Nip

The distance between adjacent rolls of a mixing mill or calender; the term is often applied also to the space between the rolls, leading to the nip proper.

Nitrile Rubber

The generic term applied to all elastomers resulting from the copolymerisation of butadiene and acrylonitrile. Nitrile rubbers are available with different butadiene/acrylonitrile ratios ranging from 18% to 50%, a high acrylonitrile content giving rubbers excellent oil resistance, a lower acrylonitrile content giving improved low-temperature flexibility.

Nitrile rubbers have high resistance to oils and organic solvents, and, although their mechanical properties are not as good as those of natural rubber, they are subject to much less deterioration in the presence of oils and solvents. They are not resistant to ozone attack.

Nitroso Rubbers

Elastomers produced by copolymerisation of a nitroso monomer with tetrafluoroethylene; they have excellent resistance to heat, to the action of solvents and to chemical attack, and are completely non-flammable.

***N*-Nitrosodiphenylamine**

NDPA, retarder.

NMR

Abbreviation for nuclear magnetic resonance.

No Mark Soling

Soling which is compounded with light-coloured fillers instead of carbon black and thus does not leave unsightly marks on floor coverings.

Nomogram

A chart which enables the value of a variable to be read off, without calculation, from the values of one or two other known variables.

Normal Latex

Latex of natural rubber which has had a preservative (usually ammonia) added, but which has not been concentrated. *See Concentrated Latex.*

Non-Staining

Applied to compounding ingredients which do not cause a colour change either in the compounds in which they are incorporated or in

other materials with which they may come in contact; also applied to synthetic elastomers which contain non-staining antioxidants or stabilisers. *See Staining.*

Non-Sulphur Vulcanisation

Elastomers (natural and synthetic) employ as vulcanising agent a quantity (2.5 phr on average) of elemental sulphur. The use of any other substance (TMT, peroxides, quinones, etc.) is termed non-sulphur vulcanisation.

Non-Woven Fabric

A fabric made by uniting a mass of staple fibres into a continuous sheet by using the adhesive properties of a bonding agent, usually rubber latex, either natural or synthetic. In textile technology the term is applied to fabrics which are not woven, such as felted fabrics. Non-woven fabrics are now being termed bonded fabrics.

NPD

Nitrogen phosphorus detector.

NR

Abbreviation for natural rubber.

NSR

Abbreviation for Nigerian Standard Rubber.

***N*-tert-Butyl-2-Benzothiazole Sulphenamide**

TBBS, accelerator.

NTP

Abbreviation for Normal Temperature and Pressure, i.e., a temperature of 0 °C and a pressure of 760 mm of mercury. Also known as STP.

Nuclear Magnetic Resonance Spectroscopy

A type of spectroscopy used in chemical analysis and the determination of the structure of organic compounds and polymers.

Nuclear Soling

A high styrene soling of microcellular rubber. The soling is termed 'solid' and has a density of about 0.9 g/cm².

Nylon

The first successful synthetic fibre. The term is applied to any long-chain synthetic polymeric amide and the best known commercial type is nylon 66 produced by the condensation polymerisation of adipic acid with hexamethylene diamine.

O**OBSH**

p,p'-Oxy-bis(benzene sulphonylhydrazide), blowing agent.

Occupational Exposure Limits

Occupational Exposure Limits (OELs) refer to airborne concentrations of substances and provide a guide to their toxicity.

In the UK a list of occupational exposure limits is published by the HSE in Guidance Note EH40, which is updated annually. There are two kinds of occupational exposure limits: maximum exposure limits (MELs) and occupational exposure standards (OESs). For substances which have been assigned a MEL, the level of exposure should be reduced so far as is reasonably practicable and in any case should not exceed the MEL. For substances which have been assigned

an OES, it will be sufficient to ensure that the level of exposure is reduced to that standard or that all reasonably practicable measures are being taken to remedy any temporary excursions. OESs are 'health based' limits. The exposure limits are defined in terms of long-term exposure limits (8 hour time-weighted average (TWA)) and short term exposure limits (15 minute TWA or STEL). See TLV.

ODPA

Octylated diphenylamine, antidegradant – staining.

ODR

Abbreviation for oscillating die rheometer.

OEP

Abbreviation for oil extended polymer.

OEL

Occupational Exposure Limit. See *Occupational Exposure Limits*.

OES

Occupational Exposure Standard. See *Occupational Exposure Limits*.

Off Centre

A defect in rubber products where a component has been misaligned in relation to the centre line, e.g., conductor in a cable, breaker strip in a conveyor belt or pneumatic tyre.

Oil Black Masterbatch

An oil extended polymer to which has been added at the latex stage a quantity of a reinforcing carbon black.

Oil Extended Polymer

A type of SBR with which has been mixed in the latex stage a quantity (usually 37.5 or 50 phr) of an emulsion of a mineral oil and the mixture coagulated and processed in the normal manner. Although other synthetic rubbers may be oil extended in this way, the abbreviation OEP usually refers only to SBR. See *Oil Extension*.

Oil Extension

The addition of a high proportion (40-50 phr) of a rubber processing oil to an elastomer with the object of improving the processibility of a tough polymer and/or cheapening the compound. See *Oil Extended Polymer*.

Oil Resistance

Resistance of an elastomer to swelling and ultimate degradation due to contact with or immersion in an oil.

Oil Seal

A rubber product designed to prevent oil leakage from bearings, rotary shafts, etc. The cross-section varies according to the particular application.

Olefins (Olefines)

A homologous series of unsaturated hydrocarbons having the general formula C_nH_{2n} , of which the first stable member is ethylene C_2H_4 .

Oleic Acid

An unsaturated long-chain organic acid found in natural fats. Its uses in rubber compounding are similar to those of stearic acid.

Open-Chain Compounds

Another term for aliphatic compounds.

Open Mill

A mill in which the rolls are exposed, in contrast to those of an internal mixer.

Open-Steam Curing

The method of vulcanising those rubber products which do not require the precision of shape given by a mould. The heat for curing is supplied by steam circulating openly in an autoclave, the products being supported on mandrels or embedded in chalk. See *Moulding*.

Optimum Cure

The best cure for a rubber product is always a compromise, but optimum cure may be defined as that time of cure necessary to bring a pre-selected property of the vulcanisate to near maximum (or minimum) value, at the same time ensuring that the other properties are satisfactory. All the physical properties of a rubber do not reach their optimum values at the same time of cure, and therefore the time must be selected so that the properties are near their optima, the most weight being given to the property considered most important.

Maximum productivity is given by the shortest possible time of cure, provided the selected time and temperature do not produce an unacceptable level of defects or early failures in service. Sufficient cure must be given to prevent porosity, since badly undercured rubber will sponge at pressure release. It is better to risk a slight overcure rather than an undercure, since if the curatives are correctly chosen (in type and quantity) the compound should show a plateau effect, which means that a reasonable overcure will not have any marked effect on the physical properties of the product.

Orbitread Process

A process used in the retreading of pneumatic tyres, whereby the new tread rubber is applied by extruding and winding a ribbon of uncured rubber (approximately 35 mm wide and 2.5 mm thick) on to the buffed and solutioned tyre casing.

Organic Chemistry

That branch of chemistry which deals with the compounds of the element carbon; the simpler carbon-containing compounds (such as calcium carbonate) are usually classed with inorganic chemistry and an alternative definition of organic chemistry is the chemistry of the hydrocarbons and their compounds.

Organometallic Compound

A carbon compound containing a metal, in which there is a direct link between at least one carbon atom and the metal atom. Many stereospecific catalysts are organometallic compounds.

Orientation

The ordering of molecules, particles or fibres so that they point in the same direction.

O-Ring

An O-shaped rubber ring of round cross-section used as an oil seal.

Oscillating Disc Rheometer (ODR)

A particular type of rheometer developed by Monsanto, now known as Alpha Technologies. The mechanical portion of the rheometer consists of a biconical disc embedded in an elastomeric specimen contained in a specially designed

cavity. The cavity is heated and closely controlled and the torque required to oscillate the biconical rotor is accurately monitored. A graph of the torque against time is a clear indication of the progression of the curing reaction. As the material cures it gets stiffer and the torque increases. *See Moving Die Rheometer.*

Oscilloscope

An apparatus employing a cathode ray tube on the screen of which varying electric currents and voltages may be displayed as visible patterns.

OSHA

Occupational Safety and Health Administration, US Department of Labor.

Osmosis

The flow of water or other solvent through a semi-permeable membrane, i.e., one which permits the passage of the solvent itself but not the dissolved substance.

Osmotic Pressure

In the case of a solution bounded by a semi-permeable membrane, the pressure which must be applied to drive the solvent molecules through the membrane is termed the osmotic pressure. *See Osmosis and Molecular Weight.*

OVA

Organic vapour analyser.

Oven

A hot air chamber used for heating or drying raw rubber, for vulcanising rubber products by the dry heat method, or for carrying out accelerated ageing by the air oven method. On the continent of Europe, the term oven is sometimes used in the sense of autoclave.

Overcure

Prolongation of cure beyond that time which gives the optimum cure. An overcure may be accidental due to variation in curing conditions; or deliberate as in laboratory determination of curing range, or with the object of enhancing a particular property of a vulcanisate, e.g., compression set.

Overflow

Another term for spew.

Oxidation

Combination with oxygen. On the basis of the electronic theory of valency the meaning of the term has been extended to include all reactions in which there occurs an increase in the ratio of the electronegative to the electropositive atoms or groups of a substance. The controlled oxidation of natural rubber produces resinous substances called Rubbones.

p,p'-Oxy-Bis(Benzene Sulphonylhydrazide)

OBSH, blowing agent.

Oxygen

An odourless invisible gas (O₂) comprising approximately one-fifth of the atmosphere; it is chemically very active. Oxygen is necessary in the mastication of rubber, but also contributes to the degradation of vulcanised rubber.

Oxygen Bomb Ageing

Accelerated ageing carried out in a pressure vessel containing oxygen at a pressure of 300 lb/in² and at a temperature of 70 °C. The procedure is covered by BS ISO 188.

Ozone

An allotropic form of oxygen (O₃) (*see Allotropy*) of considerably greater degradative effect on rubber than oxygen itself. The ozone content of the atmosphere normally varies from 0.5 to 5.0 parts per 100 million (pphm) of air, but in certain areas (notably Los Angeles, USA) it may reach as much as 40 pphm of air.

Ozone Cracking

Cracking of the surface of stretched rubber exposed to ozone. The ozone will only crack unsaturated (i.e., containing double bonds) rubbers when they are subjected to tensile strain, the cracks are at 90° to the direction of the strain.

Ozonide

An unstable organic compound formed by the addition of ozone to an olefinic compound, the addition of one molecule of ozone taking place at each double bond.

Ozonolysis

A method for determining the constitution of organic compounds containing double bonds.

P

P

Abbreviation for (1) phosphorus, (2) propylene.

PA 80

Processing aid-80, a masterbatch in the form of pressed crumb consisting of an 80:20 blend of crosslinked to ordinary natural rubber. The correct proportions of vulcanised latex and field latex are blended, coagulated and the resulting crumb pressed into 100 lb bales. The use of PA 80 confers 'Superior Processing' properties on any natural or styrene-butadiene rubber with which it may be mixed. *See Superior Processing Rubber.*

PAC

Abbreviation for polycyclic aromatic compounds.

Packing

Any material used to prevent fluid leakage in joints, flexible couplings, hydraulic glands, etc.

PAH

Abbreviation for polycyclic aromatic hydrocarbons.

Pale Crepe

Also termed 'first latex crepe'. This is the highest quality plantation crepe rubber. Extreme care is taken in preparation to ensure that the lightest possible colour is obtained.

Pallet

A platform or framework of wood or metal fitted with feet or otherwise recessed so that the forks of a forklift truck may be inserted for transportation of the load (bales of rubber, bags of compounding ingredients, etc.) as a unit.

PAN

Abbreviation for phenyl- α -naphthylamine.

Pan

A jargon term for any form of autoclave.

Paraffin Series

A homologous series of hydrocarbons of general formula C_nH_{2n+2}, of which the first member is methane CH₄.

Paraffin Wax

A white solid which melts in the range 50 °C to 60 °C. It is a mixture of the higher hydrocarbons of the paraffin series and is used in rubber compounding as a softener and as a processing aid in extrusion. It also acts as a protective agent against ozone attack in vulcanised rubber by blooming to the surface and forming a protective film, which replenishes itself if removed by the service conditions.

Para-Quinone Dioxime

A non-sulphur vulcanising agent of particular application in butyl rubber compounds, the activator being red lead.

Para Rubber

Hevea rubber from uncultivated trees growing in the Amazon Valley of Brazil and exported from Para, a town at the mouth of the river. Para rubber was the best variety of all wild rubber but the advent of plantation rubber steadily reduced its importance until it is now of no significance in world rubber production.

Parkes' Process

Another name for cold cure, named after its discoverer Alexander Parkes. Celluloid, first known as Parkesine was another discovery of Alexander Parkes.

Pascal's Law of Fluid Pressures

Pressure applied anywhere to an enclosed body of fluid is transmitted equally in all directions. This pressure acts at right angles to every portion of the surface of the container, the force per unit area being uniform throughout.

Patramold Process

The use of a special ebonite as the thermoplastic material in the printing process of electrotyping, a method of producing metal replicas of printing surfaces.

PB

Abbreviation for polybutadiene.

PBN

Abbreviation for phenyl-β-naphthylamine.

PBNA

Alternative abbreviation for phenyl-β-naphthylamine (PBN).

PCP

Abbreviation for polychloroprene.

PCPL

Pentachlorophenyl laurate, latex auxiliary.

PDMS

Polydimethylsiloxane, latex auxiliary.

PE

Abbreviation for polyethylene.

Peachey Process

A method of vulcanising thin rubber articles, now of historical interest only. The products are exposed successively to the gases, sulphur dioxide and hydrogen sulphide, which react to form active sulphur which brings about vulcanisation.

Peaky Cure

When the curve of a particular property (usually tensile strength) of vulcanised rubber plotted against time of vulcanisation shows a sharp drop after the maximum has been reached, the compound or compounding ingredient under test

is said to show a peaky cure; the opposite of flat curing.

Pelletiser

A machine for converting masticated rubber or mixed compound into pellet form. It consists of an extruder screw which forces the rubber through a drilled plate, the rods so formed being cut into small lengths and treated with a lubricant to prevent sticking. In some arrangements the cutting is performed underwater to improve partition.

Pendulum Feed

In supplying a calender with a strip of warmed compound by means of a narrow conveyor belt, the final section of the belt may be arranged to oscillate back and forth across the calender nip; the device is termed a pendulum feed.

Pentachlorophenyl Laurate

PCPL, latex auxiliary.

Peptised Rubber

Natural rubber to which has been added on the plantation a quantity of a peptising agent. Such pre-softened and easily-softened rubbers breakdown much more quickly during mastication in the factory.

Peptising Agent

A substance which added to rubber in very small amounts (0.1-0.2 phr) speeds up the normal mastication process and produces rubber of a given plasticity in a shorter time and with less power consumption. The accelerator MBT has a peptising action but certain thiophenols, mercaptans and particularly *o-o'*-dibenzoylaminodiphenyl disulphide are much more effective.

Perbunan

The Bayer trade name for a nitrile rubber formerly known as Buna N.

Perishing

An inexact term for the general deterioration of vulcanised rubber. *See Ageing.*

Permanent Set

See Compression Set and Tension Set.

Permeability

Diffusion of a gas or liquid through a semi-permeable material. The permeability of elastomers to gases varies with the elastomer type and with the gas. Butyl rubber is much less permeable to air than is natural rubber hence its use in tyre inner tubes and similar applications. The rate of permeation is generally related to the size of gas molecule, i.e., the smaller the molecule the higher the rate. The exception is CO₂ which has a rate 10 to 100 times greater than that of nitrogen.

Peroxide

Peroxides are used in the crosslinking of rubbers.

PET

Abbreviation for polyethylene terephthalate.

Petrochemical

Any chemical derived from petroleum, the main refining processes being fractional distillation, catalytic cracking and platforming (reforming the constituents with the aid of a platinum catalyst). Since sulphur may be recovered from petroleum refining and since SBR, furnace black and processing oils are all petrochemicals it is

possible to visualise a vulcanised rubber derived entirely from petroleum.

Petrolatum

A semi-solid yellowish substance consisting of a purified mixture of hydrocarbons; also known as petroleum jelly. It is used as a softener in rubber compounding.

Petroleum

Naturally-occurring oil, a mixture of hydrocarbons with a small proportion of other organic compounds containing sulphur, phosphorus, oxygen and nitrogen; the exact composition varies according to source.

Petroleum Oils

Used as processing additives at 5-10 phr and as a rubber extender and softener at >10 phr.

Petroleum Rubber Solvent

A solvent for natural rubber; a petroleum distillate with a boiling range of 100-160 °C.

pH

See hydrogen ion concentration.

Phenol

A white crystalline solid, C₆H₅OH, with a characteristic odour. It is used in the manufacture of the phenolic plastics, of dyestuffs and of rubber antioxidants. Highly toxic, avoid skin contact.

Phenol-Formaldehyde Resin

Thermosetting resin produced by the reaction of phenol and formaldehyde in the presence of either an acid or an alkaline catalyst. In rubber compounding these resins are used as plasticisers and reinforcing materials.

Phenyl- α -Naphthylamine

One of the earliest organic antioxidants, now obsolescent due to its severe staining properties, health problems, and to the production of more effective antioxidants.

Phenyl- β -Naphthylamine

A general purpose antioxidant for natural rubber, SBR and nitrile rubbers. Staining, now obsolescent.

N,N'-(*m*-Phenylene)Dimaleimide

Diamine accelerator.

Photosynthesis

Synthesis by the action of light. The term is generally applied to the formation of carbohydrates from carbon dioxide and water in the presence of sunlight and chlorophyll in green plants.

PHR or phr

Abbreviation for parts per hundred of rubber.

Phthalocyanine Dyes

Dyes manufactured from the family of chemical compounds known as the phthalocyanines. Copper phthalocyanine is a pigment where, it should be noted, the copper atom is well protected by organic radicals and does not catalyse the deterioration of the rubber compound into which it has been incorporated.

Phytophthora

A disease of rubber trees affecting the pods and leaves. The resulting pod-rot and leaf-fall seriously reduces the latex yield. It is common in most rubber growing countries with, until recently, the exception of Malaysia, where urgent

measures are being taken to stop the spread of the disease.

Pick

In textile technology, a weft thread; also termed a filling thread or shot.

Pico Abrasion Test

A type of test for determining abrasion resistance. Fixed knives, under constant load, scrape across a rotating rubber test piece. The resulting loss in weight is a measure of the abrasion resistance.

Pig

A roll of masticated rubber cut from an open mill also known as a dolly.

Pigment

Pigments are coloured, black, white or fluorescent particulate organic or inorganic solids, which are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or scattering of light.

Pigment

A colouring material mixed with rubber to give the desired colour in the product. The term has been used in the sense of any powdered compounding ingredient.

Pile Curing

Premature curing whilst in storage also known as bin curing.

Pine Tar

A tar obtained by the distillation of pine wood. It is an excellent softener and tack-producing agent in rubber compounding.

Piperidine Pentamethylene Dithiocarbamate

An ultra accelerator of particular application in the manufacture of dipped latex products.

Plain Weave

The simplest type of woven fabric construction; each thread passes alternately over and under the thread it intersects. There is thus an intersection of adjacent threads at every possible point and no thread passes over or under more than one thread at a time in either direction.

Planimeter

An instrument for measuring by mechanical means, the area of a plane surface, the perimeter of which is traced out by a moving arm.

Plantation Rubber

Natural rubber obtained from cultivated trees as opposed to that obtained from trees growing 'wild' in the jungle. The size of a plantation varies from the large estate of several thousand acres down to the smallholdings of a few acres worked by the owner and his family. Such smallholdings produce a significant proportion of the world's NR output.

Plasticator

A machine for masticating rubber. The principle is that of an extruder, the rubber being softened by working between the threads of the screw and the surface of the barrel. The best known type is the 'Gordon Plasticator'. Now obsolete.

Plasticiser

Also termed softener and processing aid. A compounding ingredient which facilitates processing by making the unvulcanised compound more plastic, aids in the incorporation

of powders, reduces the processing temperature and assists mould flow. It should be noted that the softness is carried through to the vulcanisate. Plasticisers comprise fatty acids, vegetable oils, mineral oils, and esters. *See Peptising Agent.*

Plasticity

A convenient term for the rheological properties of an unvulcanised elastomer (*see Rheology*). It has been defined as the 'susceptibility to, and retentivity of deformation', and also 'the degree of flow which takes place under given conditions of temperature and pressure'. The use of the term viscosity is a more appropriate description.

Plasticity Retention Index

There are obvious advantages in a technique whereby the behaviour of a rubber in a vulcanisate could be assessed by a test carried out on the raw rubber. The PRI test consists in measuring the Wallace Plasticity of the raw rubber before and after ageing for 30 minutes at 140 °C, the aged plasticity being expressed as a percentage of the unaged (BS 903-A59.2).

Plasti-Corder

See Brabender Plasti-Corder.

Plastics

A truncation of the term thermoplastics. Generally organic materials which in the manufacturing stage are caused to flow by the application of heat and pressure and thus take up a desired shape, which shape is retained when the applied heat and pressure are removed. Plastics are high polymers and are classified into amorphous and semicrystalline thermoplastics and thermosetting materials.

Plastimeter

An instrument for measuring the plasticity of an elastomer, e.g., Wallace Rapid Plastimeter

Plastisol

A paste of polyvinyl chloride and plasticiser. The name originated in the USA and is now in general use.

Plastograph

See Brabender Plastograph.

Plastometer

Any instrument for measuring the plasticity of an elastomer. *See Mooney Viscometer and Williams' Plastometer.*

Plateau Effect

See Flat Curing and Peaky Cure.

PLC

- (1) Abbreviation for programmable logic control.
- (2) Abbreviation for pale latex crepe.

Plucking

Tearing out of small areas of rubber from the surface of a rubbered fabric, during the subsequent assembly of the uncured product.

Ply

- (1) A sheet of rubber or layer of rubbered fabric when prepared as a component of a composite rubber article.
- (2) A single yarn of a multi-ply yarn.
- (3) The term has wide application with its normal meaning of layer, thickness, fold or strand.

Ply Separation

Lack of adhesion between the plies of a composite rubber article.

PMQ

Abbreviation for phenyl methyl silicone.

Pneumatic Tyre

An assembly of outer cover (or tyre) fitted with an inner tube and mounted on a metal rim or wheel, the inner tube is inflated with air under pressure which supports the load of the vehicle. In the tubeless tyre no separate inner tube is fitted, the outer cover itself being so constructed as to retain the inflation air.

PO

Abbreviation for copolymer of propylene oxide and allyl glycidyl ether.

Pocket

An undesired discontinuity in a rubber article (uncured or cured) resulting from ply separation or from the trapping of air during assembly or during vulcanisation.

Poise

The unit of viscosity of fluids in CGS units. It is measured in dynes/cm² per unit velocity gradient.

Poisson's Ratio

Poisson's ratio is a measure of the simultaneous change in elongation and in cross-sectional area within the elastic range during a tensile or compressive test. During a tensile test, the reduction in cross-sectional area is proportional to the increase in length in the elastic range by a dimensionless factor, Poisson's ratio. For thermosetting elastomers, typical values of 0.48 to 0.499 are seen whereas thermoplastics and metals have values of around 0.3.

Polyamide

The generic name given to the nylon type of polymer, which consists of short carbon chains connected by amide groups -NHCO-. *See Nylon.*

Polybutadiene

Polymerised butadiene, made by the use of stereospecific catalysts. *cis*-1,4-Polybutadiene is widely used in tyre tread compounds. An inherently low temperature and low loss polymer.

Polycarbonates

Thermoplastic materials of the polyester family, characterised by high impact strength and dimensional stability up to 140 °C.

Polychloroprene

See Neoprene.

Polydimethylsiloxane

PDMS, latex auxiliary.

Polyesters

Members of the family of polyurethane elastomers.

Polyethers

Members of the family of polyurethane elastomers.

Polyethylene (PE)

Tough, waxy material made by polymerising ethylene gas either at high pressure and temperature (30,000 lb/in² and 200 °C) or at atmospheric pressure and moderate temperature by the use of aluminium catalysts developed by Karl Ziegler. This 'low pressure', 'high density' or 'Ziegler' polyethylene has improved properties compared to the 'high pressure' variety—higher softening point, higher bursting strength and higher impact strength. *See Stereospecific Catalysts.*

Polyethylene Terephthalate

A condensation product of terephthalic acid and ethylene glycol.

Polyisobutylene

Polymerised isobutylene, a non-vulcanisable, rubber-like polymer. *See Butyl Rubber.*

Polyisoprene

Polymerised isoprene. Naturally-occurring polyisoprenes are natural rubber (*cis*-form) and gutta percha (*trans*-form). The use of stereospecific catalysts has made possible the manufacture of synthetic *cis*-polyisoprene and *trans*-polyisoprene both of which are now available commercially.

Polymer

A polymer is a large molecule (macromolecule) constructed from many smaller structural units called monomers. When only one species of monomer is used to build a macromolecule, it is known as a homopolymer, two species a copolymer, three species a terpolymer.

Polymeric 2,2,4-Trimethyl-1,2-Dihydroquinoline

TMQ, antidegradant – staining.

Polymerisation

A chemical reaction by which small molecules (of monomer) are joined together to form large molecules (of polymer). Polymerisation may be effected by (a) addition, in which the polymer molecule is a multiple of the monomer molecule, (b) by condensation, in which the empirical formula of the polymer differs from that of the monomer, and (c) by copolymerisation, in which the polymer molecule is built up from two or more different monomers

There are three main techniques of polymerisation; bulk, solution and emulsion. In bulk or mass polymerisation, the catalyst is added directly to the monomer and heat may be applied to start the reaction. In solution polymerisation, the monomer is dissolved in an organic solvent. In emulsion polymerisation, the monomer or monomers are stirred up with water and an emulsifying agent to form a stable emulsion. Control of the reaction is obviously much easier with either solution or emulsion polymerisation than with bulk polymerisation.

Polyphenylene Oxide (PPO)

An engineering plastic. It is chemically an aromatic polyether; it can be used across a very wide temperature range, from $-170\text{ }^{\circ}\text{C}$ to $+190\text{ }^{\circ}\text{C}$.

Polypropylene (PP)

Polymerised propylene, a polyolefin plastic with properties similar to those of polyethylene.

Polypropylene Glycol (PPG)

A heat-sensitive gelling agent for latex. *See Heat-Sensitive Latex.*

Polystyrene (PS)

Polymerised styrene, a hard, transparent, rather brittle thermoplastic material.

Polysulphide Rubbers

This group of synthetic elastomers is better known under the trade name 'Thiokol'. Polysulphide rubbers are condensation polymers of sodium polysulphide and dichloro-compounds; they have outstanding resistance to swelling by oils and solvents but tensile strength is

comparatively low; they are of particular interest in the sealant field. They are recognisable by their very distinctive and pungent smell.

Polytetrafluoroethylene (PTFE)

A wax-like polymer with resistance to a wide range of temperatures, high resistance to chemical attack and very low frictional resistance. It is widely used in O-rings, seals and gaskets; it may also be sintered on to a mould surface to assist the release of the product.

Polythene

A shortened form of the correct chemical name, polyethylene.

Polyurethane Elastomers

Elastomers resulting from a series of organic reactions, e.g., a polyglycol ester of adipic acid reacted with an aromatic diisocyanate and cured with water, glycol or further reaction with an aromatic diisocyanate. These elastomers have high tensile strength, very high abrasion resistance, and lower hysteresis than natural rubber. A major use is in the manufacture of foamed polymers.

Polyvinyl Alcohol (PVA)

A synthetic polymer which is being developed as a textile for tyre cord, etc.

Polyvinyl Chloride (PVC)

Polymerised vinyl chloride, one of the polyvinyl plastics.

Polyvinyl Methyl Ether (PVME)

A heat-sensitive gelling agent for latex. *See Heat-Sensitive Latex.*

Porosity

The presence of small cells or voids in rubber articles. Porosity may be unwanted due to lack of pressure during vulcanisation, or intentional as in cellular rubber.

Positex

The trade name for a positively-charged natural rubber latex. The normal negative charge is reversed by pouring the diluted latex into a solution of cetyltrimethyl ammonium bromide. Positex thus has greater affinity for negatively-charged textile fibres than normal latex, and is used to confer non-shrink qualities to textiles.

Post Cure

Refers to an operation carried out immediately following the cure proper, e.g., post cure inflation of nylon pneumatic tyres. Seals are often post-cured to optimise their stress relaxation properties. *See Aftercure.*

Pot Heater

A term used to describe certain types of vertical autoclaves for the vulcanising of large-size pneumatic tyres; sometimes called a 'kettle'.

Pot Life

The time a rubber solution or dough will remain usable after the addition of the curatives.

Potassium Hydroxide Number

In latex testing an expression for the ammonium salt content of the latex, it is the number of grams of potassium hydroxide required to decompose the ammonium salts present in 100 g of latex solids.

Potting

The embedding or encapsulation of articles against breakage or for protection of electrical

components, by pouring around them a vulcanisable liquid polymer such as silicone or epoxy.

Powdered Rubber

Unvulcanised rubber in the form of granules. It is used for dissolving in hot bitumen for making the surfaces of so-called rubberised roads

Power Factor

The power factor of an insulating material indicates its tendency to generate heat in service. The electrical energy loss is directly proportional to the frequency and at high frequencies only materials of very low power factor may be used as cable insulation.

PP

Abbreviation for polypropylene.

PPD

Abbreviation for piperidine pentamethylene dithiocarbamate.

PPG

Abbreviation for polypropylene glycol.

pphr

Parts per hundred rubber.

PPO

Abbreviation for polyphenylene oxide.

PE

Abbreviation for polyethylene.

Precipitated Whiting

Calcium carbonate produced by the chemical process known as precipitation.

Precipitation

The formation ('throwing down') of a precipitate, an insoluble substance in a fine state of division, as a result of a chemical reaction between substances in solution.

Preform

An imprecise term, mostly used in the sense of a blank for moulding or a subsequent process.

Premasticated Rubber

Rubber which has been masticated in an operation entirely separate from the mixing process proper. *See Mastication and Mixing.*

Premix

An imprecise term used sometimes in the sense of masterbatch, sometimes with the meaning of a blend of compounding ingredients for subsequent addition to the elastomer on a mill or in an internal mixer. Premix moulding is the same as dough moulding.

Press Curing

Vulcanisation of rubber products carried out in a daylight press.

Press Table

A movable platform (compressed air or hydraulically operated) which facilitates mould changing in a hydraulic press. The table is raised to the level of each daylight in turn and the mould is easily transferred from or to the platen.

Press Tonnage

The total pressure in tons exerted by the ram on the platens of a hydraulic press. It is calculated by multiplying the area of the ram by the hydraulic pressure and converting to tons; sometimes called press capacity or ram pressure.

Pressure Sensitive Adhesive

A rubber-based adhesive usually applied to a backing material which may therefore be applied to a surface by quite light pressure.

PRI

Abbreviation for plasticity retention index.

Printers Blanket

Printers blankets are of several different types:

- (1) In presswork - a sheet of rubber used on a press platen or impression cylinder to cushion the impression in printing.
- (2) In lithography - a rubber coated fabric mounted on a cylinder that receives the inked impression from the plate and transfers (offsets) it to the paper. Such blankets are also mounted on the impression cylinders of sheeted gravure presses.
- (3) In stereotyping and electrotyping - a yielding resilient material for backing the mat or lead sheet that is pressed into the printing form to produce the mould.
- (4) A sheet of rubber used in newspaper and poster work on the tympan of cylinder presses to secure a smooth, but not too hard, printing surface.

Processibility

The ability of a rubber compound to meet the requirements of processing, i.e., to cope with the day-to-day variations in ambient temperature, in temperature of cooling water, in amount of uncured waste available, etc., while still maintaining an acceptable level of product quality. *See Processing Safety.*

Processing

A general term applied to the variety of operations required to convert a raw elastomer into finished products. *See Calendering, Compounding, Curing, Extrusion, Mastication, Mixing, Spreading.*

Processing Safety

Indicates the ability of an unvulcanised rubber compound to accept the heat history required in processing without risk of scorching.

Profiling

Production of long lengths of a given cross-section of rubber compound by calendering. One or more of the calender bowls are grooved (in the negative) with the profile desired, which may be cut from the solid or obtained from two easily-replaceable half-shells fitted over the bowl.

Programmable Logic Control

The application of instrumentation to the automatic control of a sequence of operations, e.g., injection moulding processes. Once the mould has been loaded with inserts (assuming a rubber to metal bonded part) into the press, the operation of a push-button starts the controller which closes the press, injects the rubber, controls the cure cycle, recharges the injection unit, opens the press, operates the ejectors and presents the mould for cleaning and loading of inserts.

Promoter

The name given to certain nitroso-secondary aromatic amines which, added in small quantities to butyl rubber, result in improved resilience and higher tensile strength.

Proofing

Short for waterproofing, usually refers to the application of a rubber coating to fabrics by the process of spreading.

Propylene

CH_2CHCH_3 , propene, the second member of the olefine series of hydrocarbons. It is the monomer used in the preparation of polypropylene and ethylene-propylene rubbers.

Protective Agents

Materials used to protect vulcanisates from deterioration, including surface coatings as well as the ingredients added to the rubber at the mixing stage. *See Antioxidant, Antiozonant, Paraffin Wax.*

Protective Colloids

In the manufacture of articles direct from latex it is necessary to stabilise the latex (to prevent premature coagulation) by the addition of protective colloids such as casein soaps, gelatine and proprietary anionic surface active agents.

PSA

Abbreviation for pressure sensitive adhesive.

PSI or psi

Abbreviation for pounds per square inch; although this abbreviation is very popular it has never had official approval, the correct imperial unit is lbf/in^2 .

PSIG or psig

Abbreviation for pounds per square inch gauge. *See Gauge Pressure.*

PTFE

Abbreviation for polytetrafluoroethylene.

PU

Abbreviation for polyurethane.

Pure Gum Mix

Another term for high gum compound.

Pusey and Jones Plastometer

This is an instrument for hardness testing and not a plastometer. The Pusey and Jones tester is used for determining hardness particularly on curved surfaces, such as rubber-covered rolls. It operates on a dead-weight principle.

PVA

Abbreviation for polyvinyl alcohol.

PVC

Abbreviation for polyvinyl chloride.

PVI

Abbreviation for prevulcanisation inhibitor.

PVME

Abbreviation for polyvinyl methyl ether

PVMQ

Abbreviation for phenyl vinyl methyl silicone.

Pyrometer

An instrument for measuring temperatures, in the rubber industry the term is usually applied to an instrument for determining the surface temperature of mill and calender rolls, moulds, etc. The instrument is usually based on thermocouples or, where higher accuracy is required, platinum resistance thermometers. Infrared (IR) techniques are now used which have the advantage of non contact but require careful calibration for the emissivity of the surface.

Q

Qualitative Chemical Analysis

Analysis to determine the chemical nature of the constituents of a material, irrespective of their amounts.

Quality Control

As well as the usual meaning of the control of quality this phrase is particularly used with reference to manufactured products. *See Statistical Quality Control.*

Quantitative Chemical Analysis

The determination of the amounts in which the various constituents of a material are present.

Quaternary Ammonium Compounds

Organic compounds having four alkyl groups attached to nitrogen. A quaternary ammonium salt is employed in reversing the electric charge on natural rubber latex; quaternary ammonium dithiocarbamates are ultra-accelerators for rubber vulcanisation.

Quebrachitol

Methylinositol, one of the constituents of natural rubber latex. Although it is present at about 1% it does not appear to have any effect on the properties of either field latex or concentrated latex.

Quicklime

CaO , calcium oxide, which combines with water to give slaked lime. A dispersion of quicklime in oil or in wax is now available for use in absorbing moisture and thus reducing porosity in vulcanisates especially those cured by a fluidised bed or in a molten salt bath.

Quinone Dioxime

See Para-Quinone Dioxime.

Quinones

Quinone and some of its derivatives may be used in the non-sulphur vulcanisation of natural rubber. The best-known derivative is *para*-quinone dioxime used as a curing agent for butyl rubbers.

R

Racked Rubber

Unvulcanised natural rubber which has been cooled quickly while under tension. In this condition it behaves like a relatively inextensible fibrous material.

Radial-Ply Tyre

Formerly termed braced tread, rigid breaker or belted tyre. A pneumatic tyre in which the cords of the casing plies run directly across the tyre section from bead to bead, and not at an angle as in a cross-ply tyre; the breaker in a radial-ply tyre is an inextensible band which runs circumferentially round the tyre between tread and casing. It is made up of layers of bias cut fabric set at discrete angles to confer the required stability in the tread but maintain the flexibility in the sidewall.

Radical

(1) A molecule or atom with an odd number of electrons, often short lived, reacting rapidly with other molecules.

- (2) In a chemical compound, a group of atoms which maintains its identity during chemical changes which affect the remainder of the molecule.

Radical Acceptor

In cold mastication of rubber, a substance which prevents the recombination of the free radicals produced by the mechanical shearing forces. *See Cold Mastication, Free Radical and Mechano-Chemical.*

Radioactive Isotopes

These are unstable forms of elements which decay by the emission of radiation. A radioactive isotope of an element behaves chemically in the same way as the non-radioactive form, but its radiation may be detected and measured by a suitable instrument. In the rubber industry radioactive isotopes are used in beta ray thickness gauges, in studying the precise role of sulphur in vulcanisation, in the speedy determination of tread wear in tyres, etc. *See Beta Rays.*

Ram

The solid metal cylinder or plunger which is moved by liquid pressure, air pressure or a combination of both, in such machinery as moulding presses, bale splitters, internal mixer floating rams and bottom doors, etc.

Ram Pressure

Another term for press tonnage.

Rasping

The process of roughening the surface of vulcanised rubber preparatory to applying a layer of unvulcanised rubber as in tyre re-treading, conveyor-belt repairing, etc.

Rate of Cure

The time of vulcanisation required by the compound in question to reach a given state of cure compared to the time required by a standard compound to reach the same state of cure.

Rayon

This term was originally intended to denote all kinds of man-made textile fibres, but is now applied only to cellulose types. Viscose rayon (regenerated from a solution of cellulose xanthate in sodium hydroxide) accounts for the greater part of world rayon production. Acetate rayon and cuprammonium rayon are relatively unimportant.

Reactor

The vessel in which a chemical reaction takes place; the term is usually applied to the vessel used in pilot plant or large-scale commercial processes.

Rebound Resilience

Resilience measured by an impact or rebound method. *See Lupke Pendulum, Tripsometer.*

Recapping

A tyre retreading process in which new material is applied as tread and over the shoulders of the tyre.

Recipe

Another term for formula.

Reciprocating Screw Machine

See Injection Moulding.

Reclaim

Another term for reclaimed rubber.

Reclaimed Rubber

The product resulting from the treatment of waste rubber (flash, used tyres, etc.) by heat and chemical agents, which effect sufficient break down and softening so that the reclaim may be used as a compounding ingredient in fresh compound without excessive degradation of physical properties.

Use peaked in the 1950s and has fallen steadily since then. Recent environmental pressures have raised the profile of recycling and reclaiming and there is now much research in this field with a view to finding effective disposal methods for waste tyres. *See Refining.*

Reclaiming

The variety of processes used in the manufacture of reclaimed rubber.

Reclaiming Agents

Substances used to assist in the reclaiming of rubber. Many plasticisers and some peptisers function as reclaiming agents.

Recovery

The degree to which a raw elastomer or unvulcanised compound returns to its original dimensions on the removal of an applied stress which has caused deformation. Die swell in extrusions and increase of thickness of calendered sheet are examples of recovery.

Red Iron Oxide

Ferric oxide prepared for use as an inorganic colouring agent for rubbers. The colour varies according to type, brick-red, orange, bluish-red, etc.

Red Lead

Trilead tetraoxide, vulcanising agent.

Redox Catalysis

A chemical reaction employing a catalyst which includes both a reducing agent and an oxidising agent. The system is used in the production of 'cold' styrene-butadiene rubbers. *See Cold Rubber.*

Reduction

The removal of oxygen or the addition of hydrogen to a compound; the opposite of oxidation. On the basis of the electronic theory of valency the meaning of the term has been extended to include all reactions in which there occurs an increase in the ratio of the electropositive to the electronegative atoms or groups of a substance.

Reed

In weaving of textiles, a comb-like arrangement of flattened steel wires fixed in a frame. The reed keeps the warp threads in position, acts as a guide for the shuttle and beats up the weft to the cloth; it also determines the number of warp threads per inch of width of the cloth.

Refiner

A two-roll machine similar to an open mill but of more robust construction, having a higher friction ratio and capable of very close nip adjustment.

Refining

The operation of processing rubber on a refiner, the object being to break down any agglomerates of compounding ingredients or to remove small particles of scorched rubber. Refining is one of

the final stages in the manufacture of reclaimed rubber.

Refractive Index

The ratio of the sine of the angle of incidence to the sine of the angle of refraction when light passes from air into the substance in question. In compounding transparent and translucent rubbers it is advisable to choose fillers with refractive indices near to that of the rubber itself.

Register

In rubber moulding, those areas which contact each other when the mould is closed. Also used in the usual sense of alignment.

Reinforcement

- (1) The incorporation into rubber of certain compounding ingredients of small particle size which confer on the vulcanisate high tensile strength, high resistance to tearing, high resistance to abrasion and some increase in stiffness. *See Reinforcing Fillers.*
- (2) The term may also be used with the meaning of structural reinforcement of rubber products, generally by combining the rubber with a textile material.

Reinforcing Filler

Compounding ingredients which bring about reinforcement of rubbers. The most widely used are carbon black, silica and silicates, zinc oxide, treated whittings, high styrene resins and phenolic resins.

Relative Density

The official ISO term for specific gravity.

Relative Humidity

A measure of the dampness of the atmosphere. It is the ratio of the weight of water vapour per unit volume of the air to the weight of water vapour per unit volume of saturated air at the same temperature, usually expressed as a percentage.

Release Agent

Another term for mould release agent.

Reodorant

A compounding ingredient which masks or changes the odour of a rubber product.

Resilience

The ratio of the energy given up on recovery from deformation to the energy required to produce the deformation, expressed as a percentage. *See Heat Build-Up, Hysteresis and Rebound Resilience.*

Resiliometer

An obsolescent name for any apparatus for measuring resilience, formerly commonly applied to the Lupke Pendulum.

Resin

An omnibus term for a variety of hard, brittle, solid or semi-solid organic substances. Resins may be either natural such as rosin, or synthetic such as coumarone-indene and phenol-formaldehyde.

Resin Cure

Vulcanisation of elastomers effected by the incorporation in the compound of certain polymeric resins derived from the condensation of formaldehyde with 4-alkyl phenols. Most frequently used with butyl and EPDM compounds for enhanced heat resistance.

Resin Rubbers

Blends of natural rubber or styrene-butadiene rubber with high styrene resins used as soling material in footwear manufacture. Such resin rubbers should not be confused with combinations of rubber and phenolic resins synthesised by a controlled chemical reaction, e.g., materials sold under the trade name 'Fortiflex'.

Resistivity

Specific resistance. *See Surface Resistivity and Volume Resistivity.*

Resorcinol

m-Dihydroxybenzene, used along with latex and formaldehyde in preparing adhesives for bonding rubber to textiles. *See Latex Resorcinol Formaldehyde.*

Retarder

A compounding ingredient which retards the rate of cure of a rubber compound, thus increasing processing safety.

Reticulation

The formation of a network or net-like structure. In rubber technology this term was first applied to the anisotropy of carbon black particles, which were described as having a 'reticulate chain structure', later abbreviated simply to 'structure'.

Retracted Spew

Another term for backrinding.

Retreading

The fitting of a new wearing surface to a worn pneumatic tyre. The operations comprise rasping to remove the remaining old tread, solutioning, fitting of unvulcanised tread and, finally, curing in a suitable press or autoclave.

Reversion

Degradation of a molecularly crosslinked rubber network occurring at vulcanising temperatures. All rubber compounds in which elemental sulphur is the crosslinking agent are subject to reversion, usually shown by reduced tensile strength, reducing modulus, increased elongation and the development of tackiness.

RF Heating

Another term for dielectric heating.

RFK

A rubber to fabric bonding system comprising resorcinol, a formaldehyde donor and a hydrated silica filler. Incorporated as dry ingredients in the rubber compound and activated by heat.

RHC

Abbreviation for rubber hydrocarbon.

Rheogoniometer

An instrument for the study of the rheological properties of substances. The name is usually applied to the particular instrument designed by Professor Weissenberg.

Rheology

The science of the deformation and flow of matter; the study of a range of phenomena extending from the plastic flow of solids to the behaviour of fluids under extreme conditions.

Rheometer

An instrument for the study of the rheological properties of a substance. The name has been applied to several modified versions of the Mooney Viscometer and to the Monsanto (now

Alpha Technologies) Oscillating Disc Rheometer. Other rheometers are the Yarsley piston rheometer and the capillary rheometer.

RI
Refractive index.

Ribbed Smoked Sheet
Plantation rubber in the form of sheets which have been dried in an atmosphere of wood smoke and finally sheeted in a mill having rolls engraved with a ribbed design. Ribbed smoked sheet comprises about 60% of the output of a plantation. *See Plantation Rubber.*

Rigidity Modulus
The ratio of shear stress to shear strain. A property which determines the rate at which elastomers stiffen as the temperature is lowered. The force required to twist the test piece through 90° is measured at each temperature and the modulus calculated from a formula.

RIM
Abbreviation for reaction injection moulding.

Rind
Another term for spew.

Ring Compound
A chemical compound in the molecule of which some or all of the atoms are joined together in one or more closed rings.

Rise
In open steam curing that period of time during which the temperature is raised gradually from room temperature to the actual curing temperature.

Roelig Machine
An apparatus for measuring the dynamic modulus and hysteresis of elastomers. The stress-strain oscillogram is shown on a ground-glass screen by means of an optical system. Now superseded by modern computer controlled servo hydraulic and dynamic mechanical thermal analysis machines.

Roll Bending
The correction of calender bowl deflection by application of hydraulic pressure to counteract the forces tending to produce deflection.

Roll Crossing
See Crossed Axes.

Rolled Brown Crepe
Former name for flat bark crepe.

Rolling Ball Loss Spectrometer
An instrument designed to follow hysteresis losses in polymers by measuring the resistance to the rolling of small balls over the surface of the test piece; it can investigate transitions in polymers to as low a temperature as -120 °C. Superseded by modern dynamic mechanical thermal analysis equipment.

Rolling Resistance
The force or effort required to maintain the advance of a rolling tyre; usually expressed in pounds per ton of load.

Room Temperature Vulcanisation
Vulcanisation which takes place at normal atmospheric temperature

Rosin
The residue remaining after the distillation of turpentine. Wood rosin is obtained by the extraction of pine wood. Rosin is used in rubber compounding as a tack-producing softener.

Ross Flex Machine

A machine for determining the resistance of elastomers to flex cracking. It is used particularly in the evaluation of shoe soling materials.

Rotational Moulding

A development of slush moulding used for the production of hollow articles from plastisols. The moulds are continuously rotated in two directions during the curing cycle.

Rotocure

Trade name for an apparatus used for the continuous vulcanisation of belting, matting, etc.

Rotomill

A continuous mixing device for elastomers, consisting essentially of a fluted rotor surrounded by a stator.

Rotor

In general a rotating part of a machine; in the rubber industry the term refers particularly to the contoured rolls of an internal mixer and to the mushroom-shaped rotor of the Mooney Viscometer.

Rough Bore Hose

Suction hose in which the fabric plies are built on to a wire helix, the wire being exposed in the bore.

RPA

Abbreviation for rubber process analyser.

rpm

Abbreviation for revolutions per minute.

RSS

Abbreviation for ribbed smoked sheet.

RTECS

Registry of Toxic Effects of Chemical Substances (USA)

RTV

Abbreviation for room temperature vulcanisation.

Rubber

The name 'rubber' derives from the fact, noted in 1770 by Joseph Priestley the English chemist, that caoutchouc would erase or 'rub out' lead pencil marks. Priestley did not actually name it rubber, but at some time between 1770 and 1778 the term became popular.

Rubber Derivatives

Many chemical derivatives of rubber, produced in the course of attempts to elucidate the structure of rubber, became of practical commercial value but have been superseded by the diversity of synthetic polymers. *See Cyclised Rubber, Chlorinated Rubber, Rubber Hydrochloride, Rubbone.*

Rubber Fume

The fumes given off from hot or previously heated rubber, a very complex mixture. Exposure to rubber fumes may be a factor in the increased incidence in certain types of cancer and also in the causation of some other diseases. Fume comprises visible and invisible components.

The aerosol (visible) fraction is 'rubber fume' as defined by the UK HSE, i.e., the fume evolved in the mixing, milling and blending of natural rubber and rubber or synthetic elastomers, or of natural rubber and synthetic polymers combined with chemicals, and in the processes which convert the resultant blends into finished process dust products or parts thereof, and including any

inspection procedures where fume continues to be evolved (EH40/2000). The maximum exposure limit of 0.6 mg/m³ (EH40/2000) relates to material as determined by the HSE method MDHS 47, 'Rubber fume in air measured as total particulates and cyclohexane soluble material'.

Rubber Hydrocarbon

The hydrocarbon present in an elastomer; in natural rubber the amount varies from 93% to 96% according to type.

Rubber Hydrochloride

This derivative of natural rubber produced by the action of hydrogen chloride (liquid or gaseous) found application as a transparent food packaging film, but has now been superseded by modern packaging materials such as PET.

Rubberised Hair

A product used in upholstery and as a resilient packaging material. It is made by spraying a loose mat of curled animal hair with latex and applying heat to vulcanise the rubber. The resilience of the product comes from the fibres, the junction points of which are anchored by the rubber.

Rubber Plant Lining

Employing the corrosion- and abrasion-resistant properties of elastomers by applying a lining of suitable material to vessels, tanks, valves, pipes, etc., handling corrosive liquids.

Rubber Powder

Another term for powdered rubber.

Rubber Process Analyser (RPA)

A development of the moving die rheometer where the operation of the unit is fully computer controlled. The rate of oscillation, temperature and level of strain can all be run through a series of options. The torque measurements are also highly sophisticated. As a consequence, the unit can be set up to monitor processing parameters, then the cure behaviour and finally the finished dynamic properties of the cured material. It is manufactured by Alpha Technologies.

Rubber Process Dust

Rubber process dust is dust arising in the stages of rubber manufacture where ingredients are handled, weighed, added to or mixed with uncured material or synthetic elastomers. The aggregated maximum exposure limit in the UK is 6 mg/m³ (EH40/2000). The exception is chemicals for which specific exposure limits exist.

Rubber Substitute

Former name for factice.

Rubber Webbing

Rubber in strip form widely used in upholstery for domestic furniture and all forms of transport seating. There are two main types of rubber webbing - solid rubber and rubber reinforced with threads or fabric. There is also a woven type in which the warp threads consist of rubber filaments wrapped together in a cotton covering, the weft threads being of jute.

Rubbone

The trade name for a variety of resinous substances produced by the oxidation of rubber. Rubbones, designated A, B and C depending on the degree of oxidation, were once used in certain

paints and heat-resistant finishes, but are no longer available commercially.

RUBIAC

Rubber Industry Advisory Committee (HSC, UK).

Running Nip

A space where fabric, rubber sheet, rubbered fabric or similar material running over, under, or on to, a roller, makes a nip with itself or with any adjacent surface.

Russell Effect

The name given to the behaviour of many organic and inorganic substances in producing, especially after exposure to light, an image on a photographic plate in darkness. This effect, which is shown by unvulcanised rubber after exposure to light is considered to result from the formation of peroxides. The Russell effect shown by vulcanised rubber is very weak.

Rutile

One of the crystalline forms of titanium dioxide.

S

SAF

Abbreviation for super abrasion furnace grade of carbon black. *See Furnace Black.*

Safety Discs

Metal discs of specified shearing strength at the end housings of a roll mill; their function is to break when the mill suffers a sudden overload, thus preventing breakage of the roll neck itself.

Safety Mills

Two-roll horizontal mills, the design of which conforms to the Lunn Principles for safety in operation.

Salicylic Acid

Used as a retarder of vulcanisation.

Saturated Solution

A solution which can exist in equilibrium with an excess of the dissolved substance. The amount of dissolved substance a liquid will 'hold' depends on the temperature.

Saturated Steam

Steam at the same temperature as the water from which it was formed.

Saturation

Saturated chemical compounds are those the molecule of which contains no double or triple valency bonds; such compounds do not form addition compounds.

SBP

Abbreviation for special boiling point, a term descriptive of a series of petroleum rubber solvents of different degrees of volatility. Boiling ranges are as follows: SBP 1, 31-115 °C; SBP 2, 70-95 °C; SBP 3, 100-120 °C; SBP 4, 40-150 °C; SBP 5, 90-105 °C; SBP 6, 140-160 °C.

SBR

Abbreviation for styrene-butadiene rubber.

SBS

Abbreviation for styrene-butadiene-styrene block copolymer, a thermoplastic elastomer.

Scanning Electron Microscope

This is used for surface analysis. *See Electron Microscope.*

Scion

In bud grafting, the shoot that develops from the grafted bud.

Scleroscope

An instrument for measuring the resilience of rubber by dropping a flattened steel cone vertically on the test piece and measuring the rebound.

Scorching

Undesired premature vulcanisation of a rubber compound during the processing operations of mixing, extruding or calendaring. *See Heat History.*

Scorch Testing

The determination of the ability of a rubber compound to withstand scorching. *See Mooney Scorch Test.*

SCR

Abbreviation for styrene-chloroprene rubbers.

Scrap Rubber

A term which generally applies to vulcanised rubber unfit for any other use than reclaiming or grinding to crumb rubber. In the rubber factory 'scrap' may also refer to unvulcanised trimmings which can be reprocessed.

SDBC

Sodium dibutyl dithiocarbamate, accelerator.

SDC

Society of Dyers and Colourists

SDEC

Sodium diethyl dithiocarbamate, accelerator.

SDMC

Sodium dimethyl dithiocarbamate, accelerator.

Sealants

Rubber-like materials now superseding the traditional mastics and putties used in the building industry. Such sealants (also termed mastics) are based on butyl rubber, liquid polysulphides, silicone rubbers, polybutylene, nitrile rubbers and plasticised vinyl polymers.

SEBS

Abbreviation for styrene-ethylene-butylene-styrene block copolymer, a thermoplastic elastomer.

Second-Order Transition

Another term for glass transition.

Secondary Ion Mass Spectrometry

A surface analysis technique used in bonding failure analysis, for example.

Selenium

A non-metallic element with chemical properties similar to those of sulphur. It has been used as a compounding ingredient in low sulphur compounds to resist reversion and improve ageing. It is classed as a secondary vulcanising agent.

Self-Curing

Another term for self-vulcanising.

Self-Reinforcing Elastomer

A term applied to certain styrene-butadiene copolymers with a combined styrene content between 35% and 50%.

Self-Vulcanising

Applied to a rubber compound, dough or cement which will vulcanise at room temperature. The time taken to effect vulcanisation may be as short as 30 minutes or as long as several days.

Selvedge

That edge of a woven fabric which runs parallel to the direction of the warp threads.

SEM

Abbreviation for scanning electron microscope.

Semi-Cure

A preliminary or pre-cure given to a product or part of a product, e.g., a moulding may be given a semi-cure in a press and the cure completed in open steam; a thick section of a product may be semi-cured before assembly to the product; a component may be semi-cured to reduce the flow during the subsequent vulcanisation of the product.

Semi-Solid Tyre

A non-pneumatic tyre which has an internal cavity which may be filled with sponge rubber or may be pressurised by inflation with an air needle.

Sensible Heat

The heat which produces a rise in temperature when it enters a substance. In the generation of steam it is the amount of heat which has been added to the water to bring it up to boiling point. *See Latent Heat.*

Sequestering Agent

A substance which prevents the participation of a metal or its compounds in a chemical reaction. The catalytic effect of heavy metals, mainly copper and manganese, on the oxidation of unsaturated compounds (e.g., rubber) results in very poor ageing. If the metal can be converted into what is known as a chelate co-ordination compound, by the use of a sequestering agent, ageing is considerably improved. *See Chelating Agent.*

Serum

In rubber latex, the aqueous phase in which the rubber globules are suspended.

Set

See Compression Set, Permanent Set and Tension Set.

Setting Up

Another name for bin curing.

sg

Abbreviation for specific gravity.

Shape Factor

- (1) In rubber deformation, the ratio of the area of one loaded surface to the free area is termed the 'shape factor'.
- (2) The term is sometimes used to indicate simply the ratio of length to breadth of a body.

Shear

A type of deformation in which parallel planes in a body remain parallel but are displaced in a direction parallel to themselves, i.e., the stress is applied in the plane of one of the faces. Many designs of rubber mountings utilise rubber in shear, the rubber often being bonded to a metal support plate.

Shear Discs

Another term for safety discs.

Shearing Disc Viscometer

Another term for Mooney viscometer.

Sheeting

A calendaring process in which rubber compound (suitably warmed) is passed through the nip between two bowls set at a specified distance apart to produce a comparatively thin sheet of rubber. The name 'sheeting' is also given to the vulcanised product.

Shelf Ageing

Ageing which takes place during the storage of a rubber product, i.e., between time of manufacture and time of putting into service.

Shelf Life

The time during which an unvulcanised rubber compound (e.g., tyre, tube and belting repair materials) or a vulcanised rubber product will remain usable when stored under normal atmospheric conditions of temperature and humidity.

Shell

A hollow roller of wood or metal with an internal square housing to fit a suitable shaft, used for winding up fabric, rubber sheet, rubberised fabric, linings, etc.; also termed roller or box.

Shore Durometer

See Durometer.

Shore Hardness

Hardness measured on a Shore durometer. In addition to the commonly used Shore A scale there are several others O, OO, B, C and D, designed to open out either the soft or the hard end of the A scale.

Short

- (1) In rubber moulding, another name for light, i.e., a product where the mould has not been completely filled.
- (2) In calendaring the term indicates poor extensibility of rubber sheet usually due to the use of insufficiently warmed compound.

Short Stop

In the manufacture of synthetic rubber, the short stop or stopping agent is the substance added to the reactor to stop the polymerisation reaction.

Shrinkage

Change in dimensions of an unvulcanised rubber (calendered sheet or extruded section) on cooling from the processing temperature. Also the volume contraction of a moulded rubber product on cooling from vulcanising temperature. *See Coefficient of Thermal Expansion (Volume).*

Shrinking

The process of controlled, gentle warming of unvulcanised calendered sheet rubber to reduce its anisotropy and prevent subsequent distortion of articles made from the sheet and cured by embedding in chalk in open steam.

Shy

Another term for light.

Side Chain

Alkyl radicals attached to benzene or another cyclic group in the molecule of an organic compound.

Sighting Colours

Soluble non-fugitive dyestuffs used as identifying colours in rubber compounds.

Silica

Precipitated amorphous hydrated silica and fumed anhydrous silica, inorganic reinforcing agent.

Silica Gel

A colloidal solution of silicic acid concentrated until it contains only about 7% water. It has very high absorbent properties and is used as a desiccant.

Silicates

Calcium silicate, sodium aluminium silicate and treated varieties of aluminium silicate used as reinforcing fillers in rubber compounding.

Silicone Rubber

An elastomer of the silicone family (*see Silicones*). It is a polyorganosiloxane, the backbone structure consisting of alternating silicone and oxygen atoms with organic groups, usually methyl, vinyl or phenyl radicals, attached to the silicon member.

Silicones

A range of silicon-containing organic compounds. The backbone of the polymer chain is composed of silicon and oxygen combined as siloxanes to which the organic groups are attached. Silicones may exist as non-volatile oils, greases, resins and rubbers, their outstanding characteristics being water repellency and resistance to high temperatures. The rubber industry is interested mainly in the elastomers (*see Silicone Rubber*) and certain of the oils (*see Mould Release Agent*).

SI Metric Units

The Système International d'Unités (International System of Units) has the abbreviation SI. It includes base units, supplementary and derived units which together form a coherent system of units. Prefixes are used to form decimal multiples and sub-multiples of the SI units.

SIMS

Abbreviation for secondary ion mass spectrometry.

Sipe

A narrow slit in the tread pattern of a pneumatic tyre, formed by fitting a thin blade in the mould: often termed 'knife-cut'.

SIR

- (1) Abbreviation for Standard Indonesian Rubber.
- (2) Abbreviation for styrene-isoprene rubbers.

SIS

Abbreviation for styrene-isoprene-styrene block copolymer, a thermoplastic elastomer.

Skein

Another term for hank.

Skim Coating

Coating carried out on a calender.

Skim Rubber

When natural rubber latex is concentrated by centrifuging there are produced approximately equal volumes of concentrate containing most of the rubber, and skim latex with a low proportion of rubber. The rubber obtained by coagulation of skim latex is termed skim rubber. Due to the high content of non-rubber substances such rubber may give difficulty in processing.

Skiving

Bevelling or cutting a rubber section at an angle with the object of making a stronger splice or of tapering off a square edge to prevent air-trapping during assembly.

Slaked Lime

Calcium hydroxide, inorganic filler.

Slitter

A machine fitted with knives, spacer bars, let-off and take-up rollers, used for slitting rubber sheet, rubbered fabric, liner material, polyethylene film, etc., into narrower widths.

SLR

Abbreviation for Standard Lanka Rubber.

Slub

A defect in woven fabrics where the yarn has lost its twist and thus appears as a thicker part on the surface of the cloth. Slubs may be introduced deliberately for cloth ornamentation.

Slush Moulding

A method of manufacturing articles from latex or from a plastisol. A heated metal mould is filled with the latex compound and, after an interval for gelation, the excess ungelled latex is poured out. Further heating sets the deposit, which is removed from the mould, dried and vulcanised. *See Kaysam Process and Rotational Moulding.*

Smoked Blanket Crepe

See Blanket Crepe.

Smoked Sheet

See Ribbed Smoked Sheet.

Smooth-Bore Hose

Suction hose in which the internal wire reinforcement is completely embedded in the carcass of the hose.

SMR

Abbreviation for Standard Malaysian Rubber.

Snell's Law

When a ray of light is refracted at a surface separating two media, the ratio of the sine of the angle of incidence to the sine of the angle of refraction is a constant. *See Refractive Index.*

Soak Cure

A method of obtaining an even state of cure in thick articles. The source of external heat is shut off before cure is complete and the heat permitted to penetrate to the interior of the article. *See Drop, Hold, Rise.*

Soapstone

Another term for French chalk.

Sodium Bicarbonate

NaHCO_3 , a blowing agent, often used with a weak acid to activate its decomposition to produce CO_2

Sodium Bisulphite

NaHSO_3 , is added to latex from which pale crepe rubber is to be made. It prevents discoloration of the crepe and destroys microorganisms which may cause later deterioration of the rubber.

Sodium Dibutyl Dithiocarbamate

SDBC, accelerator.

Sodium Diethyl Dithiocarbamate

SDEC, accelerator.

Sodium Dimethyl Dithiocarbamate

SDMC, accelerator.

Sodium Hydroxide

NaOH , caustic soda, a white solid which dissolves in water to give a strongly alkaline solution.

Sodium PCP

Sodium pentachlorophenol, latex auxiliary.

Sodium Pentachlorophenate

A preservative for concentrated natural rubber latex, the use of which eliminates the ammoniation process necessary with ammonia-preserved latex. *See Low Ammonia Latexes.*

Sodium Silicofluoride

The gelling agent used in the manufacture of latex foam by the Dunlop process.

Softened Rubber

Another term for peptised rubber.

Softeners

Compounding ingredients added to elastomers (2-5 phr) to increase plasticity and facilitate processing. In larger proportions (20-50 phr) certain oil softeners are classed as extenders. *See Peptising Agent.*

Sole Crepe

Crepe rubber which has been plied up to thicknesses of 1/8 in, 3/16 in or 1/4 in and used in the soles of footwear. It has now been almost entirely superseded by a vulcanised rubber of similar appearance to that of the unvulcanised crepe.

Solid Tyre

A tyre which is composed of solid rubber bonded to a suitable wheel and without an internal air space, as in the pneumatic tyre or an internal cavity as in the semi-solid tyre. The main uses of solid tyres are on forklift trucks and armoured fighting vehicles (tanks).

Solubility

The degree to which one substance will dissolve in another. In rubber compounding it should be noted that many compounding ingredients are soluble in rubber and may also be soluble in each other. *See Blooming, Insoluble Sulphur, Staining.*

Solution

A true solution consists of molecules or ions of a solid substance uniformly distributed throughout a liquid. A rubber 'solution' is colloidal, i.e., intermediate between a true solution and a coarse suspension. Rubber solutions are used as adhesives and in the manufacture of rubber products by the dipping process.

Solution Polymerisation

See Polymerisation.

Solutioning

Another term for spreading.

Solvent

A solvent is a substance, usually liquid, in which another substance can be dissolved. Rubber solvents comprise coal-gas products, petroleum distillates, and various chlorinated solvents such as carbon tetrachloride and trichloroethylene. They are used in making rubber solutions for adhesives, doughs for spreading and in freshening uncured rubber surfaces prior to assembly with other components.

Solvent Recovery

Recovery for re-use, of the solvents used in the processes of spreading and dipping. The solvent

vapour is adsorbed on activated carbon from which it is removed by steam and separated out from the condensed water.

Spandex

The generic name given, in the USA, to stretch fibres based on elastomeric long-chain polyester polyurethanes. Trade names are, e.g., 'Lycra' and 'Vyrene'.

SPC

Abbreviation for statistical process control.

Specific Gravity

The ratio of the weight of a given volume of a substance to the weight of an equal volume of water at 4 °C. The number denoting the specific gravity of a substance is the weight in grams of 1 cm³ of the substance.

Specific Heat

The quantity of heat (J/kg/K) required to raise the temperature of unit mass of the substance through 1 °C. The specific heat of rubber (around 2000) is much higher than that of metals (around 400 for steel) and it is therefore much more expensive to heat rubber than the mould, mandrel or last on which it is cured.

Spectroscopy

The identification of chemical substances by examination of their spectra (singular, spectrum). Both infrared and ultraviolet spectroscopy are used in the study of rubber problems such as identifying the type of polymer or the nature of a contaminant.

Spew

In moulding the rubber articles, it is necessary to use a blank of slightly greater volume than the mould cavity. This excess is forced out at the mould register during vulcanisation and is known as 'spew'. It is usually accommodated in the spew groove. The term spew is also applied to the rubber extruded through release holes drilled at the edges of some extruder dies to even up the flow of rubber and produce an accurate section.

Spew Groove

A channel cut in the register of a mould to accommodate the spew.

SPH

Styrenated phenol, antidegradant – non-staining.

Spider

In the extrusion of rubber tubing, a central core determines the inside diameter. This core is supported by the spider or core-bridge which is itself fitted in the head of the extruder and may be adjusted laterally and vertically to produce a concentric tube.

Spinning

This term has two distinct meanings in textile technology: (a) the process of twisting a fibrous material into a yarn or strand, and (b) the process of producing continuous filaments of man-made fibres by extruding through a fine hole, e.g., a viscose solution to give viscose rayon, or a nylon melt to give nylon.

Spinning Cot

A revolving rubber roller which acts, in conjunction with a fluted steel roller, in consolidating the loosely formed yarn (slub) during spinning. Two sets of cots and rollers, running at different speeds, act in conjunction

with the drafting aprons, in stretching and consolidating the yarn prior to twisting.

Split Batch Technique

A procedure to prevent premature vulcanisation of very fast-curing rubber compounds, doughs or solutions. One part of the batch contains the vulcanising agent and the other contains the accelerator; requisite quantities of the two parts are mixed together immediately prior to use.

Split Curing

A technique of press curing in which the moulds are serviced while the press is closed. For example, in a two daylight press operating on a 60 minute cure, the press will be opened at 30 minutes and the mould from platen 1 removed and replaced with another mould loaded with the moulding blank. At the end of a further 30 minutes the procedure is repeated for platen 2, and the cycle of operations continued.

Sponge Rubber

One type of cellular rubber. Conventional sponge rubber has a porous structure, the cells being open and inter-communicating; it shows very high absorption of water.

The rubber compound for this product has to be of low viscosity to allow the generated gas to expand rapidly as it is formed. Inorganic blowing agents are normally used for this type of product with often a small additional amount of organic blowing agent to regularise the size of the cells being formed.

SPR

Abbreviation for superior processing rubber also known as SP Rubber

Spreader

- (1) Another name for a spreading machine.
- (2) Also a curved or fluted roller used on any machine which processes rubber-coated fabrics, with the object of 'spreading' the fabric from the centre of its width outwards and thus removing wrinkles.
- (3) A tyre 'spreader' is a device for holding open the beads of a pneumatic tyre so that the inside may be examined or repaired.

Spreading

Coating of a textile with rubber by first making the compound into a stiff dough by dissolving or 'letting-down' the compound into a suitable solvent and then applying at the back edge of a doctor knife under which the fabric is passed.

Spreading Machine

A machine which carries out the operation of coating textiles with rubber by the process of spreading

Sprues

In transfer moulding, the channels in the mould which transfer rubber compound to the actual moulding cavities.

Spue

An obsolescent term for spew.

Square Woven Fabric

A woven fabric having approximately the same number of warp threads per inch of width as weft threads.

SQC

Abbreviation for statistical quality control.

SRF

Semireinforcing furnace, carbon black grade.

SSR

Abbreviation for Specified Singapore Rubber.

Stabiliser

In latex compounding, same as protective colloid. Stabilisers are incorporated in synthetic raw rubbers to protect the rubbers from oxidation during storage. Since the chemical behaviour of these protective materials is not significantly different from that of antioxidants in a vulcanisate, it has been proposed that the use of stabiliser in this sense be dropped in favour of antioxidant.

Staining

Change of colour of a vulcanised rubber when exposed to light or change of colour in a material in contact with, or adjacent to a vulcanised rubber.

Stand

- (1) On a rubber plantation, the tree population per acre. The initial stand is sufficient to allow for losses due to disease and provides a final stand of 90-100 trees per acre.
- (2) Another name for hold.

Standardisation

An international committee (ISO/TC45) deals with the standardisation of test methods for rubber and the standardisation of rubber product specifications. There is a parallel committee for plastics, materials and products; ISO/TC61. Individual countries also have standard setting bodies such as BSI and ASTM.

Standard Malaysian Rubbers

The introduction of Standard Malaysian Rubbers represented a significant development in the marketing of natural rubber. The SMR scheme offers a complete range of technically specified natural rubbers guaranteed to meet a national standards code covering quality and presentation. The system has superseded the largely arbitrary, visual grading methods - there were thirty-one internationally recognised visual grades and, additionally, a great number of private grades used by local producers.

The first three grades of SMR were technically specified in terms of guaranteed cleanliness: SMR 5 with a guaranteed cleanliness level of 99.95%; SMR 20 a guaranteed cleanliness level of 99.8%; SMR 50 a guaranteed cleanliness level of 99.5%.

Colour plays no part in technical specification, but there is a special grade of light-coloured SMR for those who need it - SMR 5L - made to SMR 5 standards.

In addition SMR is characterised by the plasticity retention index, which gives opportunity for close control of processing and properties.

SMR is not only technically specified clean. It is delivered clean because it is film-wrapped, in small convenient bales.

SMR is available either in standard forms of sheet and crepe, or compacted crumb forms of NR.

Standing Wave

A phenomenon occurring in a pneumatic tyre running at a speed much higher than that for

which it is designed. The tyre circumference shows a series of flats since the part in contact with the ground has not had sufficient time to recover before it again meets the ground.

Staple Fibre

Man-made fibres produced as continuous filaments and then cut into short lengths to match those of some natural fibres such as cotton or wool. The 'staple' of cotton, wool, staple fibre, etc., is an indication of the average fibre length.

Stark Rubber

Another name for frozen rubber.

State of Cure

The degree of vulcanisation of a rubber compound is assessed technically by the indefinite terms of undercure, correct cure, optimum cure and overcure. It may be given precision by (a) measurement of stress-strain relationship of a range of cures, (b) measurement of the modulus at 100% elongation, (c) measurement of the volume swelling in benzene, or (d) by the use of instruments such as the oscillating disc rheometer and the moving die rheometer.

Static Electricity

Electricity at rest as opposed to moving or current electricity. Static electricity can build up on the surface of insulating materials and may either spark across to an adjacent object or give a shock to anyone handling the material. *See Anti-Static Rubber.*

Statistical Quality Control

The control of quality of a process or product by the application of the techniques of mathematical statistics.

Statistics

The classification, tabulation and study of numerical facts. Mathematical statistics is the study of the variation of natural phenomena and employs the techniques of probability theory.

Steam

Water in the gaseous state; it is a convenient source of heat widely used in the curing of rubber products. *See Open-Steam Curing, Press Curing.* Steam is really a colourless gas and what is usually termed 'steam' (issuing from an autoclave, a press, thermometer bleed pipe, etc.) is really droplets of water which result from the steam meeting the cooler air of the atmosphere.

Steam Trap

A device fitted to steam supply pipes and all steam-heated equipment to ensure that condensate formed when the steam has given up its heat is quickly discharged from the system without loss of live steam.

Stearic Acid

$C_{17}H_{35}COOH$, one of the fatty acids found in animal fats. Commercial stearic acid is a mixture of stearic and palmitic acids. It is used in rubber compounding as an organic activator of accelerators.

Stefan's Law

Also known as the Stefan-Boltzmann law. The total radiation from a black body is proportional to the fourth power of its absolute temperature.

STEL

Short Term Exposure Limit. *See Occupational Exposure Limits.*

Step Cure

In the vulcanisation of thick rubber articles the temperature may be stepped up in stages to ensure adequate heat penetration to the interior before the external surface begins to cure. Such a cure schedule is termed a step cure. Step post cures are used with thick section rubber articles to ensure that volatiles are released gradually without causing damage, such as porosity, due to an over rapid release.

Stereochemistry

Chemistry which takes into consideration the arrangement in space of the atoms in a molecule. Assuming that a molecule is three-dimensional, space isomerism is thus possible.

Stereoregular Polymers

High polymers in which the side chains are arranged either above or below the plane of the main carbon chain of the molecule in a regular pattern.

In the isotactic molecular structure the substituent groups are all on the same side of the main chain, either all above or all below.

In the syndiotactic structure the substituent groups alternate regularly above and below the plane of the main chain.

In an atactic structure the substituent groups are arranged irregularly above and below the plane of the main chain.

Stereoregular polymers are made by reactions involving the use of stereospecific catalysts.

Stereospecific Catalysts

Catalysts which bring about a spatially regular (stereoregular) configuration in high polymers. The main types are Ziegler, Phillips, Standard Oil and Metallocene

Stereospecific Polymers

Polymers synthesised by the use of certain catalysts which direct the propagation reaction so as to bring about a known and desired orderliness in the molecular chain. *See Stereoregular Polymers.*

Steric Hindrance

In organic chemistry, the retarding influence of neighbouring groups on reactions between molecules.

Stiffener

A compounding ingredient used to reduce the plasticity (increase the stiffness) of rubber compound and thus enable, e.g., an extruded section, to retain its shape or to reduce air trapping in moulding soft rubbers.

Stock

- (1) Another name for a rubber compound.
- (2) In bud grafting, the plant on which the bud is grafted.

Stokes' Law

The rate of settling of solid particles in a fluid depends on the particle-size of the solid and the nature of the fluid. The terminal velocity (v) is given by:

$$v = \frac{2gr^2(d_1 - d_2)}{9\eta}$$

where the particles have radius r , density d_1 falling through a liquid of density d_2 and coefficient of viscosity η .

STP

Abbreviation for standard temperature and pressure. *See NTP.*

STR

Abbreviation for Standard Thai Rubber.

Strain

The change in dimensions resulting from the application of a stress. In tensile testing of rubber strain is synonymous with elongation.

Strainer

A machine similar in principle to an extruder but fitted with a special head containing a wire gauze through which rubber or rubber compound may be passed to free it from foreign matter or from agglomerates of compounding ingredients. In the extrusion of thin-walled tubing a strainer plate and gauze may be fitted in the actual extrusion machine so that foreign matter is removed immediately prior to the extrudate issuing from the die-box.

Strainer-Slabber

A strainer equipped with a special die which extrudes the strained rubber as a tube, which is then slit at the head to produce a continuous sheet, which may then be cut into slabs of convenient length.

Strain Gauge

A device for measuring very small strains. The electrical type consists of a grid of thin resistance wire suitably attached with adhesive to the surface to be tested; the resistance of the wire is proportional to the strain.

Straining

Removing foreign matter and agglomerates of compounding ingredients from rubber or rubber compound by passing it through a strainer.

Stress

Force per unit area. The applied stress may deform an elastomer in three ways, i.e., extension, compression or shear.

Stress Decay

Another term for stress relaxation.

Stress Relaxation

The reduction in stress which takes place in a test strip of rubber held at constant elongation. Stress relaxation measurements are used in the study of the ageing of rubber vulcanisates, the degradation of the network structure resulting in a reduction of the tension.

Stress Softening

Another term for Mullins effect.

Stress-Strain Testing

The determination of the relationship of stress to strain when a rubber is deformed, the result being shown in the form of a stress-strain curve; unless compression stress-strain is specifically stated, the expression normally applies to the tensile characteristics of a rubber.

Strip Knives

A set of knives fitted to a mill to cut off a strip of rubber compound for continuous feeding of an extruder or calender. Similar knives may be fitted to a calender roll to produce strip or sheet rubber of specified width.

Stripping

- (1) The removal of uncured assemblies or cured products from a former, mandrel or mould.
- (2) The removal of unreacted monomers in the manufacture of synthetic rubber.
- (3) Determination of adhesion between textile and rubber in tyres, hose, belting, etc., by measurement of the force necessary to strip one from the other.

Stroboscope

An instrument used for examining any regularly repeating motion, e.g., speeds of rotating shafts. The frequency of flashing of a bright light illuminating the shaft is varied until the shaft appears stationary and a simple calculation gives the shaft speed.

Structural Formula

A formula showing how the individual atoms in a molecule are linked together by valency bonds.

Structure

This term has its normal meaning as in the 'structure of vulcanised rubber' but it now has a particular significance in relation to carbon black. See *Carbon Black Structure*.

S-Twist

In textile technology that direction of twisting yarns or threads which runs from left to right downwards, as the centre part of a letter S, when the yarn is held vertically.

Styrenated Phenol

SPH, antidegradant – non-staining.

Styrene

One of the monomers used in the manufacture of styrene-butadiene rubber. It is vinylbenzene, a liquid boiling at 146 °C and having the formula $C_6H_5CHCH_2$.

Styrene-Butadiene Rubber

A general purpose synthetic rubber made by the copolymerisation of styrene and butadiene in the proportions of approximately 25 styrene to 75 butadiene.

Sub

An obsolescent abbreviation for rubber substitute.

Substitution

Chemical reaction typical of saturated organic compounds, replacing one chemical group, e.g., hydrogen, by another.

Substrate

- (1) The substance on which an enzyme acts, as in the formation of volatile fatty acids in latex.
- (2) The underlying layer, e.g., the metal in rubber-to-metal bonding.

Sulphenamides

Organic accelerators of the thiazole class having delayed action and finding particular application in tyre compounds containing furnace blacks. Sulphenamides are manufactured from mercaptobenzothiazole by reaction with an amine, the nature of which determines the degree of delayed action.

Sulphur

Elemental sulphur mixed into rubber compounds is the agent responsible for the vulcanisation of the majority of rubber products made from natural rubber, SBR, butyl rubber and nitrile rubber. Sulphur-vulcanisable varieties of many of the newer synthetics are also available. The bulk

of the world's sulphur is produced by the Frasch process. See *Flowers of Sulphur and Insoluble Sulphur*.

Sulphur Bridges

In sulphur vulcanisation of rubber, crosslinking is considered to be effected by sulphur atoms, which are therefore termed sulphur bridges. See *Vulcanisation*.

Sulphur Donor

A curing agent which splits off active sulphur during the vulcanisation reaction. One example is di-morpholinodisulphide (Sulfasan R).

Sulphur MC

A magnesium carbonate coated grade of sulphur used in curing nitrile rubber.

Sulphur Monochloride

S_2Cl_2 , a by-product in the manufacture of carbon tetrachloride from carbon disulphide. Was used, dissolved in solvent naphtha, in the vulcanising of rubber by the cold cure process and the vapour cure process. The process was fraught with health and safety problems and has been superseded by low temperature accelerators and room temperature vulcanising (RTV) systems for silicone and polyurethane.

Superheated Steam

Steam heated out of contact with the water from which it was formed and subsequently passed over an additional heat source, known as a superheater, and is therefore at a higher temperature than that corresponding to saturation. It should be noted that a 'leak' of superheated steam cannot easily be seen. See *Steam and Saturated Steam*.

Superior Processing Rubber

A modified type of natural rubber which has many processing advantages over normal sheet and crepe rubbers. It shows reduced shrinkage, reduced die swell and much better retention of dimensions especially in complicated extrusions. It is made by adding a quantity of vulcanised latex to normal latex before coagulating. See *PA 80*.

Surface Active Agent

Materials used in latex compounding, having the power to displace other substances already adsorbed on the rubber particles. See *Emulsifying Agent, Protective Colloids and Wetting Agents*.

Surface Resistivity

The electrical resistance between opposite edges of a square or between 2 electrodes on the same surface of the material, under specified conditions of testing, e.g., BS 903-C1.

Surface Tension

The open surface of a liquid tends to contract inwards towards the bulk of the liquid, as if it were covered with an elastic skin. This phenomenon is termed surface tension.

Surfactant

Another term for surface active agent.

Suspension

A solid/liquid mixture consisting of very small solid particles suspended in a liquid. The action of gravity or the process of filtration can effect separation of the solid from the liquid.

SVR

Abbreviation for Standard Vietnamese Rubber.

Swan-Necked Press

Another term for gooseneck press.

Sweetening

The process of treating cold-cured proofings with a weak alkali to neutralise any remaining acid and so prevent subsequent tendering of the fabric.

Swelling

Increase in dimensions of an elastomer due to the absorption of any organic liquid with which it may come in contact or in which it may be immersed. Measurement of the swelling of vulcanised rubber in solvents can be used to determine state of cure and to assess the suitability of elastomers for such uses as chemical plant lining or oil seals.

SWG

Abbreviation for Standard Wire Gauge (British).

Syndiotactic or Syndyotactic

One of the terms coined by G. Natta to describe different arrangements of atoms in long-chain molecules. *See Stereoregular Polymers.*

Syneresis

The expulsion of liquid from a gel as in the coagulation of latex, where the structure of rubber particles contracts and expels the serum.

Synergistic

The 'working together' of two substances to give a result of greater effect than would be expected by the simple addition of the effects of the two substances working alone.

Synthetic

The adjective from the noun synthesis; it is correctly applied to the product resulting from the combination of two or more chemical substances to form a new substance, the process being carried out by man in either the laboratory or the factory; 'synthetic' does not mean inferior.

Synthetic Rubber

A convenient term for any material possessing the properties of a rubber but produced from other than natural sources. A synthetic version of natural rubber has been available for many years with the same chemical formula, i.e., *cis*-1,4-polyisoprene, but it has not displaced the natural form. *See also Butyl Rubber, Chloroprene Rubber, Ethylene-Propylene Rubber, Nitrile Rubber, Silicone Rubber and Styrene-Butadiene Rubber.*

Semicrystalline

A polymer in which most of the molecules are packed in a regular manner forming crystalline regions (50-95%) in the solid state, the remainder of the material forms amorphous regions.

T

TAC

Triallyl cyanurate, peroxide co-agent.

Tachometer

An instrument for measuring the speed of a revolving shaft or of belting, etc.; it may indicate the speed in either revolutions per minute (rpm) or in length per minute.

Tack

The adhesiveness of raw rubber or rubber compounds. Where tack is undesirable it may be

reduced by the use of dusting agents; assembly of uncured components is facilitated by good tack which is enhanced where necessary by the addition to the compound of tackifiers. Certain freshly-cured rubber products have a very tacky surface, and if the use of a dusting agent is undesirable the tack may be removed by treatment with chlorine water or with 'cold cure' solution (*see Cold Cure*). *See Tackiness.*

Tackifier

A compounding ingredient which enhances the surface tack of uncured rubber compounds. Tackifiers, exemplified by pine tar are classed under 'softeners and processing aids'.

Tackiness

Although tack and tackiness generally have the same meaning, the term tackiness is usually confined to surface stickiness due to environmental degradation whereas tack refers to the adhesiveness of uncured material.

Tackmeter

An instrument for measuring the surface tack of sheet materials.

Tactic Polymers

High polymers which show the stereochemical configurations known as isotactic and syndiotactic. *See Stereoregular Polymers.*

TAIC

Triallyl isocyanurate, peroxide co-agent.

Tail Gas

The lighter gases produced in the distillation of petroleum or the residual gas in the manufacture of carbon black by the furnace process.

Talalay Process

A method of manufacturing latex foam. Compounded latex is partially frothed and fully expanded by application of vacuum to the mould; the gel is frozen, set by carbon dioxide and vulcanised by raising the temperature of the mould. *See Dunlop Process.*

Talc

Another term for French chalk.

Tall Oil

A mixture of monobasic organic acids (abietic, oleic and linoleic), produced either as a by-product of paper production or synthetically. It is used as an extender.

Tapping

The operation of making a carefully-controlled incision in the bark of the Hevea tree to permit the latex to flow out. Using a specially shaped knife the tapper makes a 6 mm deep cut in the bark at an angle of 30° from left to right. The cut is shaped into a groove from which a shaving of bark about 1 mm thick is removed in subsequent tappings. *See Tapping Systems.*

Tapping Systems

Length of cut and frequency of tapping are varied to suit particular clones, e.g., a half-spiral cut every second day being denoted as 'S/2, D/2, 100%', the 100% representing normal tapping intensity.

TBBS

N-tert-Butyl-2-benzothiazole sulphenamide, accelerator.

TBTU

1,1,3-Tributyl thiourea, accelerator.

TBUT

Tetrabutyl thiuram disulphide, accelerator.

TBZTD

Tetrabenzyl thiuram disulphide, accelerator.

TCP

Tricresyl phosphate, ester plasticiser.

TCR

Abbreviation for technically classified rubber.

TDI

Toluene diisocyanate. *See Isocyanate.*

Tear Resistance

Resistance to extension of a cut or tear in a rubber sample. *See Tear Strength.*

Tear Strength

This is determined by cutting a nick of accurate depth in a crescent-shaped test piece, measuring the load required to complete the tearing.

Technically Classified Rubber

Technically Classified Rubber was introduced in about 1951. It was natural rubber which had been tested on the plantation for rate of cure. Each bale was marked with a coloured circle, red denoting slow curing, yellow medium curing and blue fast curing. When the scheme was first introduced, the shape of the symbol indicated the plasticity of the rubber, a bar for low Mooney viscosity, a circle for medium Mooney and a cross for high Mooney. The plasticity grading was then discontinued due to the plasticity change between plantation testing and receipt of the rubber by the consumer. This system was superseded in 1965 by Technically Specified Rubber.

Technically Specified Rubber

This is the generic name for the scheme originally introduced in Malaysia as Standard Malaysian Rubber (SMR). In effect it is the same specification but applied to rubber produced in other countries, e.g., Standard Indonesian Rubber (SIR). Both SMR and SIR are Technically Specified Rubbers.

Technology

The practice and description of any or all of the applied sciences which have commercial value.

Tellurium

A brittle, non-metallic element with chemical properties similar to those of sulphur. It has been used as a secondary vulcanising agent.

Tellurium Diethyl Dithiocarbamate

TDEC, accelerator.

TEM

Abbreviation for transmission electron microscopy.

Temperature

A measure of the 'hotness' or 'coldness' of a substance; it is measured in degrees. *See Celsius and Fahrenheit.*

Temperature Coefficient of Vulcanisation

This is the ratio of the rates of vulcanisation at two temperatures 10 °C (or 18 °F) apart. For rubber vulcanisation the coefficient is approximately 2 but it varies slightly with the temperature, the type of compound and the accelerator.

Temperature Control

Maintaining a specified temperature within narrow limits is essential in many processes carried out in the rubber industry, e.g.,

polymerisation temperature in the manufacture of synthetic elastomers, vulcanising temperature in the manufacture of rubber products. Control systems vary in their sophistication. Sensors are commonly based on thermocouples or platinum resistance thermometers and the most common system can be described as having three term controllers, i.e., PID or Proportional, Integral and Derivative. To be effective the PID terms need to be tuned to the process and equipment, modern systems are generally self tuning.

Temperature Scales

See Celsius and Fahrenheit.

Tenacity

The breaking strength of a textile filament, yarn or cord, expressed in grams per denier.

Tendering

Weakening of a fabric from any cause, but particularly the weakening of a proofed fabric by the acid resulting from insufficient sweetening, after vulcanisation by the cold cure process.

Tensile Strength

The breaking stress in tension of an elastomer expressed in Mpa, kg/cm² or lb/in². It is calculated on the original (unstressed) area of cross-section of the test specimen.

Tension Set

The elongation remaining after a rubber test piece has been stretched for a given time and allowed to rest for a given time; it is expressed as a percentage of the original distance between the bench marks. The term 'permanent set' (correctly, permanent set in tension) is still popularly used to denote tension set, see standard BS903-A5.

Terpenes

A class of hydrocarbons occurring in many essential oils of plants. They can be regarded as low-molecular weight polymers of isoprene (C₅H₈)_n. Dipentene is a terpene, while natural rubber, gutta percha and balata have been termed polyterpenes.

Terpolymer

A copolymer consisting of three monomers polymerised together, e.g., ethylene-propylene-dicyclopentadiene terpolymer.

Terracing

The cutting of terraces on rubber plantations situated on hilly areas, with the object of preventing the loss of top soil during heavy rain.

Terylene

The trade name of a polyester fibre used as textile reinforcement for rubber in products such as tyres, belting and hose. It is a truly synthetic fibre made from polyethylene terephthalate, a condensation product of terephthalic acid and ethylene glycol.

TETD

Tetraethyl thiuram disulphide, accelerator.

Tetrabenzyl Thiuram Disulphide

TBZTD, accelerator.

Tetrabutyl Thiuram Disulphide

TBUT, accelerator.

Tetraethyl Thiuram Disulphide

TETD, accelerator.

Tetramethyl Thiuram Disulphide

TMTD, accelerator

Tetramethylthiuram Monosulphide

An accelerator similar in properties to tetramethylthiuram disulphide, except that it cannot be used without added sulphur.

Tex

A system of designating the fineness (linear density) of yarns and fibres. It was proposed for universal adoption, to supersede the multiplicity of existing systems of yarn counts. The Tex unit is the weight in grams of 1000 metres of yarn. A 23^s cotton becomes 25.6 tex and a 1260 denier yarn becomes 140 tex. *See Count and Denier.*

Textiles

In a limited sense, any material suitable for weaving or being made into a woven fabric. In the rubber industry the term is widened to include any material used for the structural reinforcing of a product and thus includes such materials as steel and glass not normally classed as textiles. *See Cotton, Nylon, Rayon and Terylene.*

TFE

Abbreviation for tetrafluoroethylene.

T_g

Abbreviation for glass transition temperature.

TGA

Abbreviation for thermogravimetric analysis.

T-Head

An extruder die-box or head in the shape of a letter T used in wire covering. The rubber flow is thus at right angles to the direction of travel of the wire.

Thermal Black

Carbon black produced by the thermal decomposition of natural gas or atomised oil in a pre-heated refractory furnace where the fuel is cracked into carbon and hydrogen. The process is cyclic, two furnaces being used as one production unit, one furnace being heated up as the other is producing.

Thermal Conductivity

The thermal conductivity of a substance is the quantity of heat in cal/sec passing through a body 1 cm thick with a cross section of 1 cm² when the temperature difference between the hot and cold sides of the body is 1 °C.

The thermal conductivity of compounded rubber is an additive property of the rubber and the compounding ingredients, and may be calculated from the mix formula and the individual thermal conductivities.

Thermal Decomposition

Breaking down of a chemical substance by means of heat. *See Cracking and Thermal Black.*

Thermal Diffusivity

A coefficient which determines the rate of rise of temperature of a point in a body which is being heated at some other point; it is equal to the thermal conductivity of the substance divided by the product of its specific heat and its density.

Thermal Expansion

See Coefficient of Thermal Expansion.

Thermal Liquids

Liquids of high boiling point and having good heat transfer properties, used in industrial heating. They operate at atmospheric pressure but at temperatures up to 400 °C (752 °F).

Thermocouple

An assembly of two dissimilar metals often in the form of wires, used in measuring temperature by means of the thermo-electric effect.

Thermo-Electric Effect

The production of a current of electricity by heating a junction formed by two dissimilar metals. For temperature measurement the metals are usually in the form of wires (*see Thermocouple*) and the circuit has two junctions, the 'hot' junction which is exposed to the temperature to be measured and the 'cold' junction which is kept at a standard temperature. The thermo-electric effect is also termed the 'Seebeck Effect' after its discoverer.

Thermogram

The form of graph on which are displayed the results of tests done by the technique of differential thermal analysis.

Thermogravimetric Analysis

This is an analytical technique used to obtain accurate quantification of the principal compound constituents such as plasticiser, polymer, carbon black and inorganic species, by monitoring weight loss across a temperature range.

Thermoplastic

Applied to high polymers which soften by the application of heat and which may be resoftened by heating, provided chemical decomposition does not take place.

Thermoplastic Elastomers

These were originally described as 'thermoelastic polymers'. The first were block copolymers of butadiene and styrene, at room temperature one and the same molecule has segments in it which are rubber-like, as well as segments which are below their glass transition temperature and hence are rigid. The benefits of these unique rubbers lie in the fact that at temperatures of 285-430 °F (140-220 °C) they may be shaped and reshaped by the processing techniques used for thermoplastics, and on cooling their elastomeric character is regained. Thus, traditional mixing and vulcanising equipment is unnecessary and scrap may be recycled. There are a wide range of thermoplastic elastomers with properties generally intermediate between those of rubbers and plastics.

Thermosetting

Applied to a high polymer which undergoes a chemical change when it is subjected to heat, after which its shape cannot be changed by the application of further heat and pressure. Although vulcanisation of rubber is a thermosetting process the term is usually applied to 'plastics'. *See Thermoplastic.*

Thermostat

A device for maintaining a constant temperature. It may employ a bimetallic strip the twisting movement of which (due to the different coefficients of expansion of the two metals) switches heating elements on or off to maintain the specified temperature.

THF

Abbreviation for the solvent tetrahydrofuran.

Thiamer

A term that was used as a generic name for a new family of elastomers related to EPT. They are terpolymers and sulphur-vulcanisable. Sulphur atoms separate each of the ethylene and propylene repeating units in the backbone of the polymer chain, hence the name thiamer.

Thickening Agent

A substance used in latex compounding to increase the viscosity of the mix. Examples are alginates, casein, certain clays and methyl cellulose.

Thin Layer Chromatography

This is an analytical technique used for the separation and identification of additives. It can also be used in a preparative way for the isolation of sample fractions for subsequent chromatographic or spectroscopic analysis.

Thiocarbamide

Symmetrical diphenylthiourea, one of the oldest accelerators. It is slow-curing but scorchy and is little used nowadays. It survived as the accelerator for pneumatic tyre curing bags until the late 1960s.

Thiokol

See *Polysulphide Rubbers*.

Thixotropy

The property possessed by certain colloids of forming a gel-like structure on standing but which revert to a liquid form when subjected to agitation. The term has also been applied to the stiffening effect shown by uncured rubber compounds containing fillers, particularly carbon black.

Threading Diagram

A diagram showing how rubber sheet, fabric, linings, etc., are 'let off' through tensioning devices into calenders, spreading machines, etc., and finally taken up on box rollers. Direction of travel and position of rubber nips are usually included in such diagrams.

Titanium Dioxide

A white pigment for rubbers and plastics characterised by high tinctorial power, fastness to light, and chemical stability. Titanium dioxide pigments are made in two crystal forms, rutile and anatase, which differ in crystal structure and crystal size.

TLC

Abbreviation for thin layer chromatography.

TLV

Threshold Limit Values are established in the USA by the American Conference of Governmental Industrial Hygienists (ACGIH). Three categories of TLV are now commonly quoted as follows:

- (1) Threshold Limit Value - Time Weighted Average (TLV-TWA), this is the time-weighted concentration for a normal 8-hour work day or 40 hour working week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effects.
- (2) Threshold Limit Value - Short Term Exposure Limit (TLV-STEL). The maximum concentration to which workers can be exposed for a period of up to 15 minutes

continuously without suffering from intolerable irritation, chronic or irreversible tissue change, or narcosis of sufficient degree to increase accident proneness, impair self-rescue or materially reduce work efficiency; provided that no more than 4 excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA also is not exceeded.

- (3) Threshold Limit Value - Ceiling (TLV-C). The concentration that should not be exceeded even momentarily.

In the USA compliance with TLV standards is generally considered to be mandatory, although not statutory. See *Occupational Exposure Limits*.

TMCH

1,1-Bis(*tert.*-butylperoxy)-3,3,5-trimethylcyclohexane, organic peroxide.

TMQ

Polymeric 2,2,4-trimethyl-1,2-dihydroquinoline, antidegradant - staining.

TMT

Abbreviation for tetramethylthiuram disulphide.

TMTD

The preferred abbreviation for tetramethylthiuram disulphide to prevent confusion with tetramethylthiuram monosulphide.

TMTM

The preferred abbreviation for tetramethylthiuram monosulphide.

TNPP

Tris(nonylphenyl) phosphite, antidegradant - non-staining.

Toggle Press

A press for vulcanising rubber products, operated by electricity and held shut by a mechanical toggle or elbow joint. See *Daylight Press*.

Tolerance

The permissible deviation from the specified dimensions of any component or product, or from the specified conditions of temperature, pressure, time, etc., laid down for the carrying out of any processing operation.

Toluene

Toluol or methylbenzene; a hydrocarbon of the benzene series, used as a solvent for rubbers.

p-Toluene Sulphonyl Hydrazide

TSH, blowing agent.

o-Tolyl Biguanidine

OTBG, accelerator.

Ton

The British or 'long' ton weighs 2240 pounds; the American or 'short' ton is 2000 pounds, and the metric ton (tonne) of 1000 kilograms is equivalent to 2205 pounds.

Top Capping

The process of adding new tread to a worn tyre.

Topping

See *Coating*.

Torque

The turning force produced by two equal and opposite parallel forces acting on a body.

Toxicity

The term toxicity, when used in the context of industrial materials and processes, refers to the potential of chemical substances to cause adverse

effects in human beings as a result of skin contact, inhalation, or ingestion. Toxic effects may become apparent either immediately or shortly following exposure (acute toxicity) or they may become evident only after repeated exposure to amounts of chemicals which are individually too small to give rise to acute effects (chronic toxicity). Substances giving rise to chronic or delayed effects include cumulative poisons and carcinogenic chemicals.

TPAU

Abbreviation for thermoplastic polyester urethane.

TPEU

Abbreviation for thermoplastic polyether urethane.

TPT-MA

Trimethylolpropane trimethacrylate, vulcanising agent.

TPU

Abbreviation for thermoplastic urethane elastomer.

TPX Polymers

A series of thermoplastics based on 4-methylpentene-1. Polymethylpentene is the lightest of all known polymers with a density of 0.83 g/cm³. It has excellent electrical insulating and chemical resistance properties, and offers a very high melting point. Because of its low density, TPX has high acoustic efficiency (a high damping factor due to large internal losses). It also displays exceptionally low distortion and high power handling characteristics.

Trans

See Cis-Trans Isomerism.

Transfer Moulding

A method of moulding rubber products which has certain advantages over compression moulding. The transfer mould has an upper cavity or pot into which the uncured blank is placed. The closing of the mould transfers the rubber through a series of holes (feed ports) into the mould cavity proper. Cure times are shorter than for compression moulding since the rubber gains some frictional heat as it is forced through the feed ports.

Transmission Electron Microscopy

TEM is used to investigate the phase morphology of polymer blends and the dispersion of fillers. *See Electron Microscope.*

Tread

That portion of a vehicle tyre (pneumatic, semi-pneumatic or solid) which contacts the road surface. The tread pattern is so designed as to give the best combination of properties suitable for the conditions under which the tyre will be used.

Tread Rubber

The preferred, but ambiguous, name for camelback.

Treated

Applied to certain compounding ingredients (particularly zinc oxide and precipitated whiting) which have been surface-treated to improve their reinforcing power or their ease of incorporating into rubber. Also applied to a lining which has

received some treatment to facilitate the removal of the unvulcanised sheet or rubbered fabric.

Tree Lace

See Tree Scrap.

Tree Scrap

Strips of naturally-coagulated rubber removed from the tapping cut, vertical channels and spout prior to making the next tapping. The rubber is washed, dried, creped and sold as blanket crepe.

Triallyl Cyanurate

TAC, peroxide co-agent.

Triallyl Isocyanurate

TAIC, peroxide co-agent.

Triangular Calender

The three-bowl version of the Z calender.

Tricap

Triethylene glycol dicaprylate/caprate, ester plasticiser.

Tricresyl Phosphate

TCP, ester plasticiser.

Triethanolamine

A basic substance used particularly in compounds containing large quantities of white factice to offset the retarding effect of the factice. Also used to prepare emulsifying agents in latex compounding.

Triethylene Glycol Dicaprylate/Caprate

Tricap, ester plasticiser.

Trimethylolpropane Trimethacrylate

TPT-MA, vulcanising agent.

Triple Bond

The type of bond in which three valency bonds link two atoms in a molecule. *See Acetylene.*

Tripsometer

An apparatus for the determination of resilience by a rebound method. Usually termed Dunlop tripsometer. *See Resilience.*

Tris(Nonylphenyl) Phosphite

TNPP, antidegradant – non-staining.

Tritolyl phosphate

TTP, ester plasticiser.

Trixylyl Phosphate

TXP, ester plasticiser.

TSH

p-Toluene sulphonyl hydrazide, blowing agent.

TSR

Abbreviation for technically specified rubber.

TTP

Tritolyl phosphate, ester plasticiser.

TTR

Abbreviation for Thai Tested Rubber. *See STR.*

Tube

Normally refers to the inner tube of a pneumatic tyre assembly but may refer to any component of a rubber product which is in tubular form, e.g., the inner lining of a fire hose. *See Tubing.*

Tubeless

Applied to a pneumatic tyre with no separate inner tube. An air-impermeable lining, usually of a halogenated butyl, is applied to the inside of the casing. The bead construction is such as to ensure an airtight fit on the wheel rim. Inflation is done through a valve fitted directly into a valve hole in the rim.

Tuber

Another name for extruder.

Tubing

- (1) Another name for extrusion.
- (2) Rubber in tubular form such as gas tubing. Tubing differs from hose in that it has no structural textile reinforcement.

Tumbling

A process for removal of the spew or flash on moulded rubber products, by tumbling or rotating the parts in a barrel maintained at a temperature low enough to harden the spew, which is rubbed or chipped away by friction between the articles. The low temperature is usually obtained by using liquid nitrogen.

TWA

Time Weighted Average. *See Occupational Exposure Limits.*

Twaddell

A scale for expressing the specific gravity of liquids, named after William Twaddell, whereby 200 degrees Twaddell equates to a sg of 1.

Twist

The coiling together of textile staple fibres, yarns or threads to give the structure the required degree of strength, extensibility, flex resistance, etc. Twist is designated as so many turns per inch and either right hand (Z) or left hand (S). *See S-Twist and Z-Twist.*

TXP

Trixylyl phosphate, ester plasticiser.

Tyndall Effect

If a beam of light is passed through a colloidal solution, the colloidal particles will reflect or scatter the light so that the beam becomes visible when the solution is viewed from the side against a dark background. This Tyndall effect is used in the ultramicroscope.

Tyre

See Pneumatic Tyre, Semi-Solid Tyre and Solid Tyre.

Tyre Cord

A particular construction of filaments of rayon, nylon, Terylene, Kevlar or steel used as the structural reinforcement of pneumatic tyres. The cords were originally woven (cord fabric) but are now invariably used weftless.

T-50 Test

One method for determining the state of cure of a rubber compound. A sample of the rubber is stretched, cooled to a temperature of around -70 °C while stretched and then released. As the temperature rises the rubber retracts and the T-50 value is the temperature at which it has lost 50% of its original elongation. The T-50 test is now obsolescent.

U

UHF

Abbreviation for ultra high frequency.

UL Rating

Underwriters' Laboratory rating; a material is aged at various temperatures and a property is monitored, e.g., tensile strength.

Ultimate Elongation

In tensile testing of rubber, the elongation reached by the sample at its breaking point; also

termed 'elongation at break' (BS903:Part A2 Determination of tensile stress strain properties).

Ultra Accelerators

A term applied to a class of organic accelerators with a very fast and powerful accelerating action: examples are the thiuram disulphides, dithiocarbamates and xanthates. *See TMT, ZDC and ZIX.*

Ultramicroscope

An instrument used to observe particles too small to be seen by the ordinary light microscope. The ultramicroscope makes use of the Tyndall effect.

Ultrasonics

Pressure waves of the same nature as sound waves but of greater frequency, i.e., shorter wavelength, and therefore inaudible. Ultrasonic waves have been used for the detection of ply separations and other voids in rubber-textile composites such as tyres, and for thickness measurement of coatings, etc., where access is possible from only one side.

Ultraviolet Radiation

Electromagnetic waves with wavelengths between those of visible light waves and X-rays. Ultraviolet radiation is used in the examination of elastomers by spectroscopy.

Undercure

The opposite of overcure.

Uni-Rotor Mixer

A mixing machine for rubber and plastics, the ingredients being mixed by a single rotor blade in a cup-shaped chamber being grooved so as to force the mixture to the closed end of the chamber. The principle has been evaluated on laboratory-size machines and is being extended to larger mixers.

Unsaturated Polymer

Any polymer having more than one bond between two adjacent atoms usually carbon atoms and being capable of adding other atoms at that point to reduce it to a single bond.

Unsaturation

In organic compounds the linking of some of the atoms of the molecule by more than one valency bond, i.e., double or triple bonds.

Upside Down Mixing

The simultaneous addition of the elastomers and all the compounding ingredients to an internal mixer at the beginning of the mixing cycle. A saving in mixing time is claimed but dispersion may be adversely affected.

Urethane

RNHCOOR'; basic unit of polyurethane, formed by the reaction of an isocyanate group with an alcohol.

U-Ring

A sealing of U-section which is located in a housing so that the fluid pressure tends to expand the flanges of the U into fluid-tight contact with the walls of the housing.

USF Rubber

This is a type of natural plantation rubber made by flocculating formaldehyde-preserved latex. Formaldehyde is added to the latex as soon as possible after tapping, dirt is allowed to settle out; the latex is bulked, flocculated with acid and the floccs coalesced by steam heat. The coagulum is

dried without smoking. The initials USF denote US Rubber Company Formaldehyde.

U-Test

A static test for determining the adhesion of tyre cord in rubber. The test piece is in the form of a loop shaped like the letter U.

U-Value

A measure of heat transmittance; the number of British Thermal Units transmitted per square foot of surface per hour for 1 °F difference in temperature between the two surfaces. *See Thermal Conductivity.*

UV

Ultraviolet.

V

VA

Abbreviation for vinyl acetate.

Vacuum

Empty space in which there are no atoms or molecules. A perfect vacuum cannot be attained in practice and the term denotes a space containing air or other gas at a very low pressure. In industry 'vacuum' is measured in inches of mercury (in Hg) ranging from 0 in at atmospheric pressure to around 30 in at zero absolute pressure.

Vacuum Extrusion

Extrusion with the aid of a vacuum applied to the screw. The process is applied particularly in the preparation of extrudates to be vulcanised by either the liquid curing medium or fluid bed techniques. It assists in removing the volatiles from the compound and thus improves the quality of the extrudate.

Vacuum Forming

In rubber processing this means the same as vacuum moulding. In plastics manufacture it refers to the use of a controlled vacuum to support and form a sheet of heat-softened material into a desired contour.

Vacuum Moulding

A method of making products such as car floor mats where the 'mould' or contoured former is drilled with a series of small holes which lead into a backing chamber connected to a vacuum line. The vacuum holds the sheet of rubber firmly in contact with the former during curing.

Valency

The combining power of an atom; the number of hydrogen atoms which one atom of the element will combine with or replace.

Valency Bond

The link which holds the atoms together in a molecule. *See Covalency and Electrovalency.*

Valency Electrons

The electrons in the outermost shell of electrons surrounding an atomic nucleus, the number of which determines the valency of the atom.

Value Analysis

An analytical technique designed to examine all the functions of an existing product in order to determine whether or not any cost item can be reduced or eliminated while retaining all the functional and quality elements.

Value Engineering

The application of value analysis to new products in the research and development stage.

Van der Waals' Forces

Attractive forces acting between atoms or molecules of all substances. These forces are generally very small compared to other molecular forces, and are sometimes termed 'secondary forces'.

Vapour Cure

An obsolescent variation of the cold cure. The articles are vulcanised by exposing them to the vapour of sulphur monochloride in a closed chamber.

Vapour Pressure

The pressure exerted by a vapour, either alone or in a mixture of gases. When a mixture of gases is involved the partial (vapour) pressure is a measure of the relative concentrations of the constituents of the mixture. The saturated vapour pressure, the pressure of a vapour in contact with its liquid form is often termed simply vapour pressure.

Variable Intermeshing Clearance (VIC) Rotor Internal Mixer

The variable intermeshing clearance rotor mixer is designed to allow a variable clearance between the intermeshing rotors of the mixer.

Varnish

Used with the normal meaning as in a protective varnish for rubber products, but sometimes used in the sense of rubber cement.

V-Belt

A rubberised fabric belt used for the transmission of power. In cross-section the belt is rectangular with sloping sides similar to the upper part of a letter V; it operates between sheaves into which the V-shape fits.

VCV

Abbreviation for vertical continuous vulcanisation.

VdMi

Verband der Mineralfarbenindustrie.

Veneer

A thin rubber sheet applied in the replacement of the sidewall pattern details in the retreading of pneumatic tyres. A similar film of rubber specially compounded to resist oxygen or ozone or to prevent the migration of carbon black into a lighter rubber, e.g., a tyre white sidewall.

Vent

A channel or shallow groove cut on the surface of a mould or a hole drilled right through a mould wall. The object is to permit the escape of air in the initial stages of moulding and prevent the defect known as 'light' or 'bare' moulding.

Vermillion

The red form of mercuric sulphide once popular as an inorganic colouring agent for rubber.

Vertical Continuous Vulcanisation

Applied at present mainly in the vulcanisation of cables, and in fluid bed vulcanisation of extruded sections.

VF2

Abbreviation for vinylidene fluoride.

VFA

Abbreviation for volatile fatty acid.

Vinylacetylene

This is reacted with hydrogen chloride to produce chlorobutadiene (chloroprene) which is polymerised to polychloroprene. *See Neoprene.*

Vinyl Chloride

The monomer from which the vinyl plastic polyvinyl chloride (PVC) is prepared. Vinyl chloride was originally made by passing acetylene and hydrogen chloride over a mercury chloride catalyst at a temperature of about 180 °C. Now made from ethylene chloride which is converted to vinyl chloride by contact with a catalyst at about 500 °C (900 °F) or by reaction with dilute caustic alkali at about 150 °C (300 °F).

Ethylene chloride is produced by the reaction of ethylene and chlorine; it is denser than water and practically insoluble in it. It is an effective solvent for fats, waxes, greases, and numerous other organic compounds, but its use as a solvent has been largely discontinued in favour of tetrachloroethylene.

Vinyl Group

The unsaturated univalent radical CH_2CH . Many vinyl compounds undergo polymerisation forming plastics, fibres and resins. *See Vinyl Chloride.*

Vinyl Pyridine

One component of a terpolymer of butadiene, styrene and vinyl pyridine used in latex form to promote good adhesion between rubber and textiles, particularly rayon and nylon.

Viscoelasticity

That particular combination of properties possessed by high polymers, characterising the rubber-like state. Depending on the temperature and the time of stressing, a high polymer may show viscous flow or high elasticity. *See Elasticity, Glass Transition, Thixotropy and Viscosity.*

Viscometer

An apparatus for measuring the viscosity of unvulcanised elastomers. The best known is the Mooney viscometer.

Viscose Rayon

That type of rayon which is regenerated from viscose, a syrupy liquid consisting mainly of a solution of cellulose xanthate in dilute sodium hydroxide.

Viscosity

Resistance to flow or resistance to relative motion within a substance. Although viscosity is usually applied to liquid it is replacing the less precise term 'plasticity' in relation to unvulcanised elastomers. *See Viscoelasticity.*

Viscosity Gravity Constant (VGC)

A measure of the average aromatic content of a petroleum oil.

Viscosity Retention Index

Another term for plasticity retention index.

Viscosity-Stabilised Natural Rubber

Natural rubber of consistent Mooney viscosity; storage hardening has been inhibited by incorporating a small quantity of a compound which reacts with the aldehydic groups present in the rubber.

Viscurometer

An early cure instrument which combined in one operation the functions of a Mooney viscometer and of a curometer or vulcameter, i.e., it measures in one quick test the plasticity (viscosity) of the (uncured) mix, its scorch time and cure rate. Now superseded by instruments such as the moving die rheometer.

Vitacap Process

An obsolete process for retreading pneumatic tyres. The vulcanisation of the new tread rubber is not done in a mould but by the open steam method in an autoclave, and the desired pattern is cut on the tread after cure.

VMQ

Abbreviation for vinyl methyl silicone.

Volatile Fatty Acid

A test which is claimed to be a more reliable guide to the condition of a natural rubber latex than the KOH number. The test is performed by steam distillation of the latex and titration of the distillate with standard alkali solution. The VFA number is a measure of the state of degradation of the latex.

Volume Resistivity

The electrical resistance of a cube of side 1 cm to a current passed between opposite faces (BS 903:Part C2, Determination of volume resistivity).

Volume Swelling

This is the percentage increase in volume attained by immersing a vulcanised sample of rubber in a specified solvent. Volume swelling measurements are useful in determining the resistance of rubbers to solvents, but are also of value in measuring the crosslink densities of rubber vulcanisates.

VRI

Abbreviation for viscosity retention index.

Vulcameter

A general term applied to a variety of instruments for determining the curing characteristics of elastomers. The spelling 'Vulkameter' refers to a particular instrument developed by Farbenfabriken Bayer and marketed by Agfa Ltd.

Vulcanisate

A name given to a vulcanised rubber sample or product particularly where the shape or form of the rubber is not required to be specified.

Vulcanisation

This term was originally limited to the chemical reaction of rubber with sulphur to bring about the following effects: (a) reduced thermoplasticity, (b) increased tensile strength and resistance to abrasion, and (c) reduced solubility in organic solvents. Since many other substances can bring about the above changes the term has now been widened to include any treatment which will introduce crosslinks in the rubber matrix.

Vulcanised Latex

By suitable treatment (addition of curatives and careful heating) latex may be vulcanised without coagulation. The latex remains liquid and may be manufactured into products, the coagulum consisting of vulcanised rubber. A less ambiguous term is prevulcanised latex.

Vulcaniser

A traditional term applied to almost any apparatus in which the process of vulcanisation is carried out. It is not normally applied to a daylight press.

Vulcanising Agents

Any substance which will bring about vulcanisation. Elemental sulphur remains a widely used vulcanising agent, but sulphur-containing substances (such as thiuram disulphides) have important uses. Organic peroxides (benzoyl and dicumyl) and nitroso derivatives (e.g., benzoquinone dioxime) are used in vulcanising certain synthetic elastomers.

Vulcanite

Another name for ebonite.

W

Wallace Rapid Plastimeter

A plastimeter of the parallel plate type which enables a determination of plasticity to be made within about 1 minute (BS 903-A59.1).

Wallace Shawbury Curometer

An apparatus developed by Rapra for the determination of the scorch and cure characteristics of rubber compounds. The principle of operation is summarised thus: two small cylinders of the rubber are placed one on each side of a small paddle and the assembly inserted between electrically-heated platens. An electrically-driven mechanism subjects the specimen to a sinusoidal force and the movement of the paddle is magnified and printed on a chart. From the envelope so formed an estimate of plasticity, scorch time and cure time may be made. Now superseded by various rotorless machines such as the moving die rheometer.

Warming

Plasticising of mixed compound by working on an open mill or in an internal mixer, preparatory to extrusion or calendaring.

Warp

The threads of a woven structure which run lengthwise of a fabric parallel to the selvedge.

Washer

A machine of the open-mill type having grooved rolls and means for directing jets of water on the rubber passing through the nip, the object being to remove impurities such as sand and bark from the rubber. The washing process is rarely necessary nowadays except in times of emergency when wild rubber may have to be processed. *See Strainer.*

Waste Rubber

Rubber products which have ended their useful lives; a proportion of this waste may be made usable again either by grinding down into crumb rubber or by the process of reclaiming. The term 'waste' is also applied to the uncured trimmings from various processing operations, which may be remilled, and added to new mixed compound. The disposal of old tyres is a worldwide problem. Dumping is obviously an unsatisfactory and unsightly answer, indiscriminate burning offends the Clean Air Act, and reclaiming does not

absorb a sufficient quantity of waste to solve the problem nor does it produce a rubber which can meet high quality standards. Recent (1995) developments on recycling agents have yet to make any significant inroads into the problem

Wax

Although the true waxes, such as beeswax, are esters of fatty acids with alcohols, the term is often applied to certain solid substances which melt at fairly low temperatures, e.g., paraffin wax. Paraffin waxes (crystalline and microcrystalline) are obtained from the refining of petroleum, and are used in rubber compounding as protective agents. They have the property of blooming to the surface of the product, forming a thin film which replenishes itself if removed in service.

Weathering

The action of the weather on exposed materials. *See Ageing.*

Weaving

The process of interlacing two sets of textile yarns or threads to form a fabric. *See Warp and Weft.*

Web

A textile term denoting a width of cloth as woven in the loom. The meaning has been broadened in the rubber industry to include almost any sheeting such as might be positioned by a web guide, or the mat of fibres later impregnated with latex in the manufacture of non-woven fabrics. *See Rubber Webbing.*

Web Guide

A device for centring or controlling one or both edges of any material in sheet form.

Weft

The threads of a woven structure which run across the fabric from selvedge to selvedge at right angles to the warp threads.

Weftless

Applied to a tyre-cord fabric without any weft or cross-threads. The individual cords are spaced out by a reed, passed into an adhesive such as LRF, dried and coated with rubber compound by calendaring.

Wet and Dry Bulb Hygrometer

One instrument for determining the relative humidity of the atmosphere. It consists of a pair of thermometers, the bulb of one of which is surrounded by a fabric wick kept moist from a small water reservoir. Due to evaporation the temperature indicated by the wet bulb thermometer is lower than that of the other. The difference in the readings compared to the dry bulb reading enables the relative humidity to be obtained from tables.

Wet Frictioning

Frictioning using a rubber dough instead of a conventional soft 'friction' compound. *See Frictioning.*

Wet Mill

An open mill on which the final stages of preparing spreading doughs are carried out.

Wetting

In rubber reinforcement, wetting denotes the covering or completeness of contact between the

rubber and the particles of the reinforcing agent, especially carbon black.

Wetting Agents

Substances used particularly in latex compounding to decrease surface tension, thus increasing wettability and facilitating the impregnation of fibres and fabrics.

White Factice

Also termed sulphur chloride factice or cold factice. That type of factice prepared by treating unsaturated oils, such as rape oil or castor oil, with sulphur monochloride. Since the reaction is exothermic care must be taken to keep the temperature as low as possible. *See Factice.*

White Metal

An alloy of lead, tin and antimony with a melting point about 180 °C, used as a material for making moulds for articles such as soles, heels and interlocking tiles. When the mould becomes off-size or damaged it is melted down and recast.

White Spirit

A petroleum distillate of boiling point range 150-200 °C used as a solvent. *See Naphtha.*

Whiting

Finely-divided calcium carbonate obtained from natural sources (chalk, limestone or marble) or as a by-product of another chemical process - precipitated whiting. Strictly speaking, the term 'whiting' should be applied only to 'material prepared by grinding natural chalk'.

WHO

World Health Organization.

Whole Tyre Reclaim

Reclaimed rubber made from pneumatic tyres which have ended their useful lives. Tyres form the main source of material for reclaiming. *See Reclaimed Rubber.*

Wiegand Pendulum

An apparatus which demonstrates the Gough-Joule effect. It comprises a pendulum adjusted so that a rubber sample is under stretch. Heat from a lamp causes the rubber to contract and swing the pendulum. This pulls the rubber into a shaded section where it extends and moves the pendulum back to the original position, whereupon the cycle is repeated.

Many attempts have been made to develop the Wiegand Pendulum into a rubber 'engine', and although a variety of devices have been demonstrated, none has reached commercial utilisation. A 'Polymotor' was developed by Professor Natta using *trans*-butadiene as the polymer.

Wig-Wag

The form of or act of laying strip material taken off a mill or extruder into a basket in an oscillating manner. Such material is then suitable for subsequent automatic feeding of production equipment such as injection moulding machines.

Wild Rubber

Natural rubber obtained from trees growing 'wild' and not cultivated in either plantations or native small holdings. The output of wild rubber is now insignificant.

Williams' Plastometer

The earliest and best-known of parallel plate plastometers. The original model has been

modified in several ways to improve its ease of operation and its accuracy. Now obsolete.

Wintering

The annual leaf loss suffered by rubber trees. It coincides with the dry season in February and March. Since the trees are then using their reserves for refoliation there is a temporary drop in yield, and changes occur in the composition of the latex.

Wire Cord

In most modern pneumatic tyres the 'textile' reinforcement is in the form of steel wire constructed in the manner of cord fabric.

Wood Flour

Finely divided wood, used as an inert filler and stiffener in rubber compounds.

Wood Rosin

See Rosin.

Wound Response

In a rubber tree which is being tapped for the first time there is a high percentage of rubber in the latex (about 60% as against the normal 30%) and only a low yield is obtained. As tapping is continued the latex becomes more dilute and a higher yield is given. This phenomenon is known as wound response.

Wrapped Hose

Hose constructed by wrapping the reinforcing fabric and the calendered cover on to the inner tube which has been fitted over a mandrel of the desired diameter. The application of the fabric, the cover and of the wrapper may be done either by hand or by machine.

Wrapper

A length of narrow textile material which is tightly wrapped round a product, e.g., wrapped hose, to apply pressure during vulcanisation. The term is used also in the sense of lining.

X

Xanthates

Salts of the series of xanthic acids of the general formula ROCSSH. Certain xanthates such as ZIX are ultra accelerators for rubber. Cellulose xanthate is the intermediate product in the manufacture of viscose. *See Viscose Rayon.*

Xanthogen Sulphide

Diisopropyl xanthogen polysulphide, accelerator.

XNBR

Abbreviation for carboxylated nitrile rubber.

X-Ray Diffraction

The technique of using the diffraction of X-rays to study the structure of fibres, plastics and elastomers, to determine the crystalline nature of such polymers, and to measure the particle size of finely divided materials.

X-Ray Fluorescence Spectroscopy

This is a semi-quantitative elemental analysis technique.

X-Ray Photoelectron Spectroscopy

This is a surface analysis technique.

X-Rays

Electromagnetic waves of short wavelength 0.01 to 50 Ångström units, which are produced when

streams of high energy electrons impinge on matter, usually metal in commercial systems.

XPS

X-ray photoelectron spectroscopy.

XRF

X-ray fluorescence spectroscopy.

Xylene

Xylol (dimethylbenzene), used as a rubber solvent. Xylene exists in three isomeric forms, commercial xylol being a mixture of all three.

Xylyl Mercaptan

An efficient peptising agent for natural rubber; it is also used as a bleaching agent in the preparation of pale crepe rubber.

Y

Yarn

An assembly of textile fibres to form a thread. Yarns may be single, ply or cabled, the commonest used in weaving being single yarns.

Yarn Count

Yarn count or number defines the relationship between yarn weight and length. On one system it is the number of times a standard length of the yarn is contained in 1 lb weight, e.g., a 23^s cotton yarn is one of such a thickness that 23 hanks each 840 yards long weigh 1 lb. *See Denier and Tex.*

Yarn Number

See Yarn Count.

Yarn Twist

Filament yarns can exist in an almost twistless form, but this is not the case for staple fibre yarns. The twisting of fibres together is still the most practical method of making short fibres into long continuous strands of yarn suitable for weaving. *See S-Twist and Z-Twist.*

Yellowing

The development of a yellow colour on the surfaces of white or light-coloured articles, but also applied to any darkening of such surfaces.

Yersley Oscillograph

An instrument for measuring the mechanical properties of rubbers in relation to their use as materials for the absorption and isolation of vibration. These properties are resilience, modulus (static and dynamic), kinetic energy, creep and set. The introduction of an improved version has recently been announced.

Yield

The amount of dry natural rubber produced per acre per annum. The yield from the original trees established in Malaysia was only about 400 kg per hectare per annum, but the best planting material available nowadays can produce about 2000-2500 kg per hectare. *See Bud Grafting, High Yielding, Ladder Tapping, Yield Stimulation.*

Yield Stimulation

The application of plant hormones to the bark of rubber trees, or of copper sulphate placed in holes bored in the trunk, can produce a consistent increase in yield without any damage to the tree or any deleterious effect on either the latex or the rubber produced from it.

Young's Modulus

The modulus of elasticity of a material; it is the ratio of the stress to the strain produced by the stress in the material. Hooke's law is obeyed by metals but rubber obeys Hooke's law only at small strains in shear. At low strains up to about 15% the stress-strain curve is almost linear, but above 15% the stress and strain are no longer proportional. *See Modulus.*

Z

Z Calender

A four-bowl calender in which rolls 1 and 2 are situated in one horizontal plane and the other two, 3 and 4, in a lower horizontal plane. Roll 3 is below roll 2, 1 and 4 being therefore 'offset'. *See Triangular Calender.*

ZBED

Zinc dibenzyl dithiocarbamate, accelerator.

ZDBC

Zinc dibutyl dithiocarbamate, accelerator.

ZDBCX

Amine-activated zinc dibutyl dithiocarbamate, accelerator.

ZDC

Zinc diethyl dithiocarbamate, accelerator.

ZDEC

Zinc diethyl dithiocarbamate, accelerator.

ZDMC

Zinc dimethyl dithiocarbamate, accelerator.

Zeolites

Naturally occurring hydrated silicates of calcium and aluminium; the name is also given to synthetic substances with a similar crystalline structure used as the basis of molecular sieves.

ZEPC

Zinc ethylphenyldithiocarbamate, accelerator.

Ziegler Catalyst

A catalyst of aluminium and other metal alkyls in combination with metallic halides, e.g., the catalyst obtained by the interaction of a trialkylaluminium with titanium tetrachloride. Such catalysts, discovered by Karl Ziegler, are used in making stereospecific polymers.

Zinc Borate

Flame retardant.

Zinc Dibenzyl Dithiocarbamate

ZBED, accelerator.

Zinc Dibutyl Dithiocarbamate

ZDBC, accelerator.

Zinc Diethyl Dithiocarbamate

An ultra accelerator too scorchy for use as the sole accelerator in 'dry' rubber compounding, but popular in latex work. In dry rubber compounding it is a useful booster for thiazole type accelerators. In some low ammonia latices it is used as a preservative.

Zinc Di-Isononyl Thiocarbamate

Accelerator.

Zinc Dimethyl Dithiocarbamate

ZDMC, accelerator.

Zinc Ethylphenyldithiocarbamate

ZEPC, accelerator.

Zinc Isopropyl Xanthate

An ultra accelerator capable of vulcanising at temperatures as low as 38 °C (100 °F). In mixtures with dithiocarbamate accelerators it is used for room temperature vulcanisation.

Zinc Oxide

An activator in rubber compounds containing organic accelerators. In polychloroprene, zinc oxide is considered to be the accelerator rather than the activator. The use of zinc oxide as a reinforcing agent and as a white colouring agent is obsolescent. Zinc oxide is manufactured by either the French (or indirect) process or by the American (or direct) process. It can be used as a filler to impart high thermal conductivity.

Zinc Pentamethylene Dithiocarbamate

ZPD, accelerator.

Zinc Stearate

A dusting agent which is soluble in rubber and thus does not impair the vulcanised bond between rubber components of a composite product. It is also an activator combining the functions of zinc oxide and stearic acid, of particular value in transparent rubbers since it does not produce the same opacity as zinc oxide.

Zinc Sulphide

An inorganic colouring agent for rubber. *See Lithopone.*

Zinc Yellow

Zinc chromate, an inorganic colouring agent for rubber.

ZIX

Abbreviation for zinc isopropyl xanthate.

ZMBT

Zinc salt of 2-mercaptobenzothiazole, accelerator.

ZPD

Zinc pentamethylene dithiocarbamate, accelerator.

ZPDX

Amine-activated zinc pentamethylene dithiocarbamate, accelerator.

Z-Twist

In textile technology that direction of twisting yarns or threads which runs from left to right upwards, as the centre part of a letter Z, when the yarn is held vertically.

Zwitterion

An ion carrying both a positive and a negative electric charge.

Conversion Factors for Units of Measurement

To convert:	Conversion factor (multiply by)
WEIGHT	
Pounds (lb) to kilogrammes (kg)	0.4536
Kilogrammes to pounds	2.2046
Ounces (oz) to grammes (g)	28.3495
Grammes to ounces	0.03527
Imperial tons (2240 lb) to metric tons	1.0161
Metric tons to Imperial tons	0.9842
Imperial tons to US tons (2000 lb)	1.1200
US tons to Imperial tons	0.8929
Imperial tons to kilogrammes	1016.0573
LENGTH	
Metres to yards	1.09361
Yards to metres	0.9144
Metres to feet	3.2808
Feet to metres	0.3048
Inches to centimetres	2.54
Centimetres to inches	0.3937
AREA	
Square metres to square yards	1.1960
Square yards to square metres	0.836127
Square metres to square feet	10.7643
Square feet to square metres	0.092903
Square centimetres to square inches	0.1550
Square inches to square centimetres	6.4516
VOLUME	
Cubic metres to cubic yards	1.3080
Cubic yards to cubic metres	0.764554
Cubic metres to cubic feet	35.3147
Cubic feet to cubic metres	0.028317
Litres to Imperial gallons	0.2200
Imperial gallons to litres	4.5460
Litres to US gallons	0.2642
US gallons to litres	3.7853
Imperial gallons to US gallons	1.2010
US gallons to Imperial gallons	0.8327
Millilitres to Imperial fluid ounces	0.03520
Imperial fluid ounces to millilitres	28.4122
Millilitres to US fluid ounces	0.0338
US fluid ounces to millilitres	29.5727
Litres to cubic feet	0.03532
Cubic feet to litres	28.32
PRESSURE	
Megapascals (1 bar = 100,000 Pa) to pound force per square inch (lbf/in ² , psi)	145.038
Pounds force per square inch to megapascals	0.006895
ENERGY	
Joules to calories	0.2390
Calories to joules	4.1868

Note

Each of the SI units may have a prefix, the most common are:

10 ⁹	giga	G	10 ⁶	mega	M	10 ³	kilo	k
10 ⁻¹	deci	d	10 ⁻²	centi	c	10 ⁻³	milli	m
10 ⁻⁶	micro	μ	10 ⁻⁹	nano	n	10 ⁻¹²	pico	p

Section 2

Specific Gravities of Some Rubbers and Compounding Ingredients

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2.1 Specific Gravities of Some Compounding Ingredients

Common Name	Chemical Name	Specific Gravity
6PPD	<i>N</i> -1,3-Dimethylbutyl- <i>N'</i> -phenyl- <i>p</i> -phenylenediamine	1.0
77PD	<i>N,N'</i> -Bis(1,4-dimethylpentyl)- <i>p</i> -phenylenediamine	0.9
ADC	Azodicarbonamide	1.7
ADPA	Acetone-diphenylamine condensation product	1.1
Alumina	Aluminium hydroxide	2.4
Aluminium silicate		2.10
Antimony trioxide		5.40
AP	Ammonium polyphosphate	1.90
BAA	Butyraldehyde-aniline condensation product	0.9-1.0
Barium sulphate		4.30
BCUP	<i>Tert.</i> -Butyl cumylperoxide	0.94
BDMC	Bismuth dimethyl dithiocarbamate	2.1
BHT	2,6-Di- <i>tert.</i> -butyl- <i>p</i> -cresol	1.0
BiDD	Bismuth dimethyl dithiocarbamate	2.1
Bisphenol AF	2,2'-Bis(4-hydroxyphenyl)perfluoropropane	1.64
Bitumen		1.04
BPH	2,2'-Methylene-bis(4-methyl-6- <i>tert.</i> -butylphenol)	1.0
BPO	Dibenzoyl peroxide	1.1-1.3
Calcined china clay		2.50
Calcium carbonate		2.65
Calcium oxide (lime)		2.19
Calcium silicate		2.10
Carbon black		1.8
Carnauba wax		0.99
CBS	<i>N</i> -Cyclohexyl-2-benzothiazole sulphenamide	1.27
Chalk	Calcium carbonate	2.8
China clay (kaolin)		2.60
Clay	Complex hydrated aluminium silicate	2.5
Cotton fibre		1.05
CTAB	Alkyl trimethyl ammonium bromide	1.01
CTP	<i>N</i> -(cyclohexylthio)phthalimide	1.3
DBP	Di- <i>n</i> -butyl phthalate	1.04
DBTU	<i>N,N'</i> -Dibutylthiourea	1.0
DCBS	<i>N,N</i> -Dicyclohexyl-2-benzothiazole sulphenamide	1.2
DEHP	Di-2-ethylhexyl phthalate	0.98
DETU	1,3-diethyl-2-thiourea	1.1
DHBP	2,5-Dimethylhexane-2,5-di- <i>tert.</i> -butyl peroxide	0.88 (liquid) 1.50 (paste; powder)
DIBP	Di-isobutyl phthalate	1.042
Dicup	Dicumyl peroxide	1.02
Diethylene glycol		1.12
DIOP	Di-isooctyl phthalate	0.98
DNPT	Dinitroso-pentamethylenetetramine	1.4
DOA	Di-2-ethylhexyl adipate	0.922
Dolomite	Calcium magnesium carbonate	2.9
DOP	Di-octyl phthalate	0.98

Common Name	Chemical Name	Specific Gravity
DOPD	<i>N,N'</i> -Bis(1-ethyl-3-methylpentyl)- <i>p</i> -phenylenediamine	0.9
DOS	Di-2-ethylhexyl sebacate	0.91
DOTG	Di- <i>o</i> -tolyl guanidine	1.1
DPG	<i>N,N'</i> -Diphenyl guanidine	1.19
DPPD	<i>N,N'</i> -Diphenyl- <i>p</i> -phenylenediamine	1.2
DPTT	Dipentamethylene thiuram tetrasulphide/hexasulphide	1.5
DPTU	1,3-Diphenyl-2-thiourea	1.3
DTBP	Di- <i>tert.</i> -butyl peroxide	0.8
DTDM	4,4'-Dithiodimorpholine	1.32-1.38
EFA	Formaldehyde-ammonia-ethyl chloride condensation product	1.1
ETMQ	6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	1.0
ETU	Ethylene thiourea	1.45
Factice		1.05
Graphite		2.04
HEXA, HMT	Hexamethylene tetramine	1.3
Indene-coumarone resin		1.09
IPPD	<i>N</i> -Isopropyl- <i>N'</i> -phenyl- <i>p</i> -phenylenediamine	1.1
Iron oxide		4.5-5.1
Lanolin		1.08
LATU	Mixed ethyl butyl thiourea	1.01
Litharge	Lead oxide	9.30
Magnesia	Magnesium oxide	2.15-3.60
Magnesite	Magnesium carbonate	3.0
MBI	2-Mercaptobenzimidazole	1.4
MbOCA	Methylene bis-ortho-chloroaniline	1.44
MBS	2-(Morpholiniothio) benzothiazole	1.35
MBT	2-Mercaptobenzothiazole	1.4
MBTS	2,2'-Dibenzothiazyl disulphide	1.54
MDI	Diphenylmethane diisocyanate	1.22
Mica	Complex aluminium potassium silicate	2.8
Mineral oil		0.91
MMBI	4- and 5-Methyl-2-mercaptobenzimidazole	1.25
NBC	Nickel dibutyl dithiocarbamate	1.3
NDPA	<i>N</i> -Nitrosodiphenylamine	1.27
Neuberg Siliceous Earth	Natural mixture of quartz and kaolinite	2.6
NiDD	Nickel dimethyl dithiocarbamate	1.5-1.7
OBSH	<i>p,p'</i> -Oxy-bis(benzene sulphonylhydrazide)	1.4
ODPA	Octylated diphenylamine	1.0
Oleic acid		0.90
OTBG	<i>O</i> -Tolyl biguanidine	1.2
PAN	Phenyl- α -naphthylamine	1.1
Paraffin oil		0.80
Paraffin wax		0.90
PBN	Phenyl- β -naphthylamine	1.34
PCPL	Pentachlorophenyl laurate	1.25-1.27
Pine tar		1.08

Common Name	Chemical Name	Specific Gravity
PPD	Piperidinium pentamethylene dithiocarbamate	1.2
Quicklime	Calcium oxide	3.4
Red lead	Trilead tetraoxide	3.9
Rosin		1.07
SDBC	Sodium dibutyl dithiocarbamate	1.08
SDEC	Sodium diethyl dithiocarbamate	1.08
SDMC	Sodium dimethyl dithiocarbamate	1.18
Silica	Fumed anhydrous silica	2.5
Silica	Precipitated amorphous hydrated silica	2.0
Slaked lime	Calcium hydroxide	2.3
Sodium PCP	Sodium pentachlorophenol	2.0
SPH	Styrenated phenol	1.1
Stearic acid		0.85
Sulphur		2.05
Talc	Magnesium silicate	2.80
TBBS	<i>N-tert.</i> -Butyl-2-benzothiazole sulphenamide	1.3
TBTU	1,1,3-Tributyl thiourea	0.94
TBUT	Tetrabutyl thiuram disulphide	1.05-1.10
TBZTD	Tetrabenzyl thiuram disulphide	1.4
TDEC	Tellurium diethyl dithiocarbamate	1.4
TETD	Tetraethyl thiuram disulphide	1.3
Titanium dioxide	Anatase	3.90
Titanium dioxide	Rutile	4.20
TMCH	1,1-Bis(<i>tert.</i> -butylperoxy)-3,3,5-trimethylcyclohexane	1.4
TMQ	Polymeric 2,2,4-trimethyl-1,2-dihydroquinoline	1.08
TMTD	Tetramethyl thiuram disulphide	1.42
TMTM	Tetramethyl thiuram monosulphide	1.0-1.38
TNPP	Tris(nonylphenyl) phosphite	0.98
TPT-MA	Trimethylolpropane trimethacrylate	1.25 (powder)
Tricap	Triethylene glycol dicaprylate/caprate	0.96
TSH	<i>p</i> -toluene sulphonyl hydrazide	1.42
TTP(TCP)	Tritolyl phosphate (tricresyl phosphate)	1.16
TXP	Trixylyl phosphate	1.15
Xanthogen sulphide	Diisopropyl xanthogen polysulphide	1.29
ZBED	Zinc dibenzyl dithiocarbamate	1.34-1.41
ZDBC	Zinc dibutyl dithiocarbamate	1.25
ZDBCX	Amine-activated zinc dibutyl dithiocarbamate	1.09
ZDEC	Zinc diethyl dithiocarbamate	1.47
ZDMC	Zinc dimethyl dithiocarbamate	1.65
ZEPC	Zinc ethylphenyldithiocarbamate	1.34
Zinc oxide		5.55
Zinc stearate		1.10
ZIX	Zinc isopropyl xanthate	1.5
ZMBT	Zinc salt of 2-mercaptobenzothiazole	1.64
ZPD	Zinc pentamethylene dithiocarbamate	1.6
ZPDX	Amine-activated zinc pentamethylene dithiocarbamate	1.5

2.2 Specific Gravities of Rubbers

Polymer	Specific Gravity
Acrylic rubbers	1.1
Bromobutyl rubber	0.91
Butyl rubber	0.91
Chlorobutyl rubber	0.91
Chlorosulphonated polyethylene	1.11-1.28*
Epichlorohydrin copolymer	1.27
Epichlorohydrin homopolymer	1.38
Ethylene-propylene rubber	0.85
Ethylene-propylene-diene-methylene rubber (EPDM)	0.86
Ethylene-vinyl acetate copolymer	0.94
Fluorocarbon rubbers	1.41-1.86*
Polyisoprene rubber	0.92-0.93
Natural rubber	0.92-0.93
Nitrile rubbers	0.95-1.00*
Nitrile/PVC blends	1.0-1.11*
Polybutadiene rubbers	0.91-0.93
Polychloroprene rubbers	1.23-1.25*
Polynorbornene	0.96
Polysulphide rubbers	1.27-1.60*
Styrene-butadiene rubbers	0.94
High styrene SBR rubbers	1.05
* According to grade	

Section 3

Rubbers

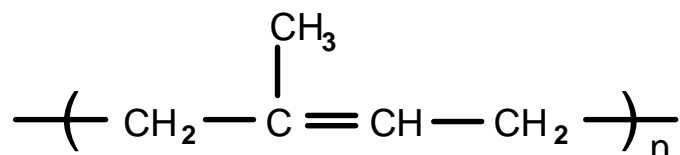
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3.1 Natural Rubber (NR)

Designation in ISO 1629 - NR

Repeat Unit



General

NR can be isolated from more than 200 different species of plant; including surprising examples such as dandelions. Only one tree source, *Hevea Brasiliensis*, is commercially significant. Latex is an aqueous colloid of NR, and is obtained from the tree by 'tapping' into the inner bark and collecting the latex in cups. The latex typically contains 30-40% dry rubber by weight, and 10-20% of the collected latex is concentrated by creaming, or centrifuging, and used in its latex form. Historically, such latex would be exported to consumer countries, but as it is expensive to ship a product with a high percentage of water, consumer companies are increasingly siting their latex processing plants in the producer countries, where the cheaper labour rates are an additional incentive.

The remaining latex is processed into dry rubber as sheets, crepes and bales. There is an International Standard for the Quality and Packing for Natural Rubber grades, the so-called 'Green Book', published by the Rubber Manufacturers' Association. The following grades of NR listed in the 'Green Book' are sold to visual inspection standards only:

- Ribbed smoke sheets
- White and pale crepes
- Estate brown crepes
- Compo crepes
- Thin brown crepes
- Thick blanket crepes
- Flat bark crepes
- Pure smoked crepe

Under each category there are generally up to 5 divisions, e.g., 1RSS, 2RSS, 3RSS, 4RSS, 5RSS for ribbed smoked sheets; the higher the number the more inferior the quality.

The Malaysian rubber industry has, however, played a pioneering role in producing NR grades to technical specifications, and this system is being followed by other producer countries. Currently the following countries sell technically specified grades:

SMR	-	Standard Malaysian Rubber
SIR	-	Standard Indonesian Rubber
SSR	-	Specified Singapore Rubber
SLR	-	Standard Lanka Rubber
TTR	-	Thai Tested Rubber
NSR	-	Nigerian Standard Rubber

Field coagulated grades break down quicker on mastication and offer inferior ageing resistance to latex coagulated grades. They also have a higher dirt content. Some of the field coagulated grades can contain a variable mixture of field and latex coagulated materials.

NR is *cis*-1,4-polyisoprene, of molecular weight 200,000-500,000, but it also contains a small level of highly important non-rubber constituents. Of these, the most important are the proteins, sugars and fatty acids which are antioxidants and activators of cure. Trace elements present include potassium, manganese, phosphorus, copper and iron which can act as catalysts for oxidation.

NR is available in a granular form (powdered rubber), and in oil extended grades.

Two chemically modified types of NR (graft copolymers of NR and polymethylmethacrylate, and epoxidised NR) exhibit useful properties. The former are used in adhesive systems, and for the production of hard compounds, whilst the latter has probably still to find its market niche.

As the name suggests, epoxidised NR is prepared by chemically introducing epoxide groups randomly onto the NR molecule. This chemical modification leads to increased oil resistance, greater impermeability to gases, but an increase in the glass transition temperature, T_g , and damping characteristics; the excellent mechanical properties of NR are retained.

A 50 mole % epoxidised NR exhibits oil resistance only marginally inferior to that of nitrile rubber.

NR can strain crystallise which results in its compounds exhibiting high tensile strength and good tear strength. Although crystallisation can occur at low temperatures, compounding greatly reduces this tendency and it can be effectively prevented from crystallising by using sulphur levels greater than 2.5 phr to cure the compound.

Since the main chain of NR contains unsaturation (residual double bonds) it, along with other unsaturated rubbers, is susceptible to attack by oxygen, ozone and light, and compounds therefore require protection against these agencies.

NR is not oil resistant and is swollen by aromatic, aliphatic and halogenated hydrocarbons. It is resistant to many inorganic chemicals, but not to oxidising acids and has limited resistance to mineral acids. It is unsuitable for use with organic liquids in general, the major exception being alcohols of low molecular weight.

NR can be crosslinked by the use of sulphur, sulphur donor systems, peroxides, isocyanate cures and radiation, although the use of sulphur is the most common method.

The sulphur vulcanisation of NR generally requires higher added amounts of sulphur, and lower levels of accelerators than the synthetic rubbers. Sulphur contents of 2-3 phr, and accelerator levels of 0.2-1.0 phr are considered to be conventional cure systems.

NR can yield a hard rigid thermoplastic with excellent chemical resistance when cured with over 30 phr of sulphur. Such a product is termed ebonite.

NR requires a certain degree of mastication (reduction in molecular weight) to facilitate processing, although the advent of constant viscosity grades, and oil extended grades has substantially reduced the need for mastication.

Peptisers are often used to facilitate breakdown of the rubber during mixing, although quantities of greater than 0.6 phr can cause a reduction in the final level of physical properties.

Uses

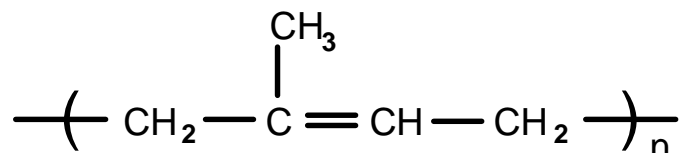
The uses of NR are myriad and a complete summary is not really possible. Its unique and excellent properties are utilised in tyres, shock mounts, seals, isolators, couplings, bridge bearings, building bearings, footwear, hose, conveyor belts, plant linings and many other moulding applications.

Latices and solutions are used to produce adhesives, carpet backings, upholstery foam, gloves, condoms and medical devices such as catheters. NR is also frequently used in blends with other elastomers.

3.2 Polyisoprene (synthetic natural rubber) (IR)

Designation in ISO 1629 - IR

Repeat Unit



General

This synthetic rubber has the same empirical formula as NR and hence closely approximates to the behaviour of its naturally occurring rival. It has the same *cis* structure as NR, good uncured tack, high gum tensile strength, high resilience and good hot tear strength. Although similar to NR it does exhibit some differences:

- i. It is more uniform and lighter in colour than NR.
- ii. Due to a narrower molecular weight distribution it exhibits less of a tendency to strain crystallise, hence green strength is inferior, as are both tensile and tear strength.

In general synthetic IR behaves like NR during processing, and it also requires protection against oxygen, ozone and light due to unsaturation in the main chain. Oil resistance is poor and it is not resistant to aromatic, aliphatic and halogenated hydrocarbons. It is resistant to many inorganic chemicals, but not to oxidising acids and has limited resistance to mineral acids. It is unsuitable for use with organic liquids in general, the major exception being alcohols of low molecular weight.

Due to the absence of the non-rubber constituents present in the NR some differences in compounding occur, although, in essence, the principles are the same. An increased level of stearic acid is generally required for cure activation and approximately 10% extra accelerator is necessary to achieve a similar cure rate to NR; similar sulphur levels are, however, used. IR can be cured by the same type of systems as NR.

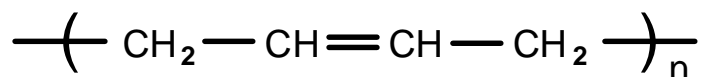
Uses

IR can be used interchangeably with NR in all but the most demanding applications, and it is often used in blends with polybutadiene, and SBR rubber, in preference to NR when improved processibility is required.

3.3 Polybutadiene (BR)

Designation in ISO 1629 - BR

Repeat Unit



General

Polybutadiene is produced by solution polymerisation, and one important feature governing the performance of the resultant polymer is the *cis* 1,4, and 1,2 vinyl contents. High *cis* 1,4 polymers (>90%) have a T_g around -90°C , and hence exhibit excellent low temperature flexibility only exceeded by the phenyl silicones. They also exhibit excellent resilience and abrasion resistance; unfortunately the high resilience gives poor wet grip in tyre treads, and hence this rubber finds limited use as the sole base for such compounds.

As the *cis* 1,4 content decreases, and 1,2 vinyl content increases, the low temperature properties, abrasion resistance and resilience become inferior.

The polymerisation of butadiene results in a polymer with a narrow molecular weight distribution which can be difficult to process. Indeed, commercially available grades present a compromise between processibility and performance. Most polybutadiene rubbers are inherently difficult to break down during mixing and milling, have low inherent tack, and the inherent elasticity of the polymer gives poor extrudability. Peptisers can be used to facilitate breakdown and hence aid processing.

Due to the unsaturation present in the main chain, protection is required against oxygen, UV and ozone. Oil resistance is poor and the polymer is not resistant to aromatic, aliphatic and halogenated hydrocarbons.

Polybutadiene based compounds can be cured by sulphur, sulphur donor systems and peroxides. Less sulphur and a higher level of accelerators are required when compared to NR. The cure of polybutadiene by peroxides is highly 'efficient' in that a large number of crosslinks are produced per free radical, the resultant highly crosslinked rubber exhibiting high resilience; this factor is utilised in the manufacture of 'superballs'.

Compounds based on this polymer only give optimum properties at high filler and oil loadings.

Uses

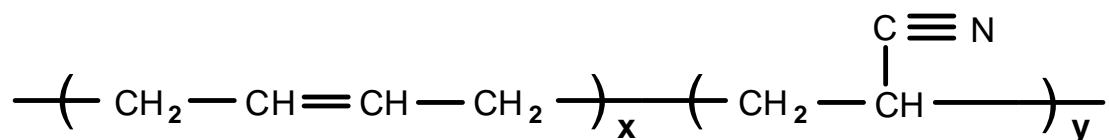
Most polybutadiene is used in tyre applications, and the majority of this use is in blends with other polymers, such as NR and SBR, where polybutadiene reduces heat build-up and improves the abrasion resistance of the blend. The friction on ice of winter tyres is also improved by using higher levels of polybutadiene in the tread blend.

When polybutadiene is used in blends for other applications, it is where the improved abrasion and low temperature flexibility conferred on a blend is advantageous, e.g., in shoes, conveyor and transmission belts.

3.4 Nitrile Rubbers (NBR/HNBR)

Designation in ISO 1629 - NBR

Repeat Unit



General

Nitrile rubbers are copolymers of butadiene and acrylonitrile which are produced by emulsion polymerisation; 'hot' and 'cold' polymerised types are available. The 'hot' polymerised types generally have higher green strength and are slightly harder to process than 'cold' copolymers.

The introduction of acrylonitrile into the polymer backbone imparts oil resistance and affects many other properties. Grades which vary in acrylonitrile (ACN) content from 18-50% are commercially available, the percentage of acrylonitrile present forming the basis of the following grade descriptions:

Low	18-24%	ACN
Medium low	26-28%	ACN
Medium	34%	ACN
Medium high	38-40%	ACN
High	50%	ACN

Many properties are influenced by the acrylonitrile content, e.g.:

	<u>% Acrylonitrile content 18% → 50%</u>
Oil resistance improvement	→
Fuel resistance improvement	→
Tensile strength improvement	→
Hardness increase	→
Abrasion resistance improvement	→
Gas impermeability improvement	→
Heat resistance improvement	→
Low temperature flexibility improvement	←
Resilience improvement	←
Plasticiser compatibility	→

A typical figure for the T_g of an 18% ACN copolymer is $-38\text{ }^\circ\text{C}$, and that of a 50% ACN copolymer $-2\text{ }^\circ\text{C}$.

Carboxylated nitriles, hydrogenated nitrile, liquid nitriles and blends with PVC are also commercially available.

The carboxylated types (XNBR) contain one, or more, acrylic type of acid as a terpolymer, the resultant chain being similar to nitrile except for the presence of carboxyl groups which occur about every 100 to 200 carbon atoms. This modification gives the polymer vastly improved abrasion resistance, higher hardness, higher tensile and tear strength, better low temperature brittleness, and better retention of physical properties after hot-oil and air ageing when compared to ordinary nitrile rubber.

Low molecular weight liquid nitrile grades are available and these can be used as compatible plasticisers in the compounding of nitrile rubber. Such plasticisers can be partially crosslinked to the main chain during cure, and hence exhibit low extractability.

PVC/NBR polymer blends can be produced as colloidal or mechanical blends, the former generally giving superior properties. Commercially available blends have PVC contents ranging from 30-55%. The blends have reduced elasticity, which gives improved extrudability, but they also exhibit superior ozone resistance, improved oil swell resistance, and tensile and tear strength; this, however, is achieved at the expense of low temperature flexibility and compression set. The ozone resistance of such blends is, however, only improved if the PVC is adequately distributed and fluxed. This is harder to achieve in mechanical blends, but if it is not achieved failure due to ozone attack can occur.

Another method by which the ozone resistance of nitrile rubber can be improved is the removal of the double bonds in the main chain of the copolymer by hydrogenation. Hydrogenated nitrile rubbers (HNBR) also exhibit much greater resistance to oxidation, and extend the useful service temperature range of nitriles up to ca. 150 °C. Commercially available grades offer different degrees of hydrogenation with residual double bonds ranging from ca. 0.8%-6%.

Nitriles have good resistance to oil, aliphatic and aromatic hydrocarbons and vegetable oils, but are swollen by polar solvents such as ketones. The unsaturated main chain means that protection against oxygen, ozone and UV light is required.

In compounding, choice of the correct grade is required if the required balance of oil resistance and low temperature flexibility is to be achieved.

Nitrile rubber can be cured by sulphur, sulphur donor systems and peroxides. However, the solubility of sulphur in nitrile rubber is much lower than in NR, and a magnesium carbonate coated grade (sulphur MC) is normally used; this is added as early in the mixing cycle as possible. Less sulphur and more accelerator than is commonly used for curing natural rubber is required. A cadmium oxide/magnesium oxide cure system gives improved heat resistance, but the use of cadmium, a heavy metal, will increasingly be restricted.

The hydrogenated nitrile (HNBR) grades which contain the lowest level of residual double bonds can only be crosslinked by the use of peroxides and radiation, whilst those with a level of residual double bonds greater than about 3.5% can be cured by sulphur.

In addition to the normal sulphur cure systems, metal oxides can be used to cure the carboxylated nitriles.

The low temperature properties of nitriles can be improved by the use of suitable plasticisers, e.g., ester plasticisers.

Uses

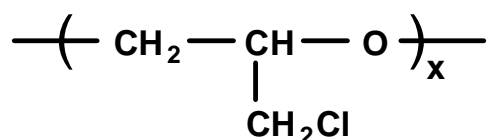
Nitrile rubber, due to its oil resistance, is widely used in sealing applications, hose liners, roll coverings, conveyor belts, shoe soles and plant linings. Nitrile rubber is also available as a latex.

3.5 Epichlorohydrin Polymers (CO/ECO/ETER)

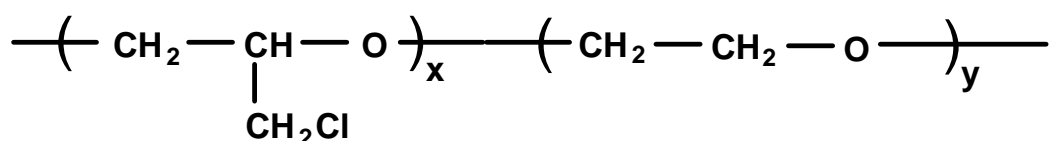
Designation in ISO 1629 - CO & ECO

Repeat Unit

Epichlorohydrin homopolymer (CO)



Epichlorohydrin copolymer with ethylene oxide (ECO)



General

Epichlorohydrin is also available as a terpolymer with a small amount of unsaturated allyl glycidyl ether. There is no ISO designation for the terpolymer, but ETER is used by ASTM.

As with EPDM, the unsaturation is pendant to the main chain and this allows vulcanisation with sulphur, whilst preserving the stability of the main chain. The ability to be cured by sulphur also allows the terpolymer to be used in blends with other polymers, e.g., nitriles.

As might be expected, the homopolymer having the highest polarity exhibits the best oil resistance, but this is at the detriment of low temperature flexibility. The homopolymer also has a low permeability to gases. The unsaturated backbone gives these materials good resistance to oxygen, ozone and light.

Resistant to oils, aliphatic hydrocarbons and alcohols, alkalis and dilute mineral and oxidising acids. Attacked by strong mineral and oxidising agents and chlorine.

The main method of crosslinking the homopolymer and copolymer is by use of thioureas, and, as the cure reaction requires basic conditions, an acid acceptor is also added. Litharge, red lead, magnesium oxide and dibasic lead phosphite are commonly used acid acceptors, and the most commonly used thiourea is ethylene thiourea, but this has a tendency to promote mould fouling.

The Echo S cure system has been commercialised by BFGoodrich and this is said to give improved scorch safety and reduced mould fouling over the use of thioureas. Inorganic acid acceptors other than those based on lead are recommended for use with the Echo S cure system.

The terpolymers can, in addition to the use of thioureas, be cured by the use of sulphur and peroxides.

Uses

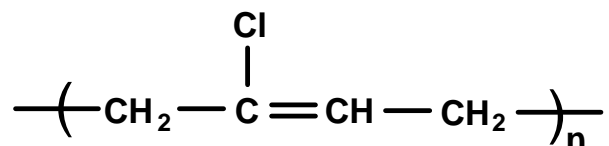
The main use of epichlorohydrin is in the automotive sector for various seals and hoses, gaskets, o-rings and diaphragms.

The terpolymer is used in roller production and in many low temperature applications.

3.6 Polychloroprene (CR)

Designation in ISO 1629 - CR

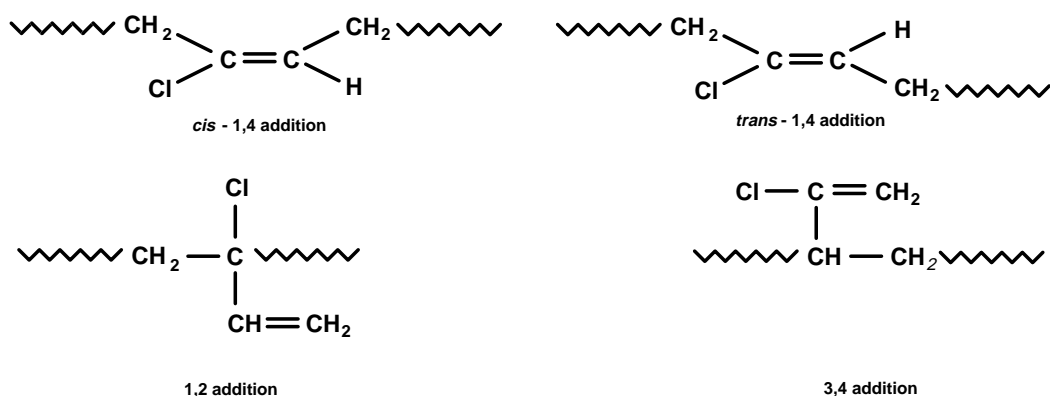
Repeat Unit



General

This polymer is frequently, but incorrectly, referred to as Neoprene which is a trade name.

Polychloroprene is produced by emulsion polymerisation, during which the following forms of addition are possible:

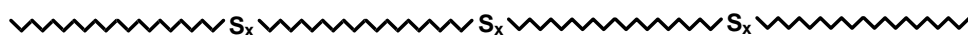


Since it is not possible to commercially produce a polymer that is based on the *cis* 1,4 form, commercial polymers are based on the *trans* 1,4 form which has a crystalline melting point, T_m , of +75 °C and a T_g of -45 °C. Pure 1,4 *trans* polychloroprene thus crystallises readily and would normally be considered to be of limited use for a rubber. Such a polymer, however, does not crystallise when dissolved in a solvent, but will do so when the solvent evaporates. This feature is used to good effect in the production of contact adhesives.

The temperature of polymerisation, however, influences how closely the polymer attains the *trans* 1,4 form. Raising the polymerisation temperature from -40 °C to +40 °C increases the percentage of 1,2 and 3,4 forms both of which reduce the regularity and hence the tendency to crystallise. Thus chloroprene based polymers that are intended to be rubbery are polymerised at higher temperatures. The 1,2 grouping in the main chain is the site of crosslinking reactions during cure. The ability to crystallise can also be controlled by copolymerising chloroprene with small amounts of other monomers.

Two different mechanisms are used to control the molecular weight of the polymer during polymerisation:

- In the so-called G types, sulphur is copolymerised with the chloroprene to yield a product as shown schematically below:



The G types are stabilised with TETD, with the result that the G types do not require further acceleration to cure.

- In the so-called W types, the molecular weight is controlled by the use of a mercaptan.

The following differences are apparent between the G and W types:

G types

G types can break down during mixing or milling via cleavage at the Sx group; this decreases molecular weight and hence reduces the elasticity, or nerve, during processing. The extent of breakdown is somewhat dependent on the exact grade, Neoprene GW being virtually unaffected by milling. Cleavage at the Sx group can also occur during long-term storage, and the G types therefore have the disadvantage of a limited storage life.

The G types do not require further acceleration during cure, but exhibit slightly inferior ageing characteristics. Resilience and tack are generally better than with the W types.

W Types

These types exhibit superior storage life, and ageing characteristics, but require the addition of accelerators to achieve an acceptable rate of cure. They do not break down during mixing. During processing they are less prone to scorch, and will accept higher loadings of filler. The cured compound generally exhibits a lower compression set, and a greater ability to resist heat ageing.

The chlorine atom in the repeat unit has a tendency to deactivate the double bond in the main chain, thus polychloroprene tends to resist oxidation, ozone and UV light to a higher degree than the other unsaturated rubbers, although they still require protection if the maximum performance is to be obtained. Unfortunately, this deactivation of the double bond means that the polymer cannot be crosslinked by sulphur.

The chlorine atom also confers an increased level of resistance to oils, so that the oil resistance of polychloroprene is roughly intermediate between natural rubber and nitrile rubber, and is often sufficient for many applications. Polychloroprene is also self-extinguishing in flame tests.

Metal oxides are principally used for curing these materials; peroxides are generally not used. The most widely used cure system is based on magnesium oxide/zinc oxide, the cured properties achieved being dependent on the ratio of the two; the most common ratio is magnesium oxide 4.0 and zinc oxide 5.0. As the zinc oxide tends to promote scorch it is added late in the mixing cycle, whilst magnesium oxide is added early. One drawback of the MgO/ZnO cure system is that chlorine liberated during cure reacts with the oxides to yield chlorides which are hydrophilic and compounds containing this cure system can swell in hot water; even in cold water swell can be progressive and eventually large.

Lead oxide (PbO or Pb₃O₄) up to levels of 20 phr can be used to improve resistance to water as the chloride formed during cure is insoluble.

The W types require additional acceleration and ethylene thiourea (ETU), gives the best balance of all properties. However, the use of this accelerator is increasingly being restricted due to fears of its effects on pregnant women, and more recently men. DETU, thiurams and guanidines can also be used. Sulphur is sometimes used to increase the degree of cure in the W types, but this detracts from the ageing performance of the vulcanisate.

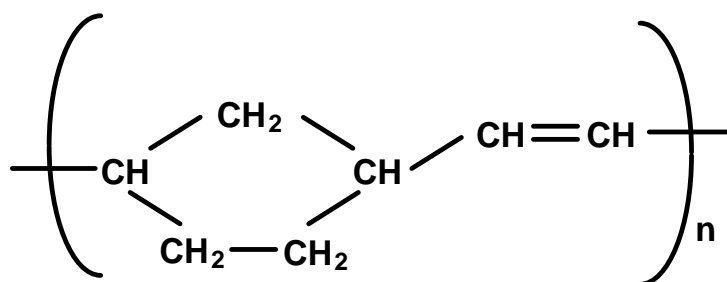
Uses

Due to its balance of strength, oil resistance, inflammability, increased resistance to ozone, ageing and weathering, polychloroprene finds widespread industrial use. Typical uses are V-belts, conveyor belts, wire and cable jacketing, footwear, wet suit applications, coated fabrics, inflatables, hoses, extrusions and many other goods. Adhesives are also a strong market area.

3.7 Polynorbornene

Designation in ISO 1629 - N/A

Repeat Unit



General

The large ring structure in the main chain gives this material a high T_g of +35 °C, and thus it is not rubbery at normal ambient temperatures and requires plasticisation to achieve elastomeric behaviour.

This material exhibits some desirable advantages. It can be extended by large quantities of oils to give very soft vulcanisates (ca. 20 Shore A) with acceptable strength, and it gives high damping which can be useful for vibration and noise reduction applications. However, since plasticisation is required particular care has to be exercised in the choice of plasticiser if exposure to higher than ambient temperatures is anticipated.

Polynorbornene is not oil resistant, and solvents which can extract the plasticiser will obviously be detrimental to its performance.

The material can be cured by both sulphur and peroxides, but requires protection against oxygen, ozone and UV light.

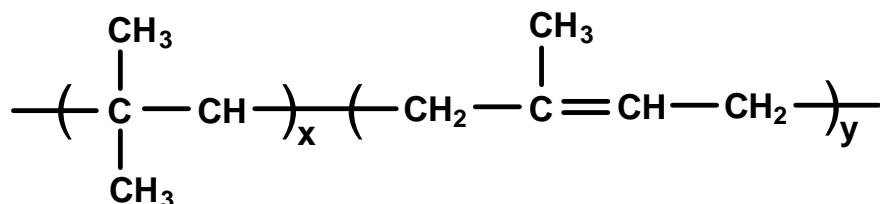
Uses

Roll covers, and elements designed to utilise the high damping properties of this material are thought to be the major uses.

3.8 Butyl Rubbers (IIR/BIIR/CIIR)

Designation in ISO 1629 - IIR, BIIR & CIIR

Repeat Unit (IIR)



General

Commercial grades of IIR (butyl rubber) are prepared by copolymerising small amounts of isoprene with polyisobutylene. The isoprene content of the copolymer is normally quoted as the 'mole percent unsaturation', and it influences the rate of cure with sulphur, and the resistance of the copolymer to attack by oxygen, ozone and UV light. The polyisobutylene, being saturated, however, naturally confers on the polymer an increased level of resistance to these agencies when compared to natural rubber. Commercial butyl rubbers typically contain 0.5-3.0% mole unsaturation.

The close packing of the isobutylene chain confers on the polymer a high degree of impermeability to gases, but also results in a very 'lossy' rubber. The high hysteresis loss can be utilised in some circumstances to provide good friction in wet conditions.

Chlorobutyl (CIIR) and bromobutyl (BIIR) are modified types containing 1.2% wt of chlorine or bromine, the isoprene unit being the site of halogenation. Introduction of the halogen gives greater cure flexibility, and enhanced cure compatibility in blends with other diene rubbers. It also confers increased adhesion to other rubbers and metals.

Butyl rubber is not oil resistant.

Butyl, and the halogenated butyls, can be cured by sulphur, dioxime and resin cure systems. In addition, the halogenated types can be crosslinked with zinc oxide, and diamines. Peroxides cannot be used because they tend to depolymerise the polyisobutylene.

Due to the low level of unsaturation in the main chain, sulphur cures require the more active thiuram and dithiocarbamate accelerators to achieve an adequate state of cure.

Dioxime cures yield vulcanisates with good ozone resistance and moisture impermeability and, as such, are frequently used for curing electrical insulating compounds.

Resin cures utilise phenol-formaldehyde resins with reactive methylene groups and a small added amount of either a chlorinated rubber, e.g., polychloroprene, or stannous chloride. If halogenated phenolic resins are used the additional source of a halogen may not be required. Resin cures give butyl compounds excellent heat stability and are used to good effect where this is required, e.g., in tyre curing bags which have to resist service at 150 °C in a steam atmosphere.

Calcium stearate has to be added to stabilise the chlorobutyl during processing.

Uses

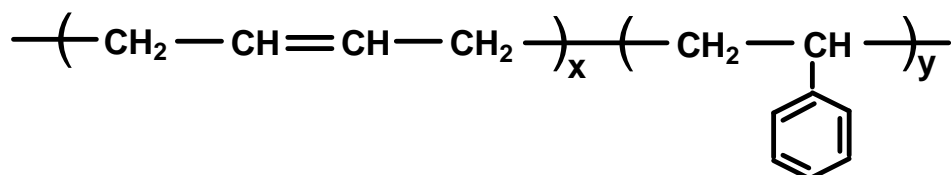
The main applications of butyl rubber are in wire and cable applications, inner tubes, inner liners in tubeless tyres, tyre curing bladders, and pharmaceutical closures, the latter utilising the low

impermeability of butyl to gases. Other applications include vibration isolation, caulk and sealants, and sheeting for pond liners and roofing.

3.9 Styrene-Butadiene Rubber (SBR)

Designation in ISO 1629 - SBR

Repeat Unit



General

When the USA and Germany were cut off from the supplies of natural rubber during the Second World War both countries sought to produce a synthetic alternative; SBR was the result, and at one stage it was the most commonly used synthetic rubber. It can be produced by both emulsion and solution polymerisation techniques, with the emulsion grades being the most widely used. Emulsion polymerisation yields a random copolymer, but the temperature of the polymerisation reaction also controls the resultant properties obtained. 'Cold' polymerisation yields polymers with superior properties to the 'hot' polymerised types.

Solution polymerisation can yield random, di-block, tri-block or multi-block copolymers. It is important to note that the tri-block, or multi-block copolymers, belong to that class of material termed thermoplastic elastomers and it is only the random copolymer types that are considered here.

Both random emulsion and solution polymerised SBR contain about 23% styrene.

SBR continues to be used in many of the applications where it earlier replaced natural rubber, even though it requires greater reinforcement to achieve acceptable tensile and tear strengths, and durability. SBR exhibits significantly lower resilience than NR, so that it has a higher heat build-up on flexing which restricts its use in lorry tyres with their thicker sections. This inferior resilience to natural rubber is an advantage in passenger car tyre treads because the higher hysteresis loss gives increased wet grip and this, combined with the good abrasion resistance that can be obtained from tyre tread compounds, ensures that SBR has a high volume use in tyre production.

The oil resistance of SBR is poor, and the polymer is not resistant to aromatic, aliphatic or halogenated solvents. Due to the unsaturation in the main chain, protection is required against oxygen, ozone and UV light.

Oil extended SBR, and SBR carbon black masterbatches are supplied by the polymer producers and such grades give the advantage of reducing the necessity of further additions of filler and oil at the mixing stage.

SBR can be cured by the use of sulphur, sulphur donor systems and peroxides. Sulphur cures generally require less sulphur (1.5-2.0 phr) and more accelerator than is normally required to cure natural rubber.

Uses

The major use of SBR is in tyres, predominantly car and light truck; in the latter use it is frequently blended with NR and BR.

SBR also finds use in conveyor belts, moulded rubber goods, shoe soles, hose and roll coverings.

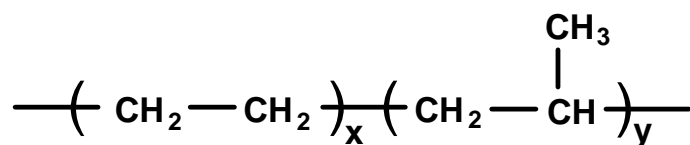
SBR is also available as a latex which is used in carpet backing and other applications.

3.10 Ethylene-Propylene Rubber (EPM/EPDM)

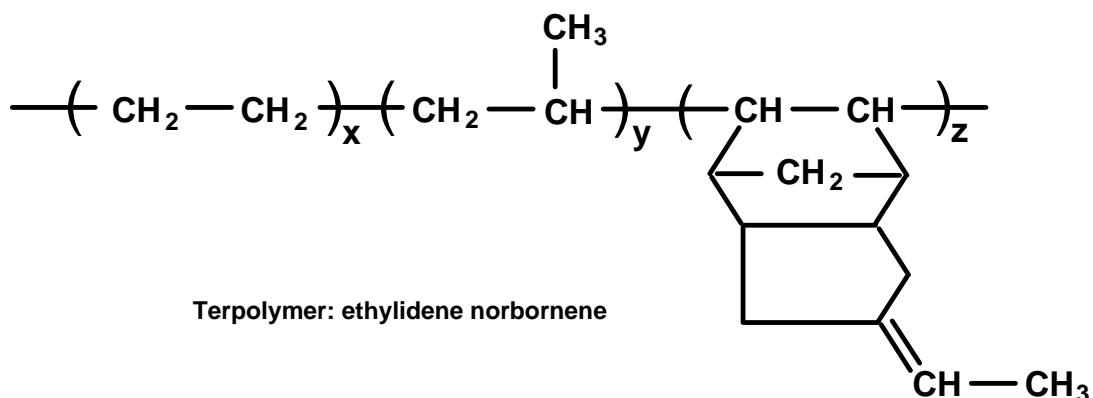
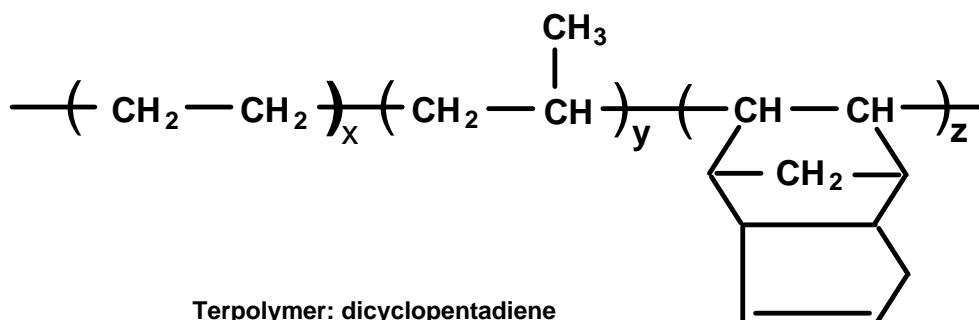
Designation in ISO 1629 - EPM / EPDM

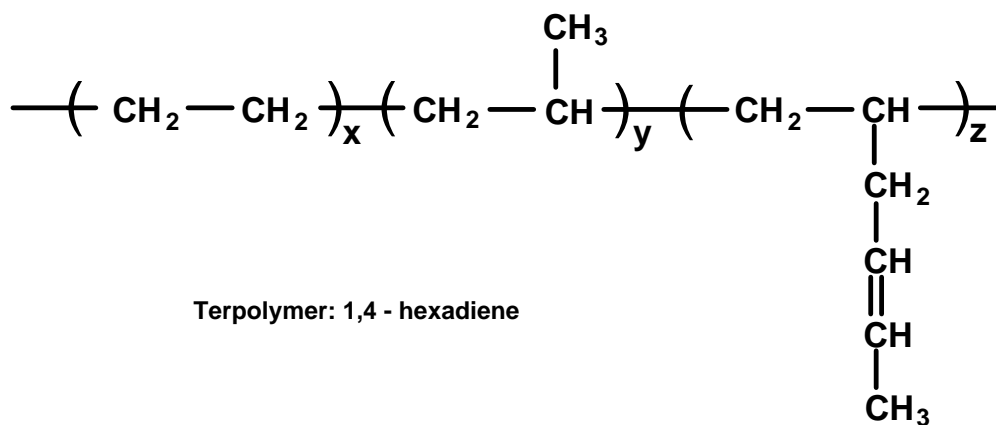
Repeat Unit

Ethylene-propylene rubber (EPM)



Ethylene-propylene-diene-methylene rubber (EPDM)





General

The copolymerisation of ethylene and propylene yields useful copolymers, the crystallisation of both polymers being prevented if the ethylene content is in the range 45-60%; grades with higher ethylene contents, 70-80%, can partially crystallise. The lower ethylene types are generally easier to process, whilst green strength and extrudability improve as the ethylene content increases. One disadvantage of the copolymer is that it cannot be crosslinked with sulphur due to the absence of unsaturation in the main chain. To overcome this difficulty a third monomer with unsaturation is introduced, but to maintain the excellent stability of the main chain the unsaturation is made pendant to it. The three types of third monomer used commercially are dicyclopentadiene, ethylidene norbornene, and 1,4-hexadiene. Generally 4-5% of the termonomer will give acceptable cure characteristics, whilst 10% gives fast cures; dicyclopentadiene gives the slowest cure rate and ethylidene norbornene the highest.

Since the main chain of both EPM and EPDM rubbers is saturated, both co- and terpolymers exhibit excellent stability to oxygen, UV light, and are ozone resistant.

EPM and EPDM are not oil resistant, and are swollen by aliphatic and aromatic hydrocarbons, and halogenated solvents. They have excellent electrical properties and stability to radiation. Their densities are the lowest of the synthetics, and they are capable of accepting large quantities of filler and oil. They exhibit poor tack, and even if tackifiers are added, it still is not ideal for building operations. Adhesion to metal, fabrics and other materials, can be difficult to accomplish.

The copolymers can only be cured by peroxides or radiation, whilst the terpolymers can be cured with peroxides, sulphur systems, resin cures and radiation.

The dicyclopentadiene terpolymer can give higher states of cure with peroxides than the copolymer, although in peroxide curing of both the copolymer and terpolymer it is common practice to add a coagent, to increase the state of cure. Triaryl isocyanurate or sulphur are the most common coagents.

Bloom can be a problem in sulphur cures, so selection of the accelerator system is important.

Resin cures utilise the same resins that are used for butyl rubber, but more resin (ca. 10-12 phr) and a halogen donor (10 phr), typically bromobutyl, or polychloroprene, are required. Although heat stability is slightly improved by resin curing when compared to sulphur cures, the effect is not as marked as in the resin curing of butyl.

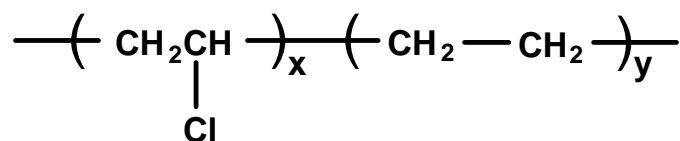
Uses

Wire and cable applications and extrusion profiles, e.g., window seals and car door seals, probably form the major applications for EPM and EPDM rubber, although they are also used in a wide variety of other extrusion and moulding applications. Washing machine door seals moulded from EPDM are starting to replace NR as washer/dryers are becoming more common.

3.11 Chlorinated Polyethylene (CPE, CM)

Designation in ISO 1629 - CM

Repeat Unit



General

Although polyethylene has a low T_g it is highly crystalline and hence it is a thermoplastic and not a rubber at ambient temperatures. If the regularity of the main chain could be interrupted, and crystallisation effectively prevented, a useful elastomer might result. The chlorination of polyethylene is one method by which crystallisation can be prevented and chlorinated polyethylene is commercially available; the degree of chlorination, however, determines how rubbery the modified polymer is. Polymers with a chlorine content of ca. 25% are still relatively crystalline, whilst those with a chlorine content of greater than 40% become increasingly brittle due to interaction between the now highly polar polymer chains. The most desirable polymers, in terms of the absence of crystallinity and flexibility of the chains, are obtained when the degree of chlorination is around 35%.

As with other polar polymers, these materials will resist oil, and the absence of a double bond in the main chain confers excellent stability to the deleterious effects of oxygen, ozone and light.

Due to the absence of double bonds in the main chain, these materials can only be crosslinked by the action of peroxides or radiation. It is recommended that metal oxides are added to act as acid acceptors during vulcanisation, the oxides of magnesium and lead being used; zinc oxide is not used as it decreases the stability of the polymer.

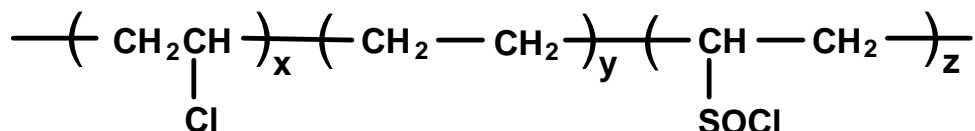
Uses

It is fairly true to say that the use of chlorinated polyethylene has not been large, possibly due to the greater ease with which the chlorosulphonated polyethylene (Hypalon), a closely related competitor material, can be cured. When used, chlorinated polyethylene has found its major use in the wire and cable industry. It is also used in pond liners.

3.12 Chlorosulphonated Polyethylene (CSM, CSPE)

Designation in ISO 1629 - CSM

Repeat Unit



General

The level of chlorination in these materials varies, and influences the properties of the material in exactly the same manner as the closely related chlorinated polyethylene. The introduction of the chlorosulphonyl group in small amounts, <1.5%, gives greater choice in the methods used to crosslink the polymer. However, in general, the properties exhibited by these materials are equivalent to those of chlorinated polyethylene.

DuPont have produced a modified chlorosulphonated polyethylene based polymer (trade name Acsium). In this modified polymer the chlorine content is reduced, but an additional pendant alkyl group is used to restrict the ability of the polymer to crystallise. The result is a polymer with a lower T_g than the conventional CSM polymer.

In addition to the use of peroxides for crosslinking, metal oxide, polyfunctional alcohols, amines and epoxide resin cure systems can be used with CSM rubbers. In the metal oxide based cure systems it is usual to add a weak acid, such as stearic acid, and accelerators, such as MBT, MBTS or TMTD; magnesium or lead oxides are generally used.

The most common polyfunctional alcohol used is pentaerythritol, but a base is also required to complete the cure system, magnesium and calcium oxide giving more controlled cure rates than stronger bases.

As with chlorinated polyethylene rubber, chlorosulphonated polyethylene exhibits good resistance to oxygen, ozone and light. The polar nature of the polymer chain also confers oil resistance.

Uses

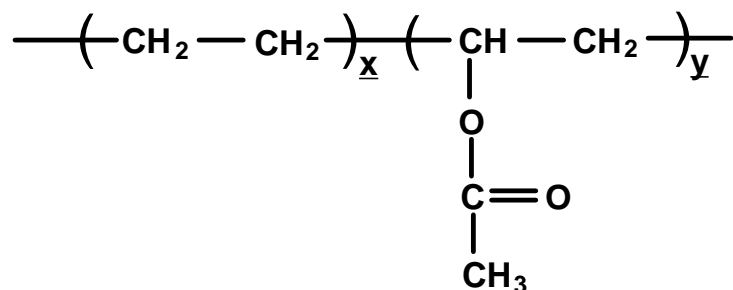
The excellent UV stability of chlorosulphonated polyethylene has led to wide use as a roof sheeting material, the ability to compound this material to slowly cure at ambient temperatures being an added advantage; another sheeting application is pond liners. Wire and cable applications, coated fabrics, and items made from them, hoses and moulded goods are other areas in which this material finds use.

Acsium is said to have been designed for use in synchronous drive belt applications.

3.13 Ethylene-Vinyl Acetate Copolymer (EVA, EAM)

Designation in ISO 1629 - EAM

Repeat Unit



General

The copolymerisation of ethylene with vinyl acetate (VA) is another method by which the crystallinity of polyethylene can be reduced and a rubbery polymer obtained. The final properties of the copolymer depend on the VA content; at a VA level of 50% the copolymer is entirely amorphous, and elastomeric grades generally contain 40-60% VA by weight. The oil resistance of the copolymer is also dependent on the VA content; in general, however, this lies between that of SBR and polychloroprene. It is swollen by most organic solvents and not resistant to animal and vegetable oils, but has some resistance to weak acids and alkalis at ambient temperature.

The saturated main chain of the copolymer confers excellent resistance to oxygen, ozone and light, but means that these materials cannot be crosslinked by sulphur. Peroxides and radiation are the only methods by which crosslinking can be accomplished, and coagents are often required to achieve the required state of cure.

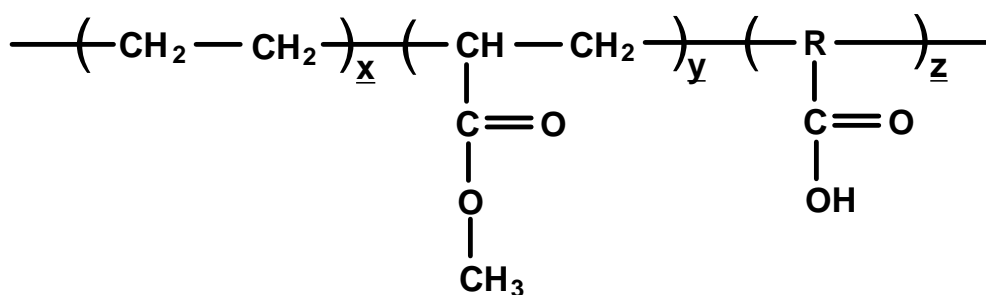
Uses

The main use of EVA is in wire and cable applications, although the electrical properties are inferior to those of EPDM. EVA is used for some medical extrusions and can be blended with other polymers to improve ozone resistance.

3.14 Ethylene-Acrylic Rubber (EACM, AEM)

Designation in ISO 1629 - N/A

Repeat Unit



General

This terpolymer is formed from methyl acrylate and ethylene with a carboxylic cure site monomer (Vamac, produced by DuPont and Denka ER from Denki Kagaku kogyo kk) it exhibits properties generally comparable to those of an acrylate. The introduction of ethylene into the main chain gives low temperature performance similar to a polyoctyl acrylate polymer, and oil resistance similar to a butyl acrylate polymer. The high temperature performance is slightly inferior to the acrylates, but this is compensated for by the generally higher physical strength. Chemical resistance is generally poor apart from mineral oils, natural fats and some salts. It is swollen by aliphatic, aromatic and chlorinated hydrocarbons.

Vamac is generally cured with diamines, with DPG as an accelerator, but it is also possible to crosslink this material with peroxides.

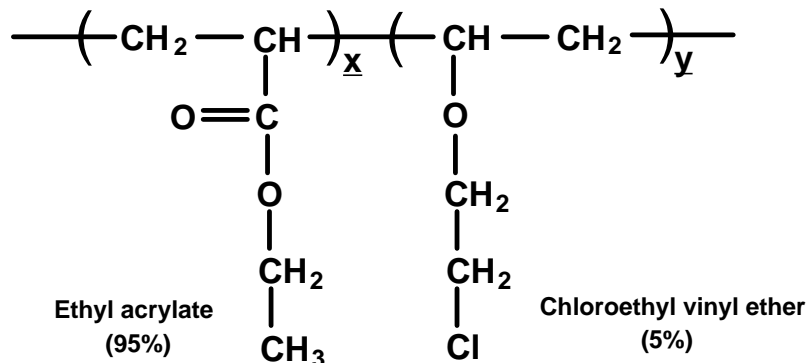
Uses

This material finds use as a sealing material in automotive applications and marine motor lead wire insulation. It has also been used as the base polymer for low flammability, halogen free, cable jacketing compounds.

3.15 Polyacrylate Rubbers (ACM)

Designation in ISO 1629 - ACM

Repeat Unit



General

Although the above chemical structure is used as an example, acrylates are a class of materials rather than one single type. These polymers are formed by the copolymerisation of an acrylic ester and a cure site monomer, ethyl acrylate and chloroethyl vinyl ether respectively being illustrated above.

The properties of alkyl acrylate homopolymers vary accordingly to the number of carbon atoms in the alkyl radical. As the number of carbon atoms increases the T_g decreases from room temperature to well below 0 °C until the number exceeds 10. However, as the carbons in the side chain increase oil resistance decreases. When carbon atoms in the alkyl radical are replaced by oxygen, oil resistance improves.

The choice of acrylic ester, and hence its polarity, determines the low temperature flexibility, and the heat and chemical resistance of the polymer; both alkyl and alkoxy acrylic esters are used as monomers. Within the alkyl acrylic esters, ethyl acrylate has the highest polarity and hence gives

the best oil and heat resistance, but the worst low temperature performance. Low temperature properties improve as the alkyl acrylic ester changes from ethyl to butyl, and on to higher analogues, but this is at the expense of heat stability and oil resistance.

It is, of course, possible to copolymerise mixed alkyl acrylic esters to achieve a compromise in these properties. Alkoxy acrylic esters also confer improved low temperature properties.

One factor that has perhaps slowed down the use of these materials is the perceived difficulties in their processing. The acrylates are soft, and thermoplastic, and prone to scorch if tight process control is not in force in a factory.

The absence of main chain unsaturation confers good resistance to oxygen, ozone and light, whilst the polarity contributes oil resistance to the copolymer.

The cure site monomer directly controls which cure systems can be used to vulcanise the rubber. Since the cure behaviour is determined by the cure site monomer, and this can differ between suppliers, and presumably grades, it is advisable to read the manufacturers recommendation when deciding on the choice of cure system to use.

The first acrylates to be developed were cured by:

- (i) Amines, e.g., trimene base, triethylene tetramine, Diak No. 1 (DuPont)
- (ii) Red lead and ethylene thiourea

Of the amines, Diak No. 1, is the most efficient since it does not volatilise during processing. Sulphur, and sulphur bearing materials, act as retarders in this type of cure, and also act as a form of antioxidant.

Newer polyacrylate rubbers can be cured with certain amines and are more responsive to a broad range of curative systems, e.g., alkali metal stearate/sulphur or sulphur donor, methyl zimate and ammonium adipate.

Good, or best, compression set requires a post cure, although at least one manufacturer has introduced a new series of polyacrylates that only require a press cure.

The use of softeners and plasticisers presents a problem. TP90B, thioethers and certain adipates can give low temperature flexibility to $-45\text{ }^{\circ}\text{C}$, but these are volatile at post cure temperatures, and hence their effect is easily lost.

Uses

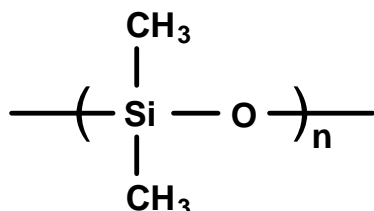
The main use for acrylates is in sealing applications where the improved heat stability over nitrile rubber is the benefit. Automotive transmission seals are probably the major use, other automotive applications include O-rings, hose, tubing, cable covering and spark plug boots. Also used in adhesive formulations.

3.16 Silicone Rubbers (MQ, VMQ, FVMQ, PVMQ)

Designation in ISO 1629 - Various (see text below)

General

Silicone rubbers contain the following dimethyl siloxane unit:



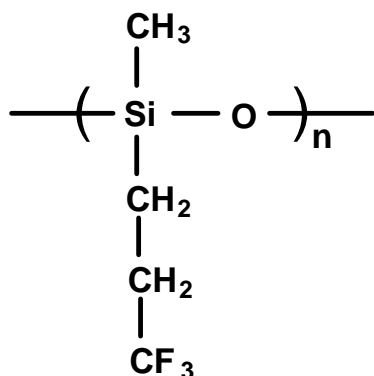
The millable gums, which will be the only type considered here, would generally contain 5,000-9,000 of the dimethyl siloxane unit.

Polymers which just contain the above repeat unit are termed methyl silicones, and are given the ISO designation **MQ**.

It is possible to replace a few of the methyl groups (<0.5%) with a vinyl group, and the resultant vinyl methyl silicones (ISO designation **VMQ**) exhibit improved vulcanisation characteristics and lower compression set.

The replacement of 5-10% of the methyl groups on the silicon atom with phenyl groups gives polymers which exhibit superior low temperature properties. Brittleness temperatures of approximately $-117\text{ }^\circ\text{C}$ can be achieved compared to the approximately $-70\text{ }^\circ\text{C}$ for the VMQ types. The ISO designation for the phenyl modified silicones is either **PMQ** or **PVMQ** depending on whether the grade is vinyl modified.

To improve the solvent resistance of the polymer, a fluoroalkyl group can be substituted on each silicon atom for one of the methyl groups, the resultant polymer (ISO designation **FMQ** or **FVMQ**) having the following repeat unit.



Silicone rubbers exhibit good resistance to heat ageing, and are considered to be usable up to temperatures of $200\text{ }^\circ\text{C}$. Although silicones do not exhibit high strength at room temperature, they do retain their properties at high temperatures to a much greater extent than other rubbers.

The long term performance of silicones is generally excellent, although exposure to steam at high pressure, and ageing in closed systems (oxygen essentially excluded) can lead to degradation via a hydrolysis reaction; this is especially true if acidic peroxide remnants have not been driven off during post curing.

The oil resistance of silicone is roughly equivalent to that of polychloroprene, whilst that of the fluorosilicones approaches the fluorocarbons.

Two further interesting points of note are that on burning silicones form silica which is an insulator, and thus cables insulated with silicone can function after short term exposure in a fire situation; silicones are also physiologically inert and this has led to their use in a wide variety of medical applications, including medical implants.

Being saturated, the resistance of silicones to oxygen, ozone and UV light is excellent, but means that peroxides have to be used for vulcanisation.

Silica fillers are generally used to reinforce these materials, carbon black being less reinforcing, and its use being somewhat specialised.

Silicones are readily available in liquid form (LR or LSR), room temperature vulcanising (RTV) and high temperature vulcanising (HTV).

Uses

Silicones are widely used in many applications, such as pharmaceutical, medical, wire and cable, automotive and aerospace, which utilise the excellent general inertness of silicone. They do, however, have a high price.

3.17 Ebonite

To convert an elastomer into ebonite, the glass transition temperature, T_g , has to be raised to above 20 °C, or above the operating temperature of the product, in order to remain rigid in use. This is achieved by crosslinking the rubber with a large amount of sulphur. Typically, 25 to 50 phr is used for natural rubber ebonites. Ebonites can be produced from NR, BR, IR, SBR and NBR. Rubbers with low unsaturation, e.g., IIR and EPDM, do not form ebonites.

A true ebonite has a Young's Modulus of >500 MPa (equivalent to 100 IRHD, 75 Shore D) and elongation at break is typically <15%.

The chemical resistance of ebonite is a function of composition and vulcanisation. Properly cured ebonites are resistant to non-polar liquids, e.g., aliphatic hydrocarbons, low molecular weight alcohols, glycerol, ethylene glycol and vegetable oils. Aromatic hydrocarbons, halogenated hydrocarbons, amines, phenols and low molecular weight esters are slowly absorbed. Ebonite is attacked by concentrated sulphuric acid, oxidising acids (>10% w/w), 50% chromic acid and dry halogens.

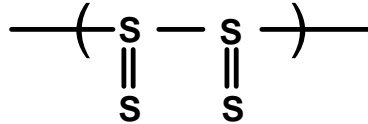
Ebonite is mainly used as chemically resistant plant linings.

3.18 Polysulphide Rubber (OT, EOT)

Designation in ISO 1629 - OT and EOT

General

These materials are formed by the reaction of a dihalide with sodium polysulphide, the main chain of the polymer formed from this reaction containing the following grouping:



The first type was produced from ethylene dichloride and sodium polysulphide. A high molecular weight polymer is obtained with predominantly hydroxyl end groups on the polymer chain. This type of polysulphide rubber was the first commercial grade but has, to a large extent, been superseded.

Three types of polymer are currently available from Morton International, the only manufacturer of this type of material.

(1) FA Polysulphide Rubber

This type is produced from a mixed dihalide, di-2-chloroethyl formal and ethylene dichloride, and sodium polysulphide. A high molecular weight polymer, ca. 100,000, is produced with predominantly hydroxyl end groups on the polymer chain. The sulphur content of the resultant polymer is 49%.

(2) ST Polysulphide Rubber

This type is produced from di-2-chloroethyl formal with a small percentage of 1,2,3-trichloropropane to provide a branch point for improving the cure state obtainable, and hence compression set. A much lower molecular weight polymer, ca. 80,000, is produced with predominantly mercaptan (SH) end groups. The sulphur content of the resultant polymer is 37%.

(3) Thiokol LP

The LP grades are liquid polymers used in sealant and mastic applications, and are formed by breaking down a high molecular weight polymer in a controlled manner. The liquid polymer again has mercaptan end groups.

The polysulphide grouping in the polymer confers an excellent resistance to solvents, with the sulphur content of the polymer determining the degree of swell.

The solvent resistance of these materials, especially to ketones, is good and is often the major reason for their use.

The resistance to ozone and UV light are excellent, although the use of 0.5 phr of nickel dibutyl dithiocarbamate (NBC) will improve ozone resistance further at high ozone concentrations.

Polysulphides are combustible, evolving sulphurous fumes, they are also malodorous.

The A and FA types both require peptisation to ensure ease of processing, and this is normally accomplished by the addition of MBTS and DPG onto a two roll mill maintained at 160°F prior to the addition of other ingredients.

The ST types do not require peptisation.

The A and FA types can be cured by the addition of zinc oxide alone at ca. 10 phr. Further additions of sulphur, at up to 1 phr, act as accelerators, but these are only needed if very fast curing compounds are required.

Either of the following three systems are used to cure the ST polymers:

<i>p</i> -quinonedioxime	1.5 phr
zinc oxide	0.5 phr
stearic acid	0.5-3.0 phr

<i>p</i> -quinonedioxime	1.0 phr
zinc chromate	10.0 phr
stearic acid	1.0 phr

zinc peroxide	6.0 phr
stearic acid	1.0 phr

Uses

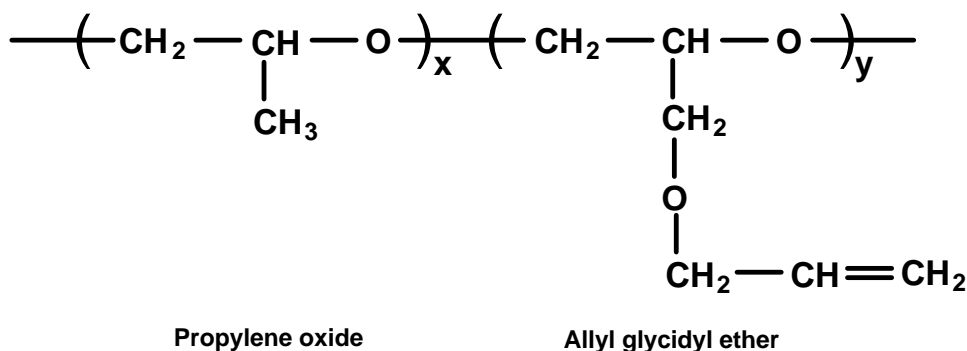
As well as moulded goods, polysulphide polymers are used in roller covering applications, and hose liners.

The sealants find use in the construction and aerospace industries.

3.19 Propylene Oxide-Allyl Glycidyl Ether Copolymer (PO, GPO)

Designation in ISO 1629 - GPO

Repeat Unit



General

The only commercially available material in this class, Parel, is a copolymer of propylene oxide and allyl glycidyl ether.

The absence of any polar grouping gives this material superior low temperature performance when compared to the epichlorohydrin terpolymers, but this is at the expense of oil resistance. The unsaturated nature of the main chain confers excellent resistance to oxygen, ozone and UV light.

The only cure systems seen for this material are based on sulphur vulcanisation.

Uses

Little comment can be made on the uses of this material except that it is used in some mouldings where the advantages of heat resistance, low temperature performance and oil resistance, roughly equivalent to that of polychloroprene, can be utilised. It has been investigated for use in engine mounts and transmission belting.

3.20 Polyurethane Elastomers (AU, EU, PU)

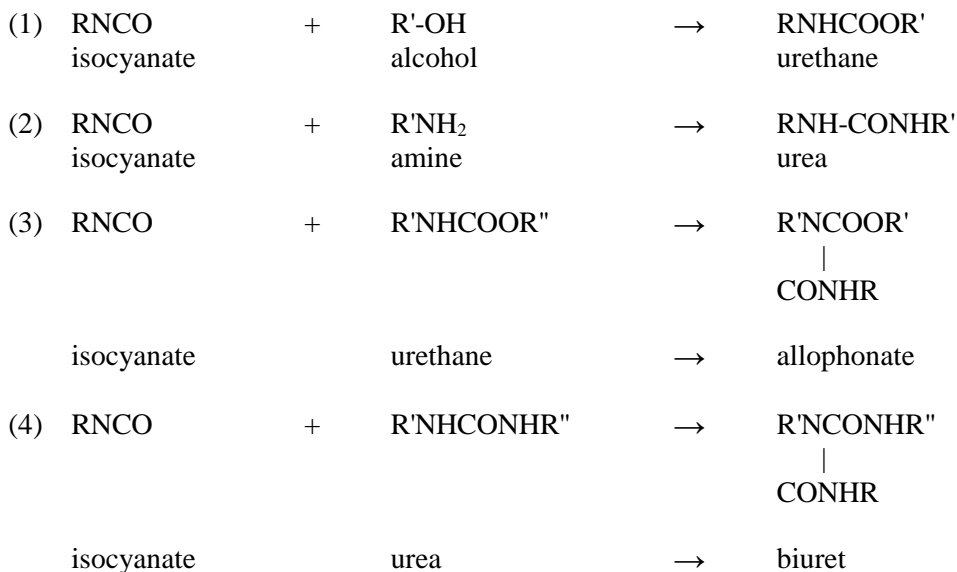
See also thermoplastic urethanes TPAU and TPEU.

Designation in ISO 1629 - AU and EU

General

Polyurethanes, as a class of materials, are one of the most versatile available. By varying the reactants, their amounts and the reaction conditions, one can obtain millable elastomeric gums, hard rigid plastics, reactive liquids, and foams. The versatility is such that it is very difficult to provide a brief summary.

The basic reactions utilised in polyurethane chemistry are:



In reactions (3) and (4) the isocyanate is capable of reacting with the active hydrogen in a urethane, or urea group, to give branching, or crosslinking by the formation of an allophonate or a biuret group.

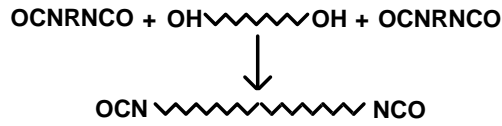
The most important reactions for the production of elastomers, however, utilise diisocyanates and polyols, and the elastomeric products formed can be of the following types.

Castable Polyurethanes

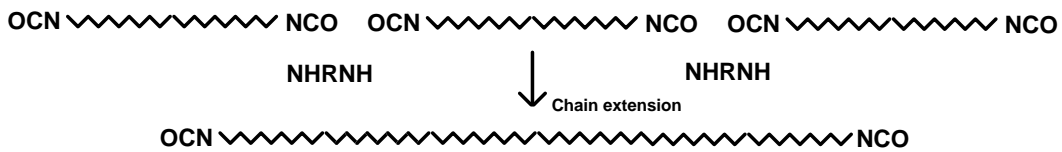
These are liquid systems that can be produced either in a one shot system (i.e., the diisocyanate, polyol and chain extender reacted in one stage) or, more usually, as a prepolymer which is chain extended and crosslinked at a later stage.

In the prepolymer system, the diisocyanate and polyol (either a polyether or a polyester) are reacted to give a prepolymer which may be either a liquid or a waxy solid. The reactant ratios used ensure the prepolymer contains isocyanate groups at the chain ends.

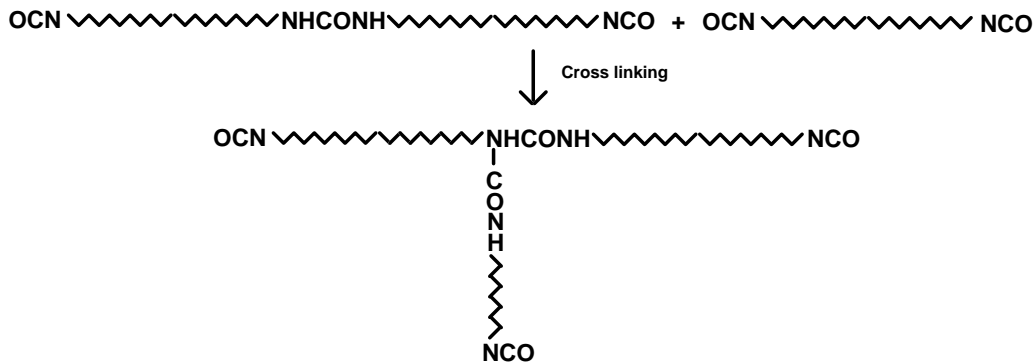
Isocyanate terminated prepolymer:



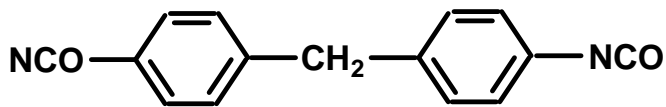
The prepolymer can, when required, then be chain extended to give a high molecular weight crosslinked product:



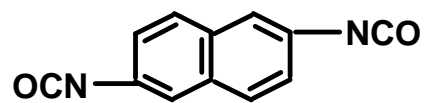
Crosslinking and branching can be promoted either by the use of a triol as a chain extender, or by using less chain extender than is theoretically required; the unreacted isocyanate end groups then react with urethane groups in the main chain to form allophanate or biuret crosslinks.



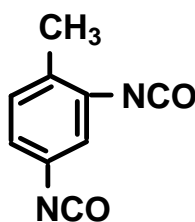
Typical diisocyanates that are used are:-



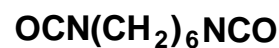
MDI (diphenylmethane 4,4'-diisocyanate)



NDI (naphthalene 1,5-diisocyanate)

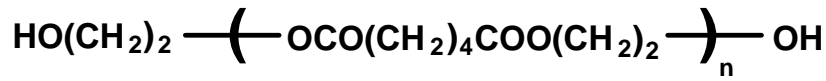


TDI (toluene diisocyanate)

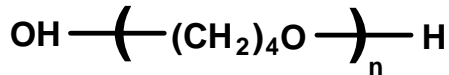


HDI (hexamethylene diisocyanate)

Typical polyols that are used include:



Polyethylene adipate (a polyester)



Poly(tetramethylene ether) glycol (a polyether)

Typical chain extenders that are used are MOCA (4,4-methylene bis orthochloro- aniline), butane diol or trimethylolpropane.

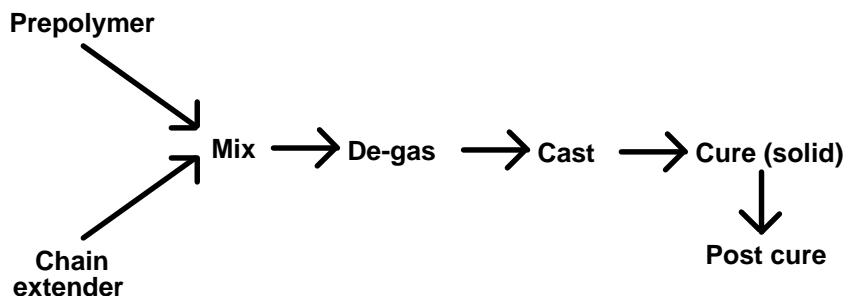
The following compositional variations can be made:

- i. type of diisocyanate
- ii. type of polyol and its molecular weight
- iii. type of chain extender
- iv. ratio of prepolymer to chain extender

By altering the above it is possible to make products elastomeric or rigid and, by the inclusion of water or a blowing agent, cellular products can be obtained. Clearly, with such possible variations, it is difficult to make general comments, but the following are generally accepted:

- i. Polyester polyurethanes generally give superior mechanical properties and chemical resistance, but inferior hydrolytic stability.
- ii. Polyether polyurethanes give superior low temperature properties and hydrolytic stability.
- iii. Diamine chain extenders give superior properties to diol cured elastomers.
- iv. Mechanical properties are generally improved as the hardness increases.

Processing of liquid systems proceeds as follows:



The mixing can be done by hand, or in low pressure mixer/dispensers, and in reaction injection moulding (RIM) machines. In the latter operation the de-gassing operation is not required.

Millable Gums

The diisocyanates and polyols are reacted to form a high molecular weight hydroxyl terminated millable gum. These millable gums are compounded and processed as conventional elastomers, both sulphur and peroxides being used to cure the polymers. Here again, polyether and polyester types are available, and the differences between these two types referred to above also apply here.

Other Types of Polyurethane

These are listed below, but not discussed further:

- i. One-component, blocked, cast polyurethanes. Here, reactive end groups are prevented from reacting by a 'blocking agent'. Upon heating to cure temperatures, the blocking agent splits off and cure commences.
- ii. Cast systems to give rigid plastics.
- iii. Polyurethane foams and microcellular products.
- iv. Spandex fibres.

Polyurethane elastomers are exceptionally tough, abrasion resistant, and resist attack by oil. The polyester types (AU) are susceptible to hydrolytic attack at above ambient temperatures, and certain polyester thermoplastic polyurethanes have been known to stress crack in cable jacketing applications when in contact with water at ambient temperatures; this latter effect has sometimes, incorrectly, been ascribed to fungal attack. Polyether types (EU) are far more resistant to hydrolytic attack. Certain polyurethanes can be attacked by UV light, the resistance to this agency primarily being determined by the isocyanate used.

The polyurethanes are resistant to ozone attack.

Uses

Polyurethanes are used in a wide variety of applications, seals, metal forming dies, liners, coupling elements, rollers, wheels and conveyor belts being examples. The thermoplastic polyurethanes are used as cable jacketing materials, conduits, fabric coatings, in ski boots and other rigid boot soles, automotive body components, gear wheels and other business machine parts.

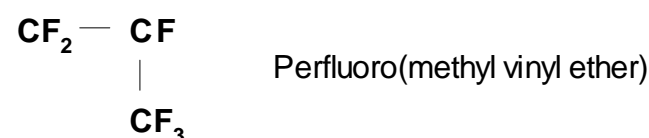
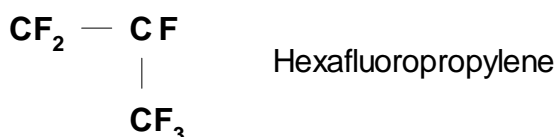
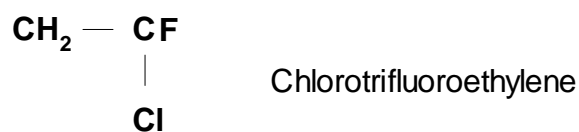
3.21 Fluorocarbon Rubber (FPM, FKM)

Designation in ISO 1629 - FPM

General

The importance of fluorine in polymer chemistry has been known since the discovery of polytetrafluoroethylene (PTFE) in 1938. Highly fluorinated polymers are very stable and have remarkable resistance to oxidative attack, flame, chemicals and solvents.

The fluorine containing compositional units generally used to produce commercial polymers are shown on the following page:



The heat resistance and chemical resistance of the fluoropolymers is mainly dependent on the extent of fluorination and stability of the crosslinks. For example, most fluorocarbons have fluorine contents of 50-70%, more chemically resistant types 65-69%. For comparison, fluorosilicones contain about 36% fluorine.

The fluorocarbons have the best heat stability of all rubbers, being capable of giving extended service life at over 250 °C. As a group, fluorocarbons resist aliphatic, aromatic and chlorinated hydrocarbons, and most oils and mineral acids. They are also highly resistant to oxygen, ozone and UV light.

There are several methods by which the fluorocarbons can be cured, and the principle methods are summarised below:

Cure Agent	Metal oxide acid acceptor	Comments
Diamine, e.g., hexamethylene diamine	Magnesium oxide or Calcium oxide	General purpose cure system, fairly resistant to scorch. Best heat resistance, but not particularly resistant to acids.
	Red Lead	Best acid and steam resistance, but exhibits strong tendency to scorch.
	Zinc oxide/dibasic lead phosphite	Least tendency to scorch, intermediate acid resistance.
Bisphenol A /Organo phosphonium salt	Magnesium oxide/calcium hydroxide	Improved compression set, reduced fissuring and shrinkage. Most common cure system for sealing applications. Changes in the acid acceptor generally give the same trends as in the use of diamine cures.
Peroxide (not for all grades)	Acid acceptor required	Inferior compression set to the Bisphenol cure. Improved resistance to amine stabilised oils.

Only the large particle sized blacks, MT or Austin Black, and mineral fillers are used in the compounding of these materials.

Some examples of fluorocarbon rubbers are listed here.

(1) Copolymers of vinylidene fluoride and hexafluoropropylene (VF2/HFP)

The commercially available materials are copolymers of vinylidene fluoride and hexafluoropropylene, and generally have a fluorine content in the range of 65-69% fluorine.

High heat resistance and oil resistance. Self extinguishing. Relatively poor cold performance. High cost. Slightly inferior heat and chemical resistance to the fluorocarbon terpolymers.

High resistance to almost all inorganic chemicals, ammonia being the most important exception. Resistance to most organic compounds, except low molecular weight polar organics. Least resistant of the fluorocarbon rubbers to methanol and phosphate ester based hydraulic fluids.

(2) Terpolymers of vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene (VF2/HFP/TFE)

Terpolymers generally have an increased fluorine content of 66-71%. Several different types can be identified, depending on the monomer used.

Some terpolymers contain an additional cure site monomer, for example, bromotetrafluorobutene, to permit crosslinking with peroxides. Peroxide curing gives vulcanisates more resistance to amine stabilisers in motor oils, more resistance to methanol containing motor fluids. Resistance to acids, aqueous media and steam is also improved. Compression set and heat resistance are slightly inferior to bisphenol A cure systems.

High heat resistance and oil resistance, superior in this respect to the fluorocarbon copolymers. Self extinguishing. Relatively poor cold performance, inferior in this respect to the fluorocarbon copolymers. High cost.

High resistance to almost all inorganic chemicals, ammonia being the most important exception. Resistance to most organic compounds, except low molecular weight polar organics.

(3) Terpolymers of vinylidene fluoride, perfluoro(methyl vinyl ether), tetrafluoroethylene (VF2/PVME/TFE)

These grades give superior low temperature performance. Commercial grades are generally peroxide curable.

High heat resistance and oil resistance. Superior low temperature performance when compared to the other fluorocarbon types. Self extinguishing. Relatively poor cold performance. High cost.

High resistance to almost all inorganic chemicals, ammonia being the most important exception. Resistant to most organic compounds, except low molecular weight polar organics.

(4) Terpolymers of vinylidene fluoride, tetrafluoroethylene, propylene (VF2/TFE/P)

These grades have been developed to give improved chemical resistance to automotive fluids such as gear lubricants, transmission and power steering fluids, engine oils, and rust inhibited engine coolants. Resistance to aromatic hydrocarbons is reduced.

High heat resistance and oil resistance. Superior resistance to automotive fluids than other fluorocarbon types. Self extinguishing. Relatively poor cold performance. High cost. Lower resistance to aromatic hydrocarbons than other fluorocarbon types.

High resistance to almost all inorganic chemicals, ammonia being the most important exception. Resistant to most organic compounds, except low molecular weight polar organics. Inferior in resistance to aromatic hydrocarbons, but superior in resistance to aqueous solutions and automotive fluids such as gear lubricants, transmission and power steering fluids, engine oils, and rust inhibited engine coolants, when compared to other fluorocarbon rubbers.

Uses

The main uses of the fluorocarbons are in sealing applications. Hose, tubing and expansion joints are another area of use.

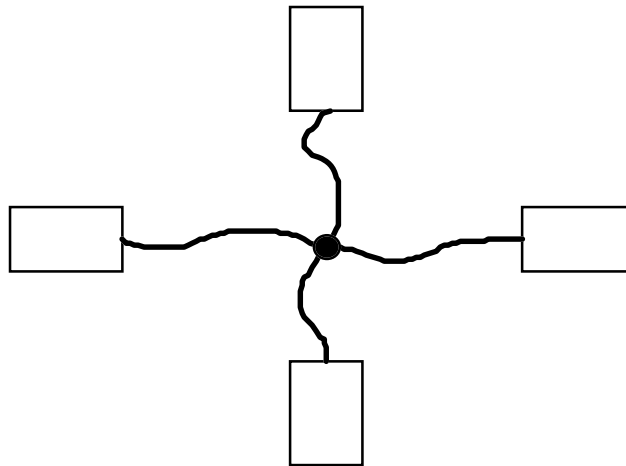
3.22 Thermoplastic Elastomers - General Description

Thermoplastic elastomers are materials which exhibit elastomeric behaviour at room temperature, but which can be processed as thermoplastics. Before one can understand the performance of these materials an understanding of how they can give their unique properties of elasticity and thermoplasticity is required; this is best done by considering the styrene-butadiene-styrene (SBS) thermoplastic elastomers.

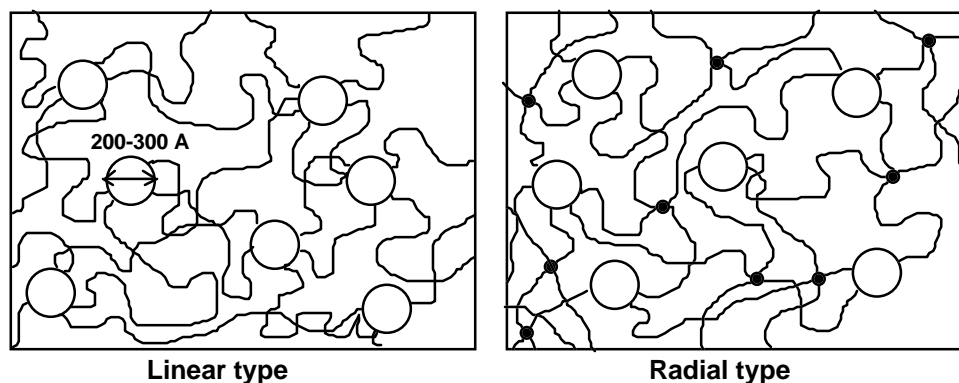
It is possible to produce a block copolymer by the anionic polymerisation of styrene and butadiene as depicted below. The polystyrene and polybutadiene are mutually incompatible and hence phase separate to give the morphology also depicted below:



Linear SBS type



Radial (tetrachain) SBS type



Simplified schematic representation of the structure of SBS block copolymers

This simplified representation of the morphology shows spheres of polystyrene embedded in a continuous soft elastomeric polybutadiene phase. Here the polystyrene domains act as ‘pseudo crosslinks’ and the polybutadiene conveys elasticity to the material. When heated above the T_g of polystyrene, the domains soften, disassociate, and the material can be made to flow. When cooled, the polystyrene domains reform and elastomeric behaviour returns.

The following features are therefore required for a material to act as a thermoplastic elastomer:

- i. A structural feature which acts as a pseudocrosslink at room temperature, but which will disassociate at elevated temperatures
- ii. A soft elastomeric phase for the development of elasticity.

The materials listed below are the major types of thermoplastic elastomer available commercially:

Major type	Subtype	Examples of trade names
Styrenic	SBS/SIS (styrene-isoprene-styrene block copolymers)	CariflexTR, Kraton
	Styrene-ethylene-butylene-styrene block copolymer (SEBS)	Kraton G, Elexar
Elastomeric alloys	EPDM/PP	Levaflex, Santoprene
	NR/PP	Vynamar
	NBR/PP	Geolast
	Chloro-olefin	Alcryn
Polyurethane	Ether/ester	Desmopan, Estane
Copolyether esters		Hytrel, Arnitel
Polyether amides		Pebax
NBR/PVC		Chemigum P83 ^a

^a Used as an additive to PVC to produce a TPE. This type is not discussed further.

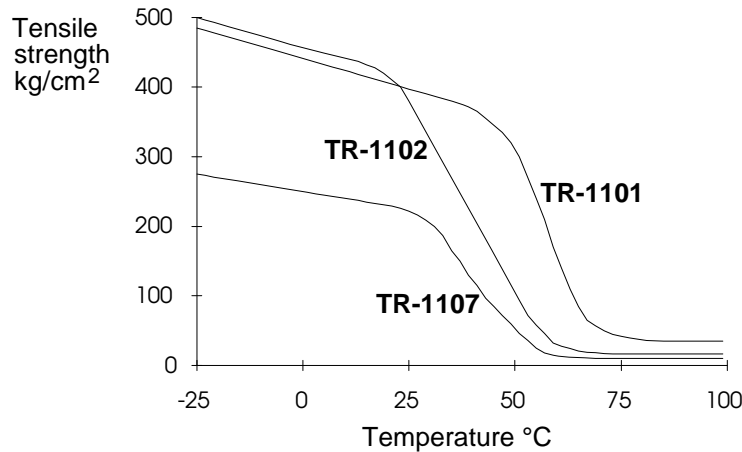
Before briefly discussing each type it is necessary to consider the performance of thermoplastic elastomers, and the problem of defining service temperature limits for them. The structural features that convey the ability to be processed as a thermoplastic are also a limiting factor in their use. Since it is the ‘pseudocrosslinks’ that allow these materials to develop elastomeric behaviour, any factor which interferes with the integrity of the pseudocrosslinks will weaken the material, and allow excessive creep or stress relaxation to occur under the sustained application of stress and strain. Temperature is obviously one such factor.

A method commonly used to derive a maximum service temperature limit is the UL rating; here, a material is aged at various temperatures and a property, say tensile strength, monitored. The

maximum service temperature is then defined as the temperature at which the property being monitored decreases by 50% after 100,000 hours ageing. Another method by which the effect of temperature can be assessed is the heat distortion temperature, which has the advantage of assessing the effect of temperature whilst the material is stressed. For example the following limits are found for one thermoplastic:

heat distortion temperature, 0.45 MPa 70 °C
heat distortion temperature, 1.8 MPa 50 °C

It can therefore be seen that the UL rating is not an adequate method of assessing maximum service temperature if a material is to support stress or undergo strain in service.



Dependence of tensile strength on temperature for Cariflex TR grades

The above illustrates the dependence of the tensile strength of SBS block copolymers on temperature. When this figure is viewed it has to be remembered that tensile strength is a short term measure of the ability of a material to resist stress and strain. One might ask the question, what would happen to the material if it was strained to 200% extension at 40 °C and held there. The answer is that one would expect a high rate of stress relaxation, the rate being an order of magnitude higher than would be expected of a conventional elastomer. It is therefore unfortunate that the manufacturers of TPEs do not generally include data on the creep and stress relaxation behaviour at elevated temperatures; they tend to rely on the UL approach to determine maximum service temperatures, or at best furnish data on the variation of hardness and tensile strength with temperature. The maximum service temperatures quoted in the following descriptions therefore need to be treated with a high degree of caution, and it is interesting to note, but not really surprising, that the major uses of TPEs are in applications where their general toughness is utilised, but where they do not have to support high applied stresses and strains.

TPEs find use in automotive, wire and cable, footwear, polymer modification, hose and tube, mechanical, bitumen modification, construction, adhesives and coatings, and film/sheet applications.

3.23 Thermoplastic Urethane Elastomers (TPAU, TPEU, TPU)

Designation in ISO 1629 - N/A

Consider the polyurethane:



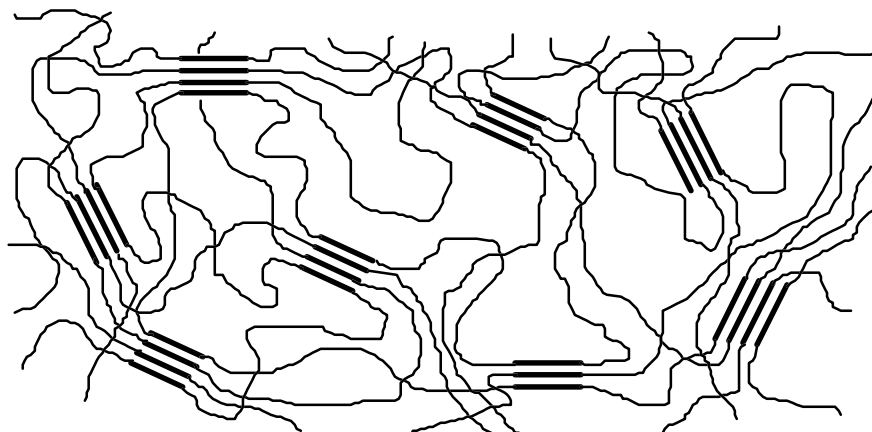
When R is small, such as the tetramethylene group (CH₂)₄, and R' is diphenylmethane, the polymers that result are rigid plastics similar to polyamides.

If R is a polymeric ester, or ether, of molecular weight 1000-3000 a flexible elastic material will result. By reacting MDI and active hydrogen components (polyether/ester and a short chain glycol) in equivalent stoichiometric quantities, a linear polymer with virtually no crosslinks is obtained.

If U is used to represent the diisocyanate, G the short chain glycol, and a wavy line to represent the higher molecular weight flexible polyether, or polyester, then the resultant polymer can be represented as:



This is a copolymer of the (AB)_n type, where the UGU sequences represent the urethane 'hard segment', and the wavy line represents the 'soft' flexible segment. Microphase separation of the hard segment occurs as illustrated below:



The thicker lines represent the sequences of 'hard' urethane segments, and the clusters of these effectively act as crosslinks, making the material act as a conventional elastomer. When the temperature is raised high enough, the clusters disassociate and the material can be made to flow; when subsequently cooled, the clusters can reform and the material again exhibits elastomeric properties. Thus these materials show elastomeric behaviour at room temperature, but can be processed as thermoplastics. Hence the name of the material class - thermoplastic elastomers.

Thermoplastic polyurethanes do not require compounding as do the conventional rubbers, and exhibit the same general properties as the cast and millable types.

The thermoplastic polyurethanes are available in a more limited hardness range than the styrenics, and are characterised by excellent strength and toughness, and oil resistance. Of the two major types available, polyester (TPAU) and polyether (TPEU), the latter exhibits superior hydrolytic stability and low temperature performance.

The electrical properties of the polyurethanes are not adequate for use as primary insulations, but their general toughness leads to their use as cable jacketing materials.

The following summarises these materials:

Typical properties

Hardness (Shore)	86A	95A (56D)	73D
Tensile strength (MPa)	40	40	50
Elongation @ break (%)	450	400	250
Tear strength (kN/m)	70	110	>120
Compression set (%)			
24 hrs @ 70 °C	30	30	--
70 hrs @ 70 °C	55	50	--

General

Hardness range:	75 Shore A to 75 Shore D
Maximum temperature:	120 °C
Minimum temperature:	-40 °C

Advantages

- Resistant to oxygen and ozone
- Oil resistant
- Strong/tough

Disadvantages

- Limited hardness range
- Hydrolytic stability
- UV stability of some grades
- Electrical properties not adequate for primary insulation
- Cost

Uses

Cable jackets, conduits, fabric coatings, ski boots and other boot soles.

Automotive: body components, bellows and lock compartments.

Also hose jackets, protective bellows, mechanical parts, animal ear tags, amongst other uses.

3.24 Styrenic Block Copolymers: SBS and SIS

Designation in ISO 1629 - N/A

These are block copolymers where the centre elastomeric block is either polybutadiene (SBS) or polyisoprene (SIS). The unsaturated nature of the mid-block renders them susceptible to attack by oxygen, ozone and light. The morphology of these materials is illustrated in Section 3.22, as is the dependence of their strength on temperature. It should be noted that their ability to function at elevated temperatures is restricted, and this is best illustrated by the fact that they cannot be used as shoe soling materials for trainers worn in indoor sports halls; the frictional heat developed by stopping, and turning quickly, softening the material and causing excessive wear.

The styrenic thermoplastic elastomers are the only type which are fully compounded in the manner of conventional elastomers. In this case, however, the addition of carbon black, or other fillers, does not give reinforcement. Additions of polystyrene, or high impact polystyrene, and oil are used to vary hardness and tear strength, and fillers can be used to cheapen the material. Other added polymers, e.g., EVA, can be used to increase ozone resistance. These materials also require antioxidants for protection during processing and service life, and the poor UV stability restricts their use in outdoor applications.

Whilst the poor resistance to oil and solvents is a drawback in some applications, it is a positive advantage in solution processing applications, e.g., adhesive production.

The following summarises this type of material. There may be some disquiet over the apparent use of these materials as glazing strips given the quoted temperature range.

Properties

Hardness range (Shore)	35A to 40D
Maximum temperature (°C)	65
Minimum temperature (°C)	-70

Advantages

- Fully compoundable, especially for tack
- Good wear characteristics in certain shoe sole applications
- Ability to be solution processed
- Good electrical characteristics
- Wide hardness range

Disadvantages

- Low maximum service temperature
- Not resistant to oxygen, ozone and light
- Not oil or solvent resistant

Uses

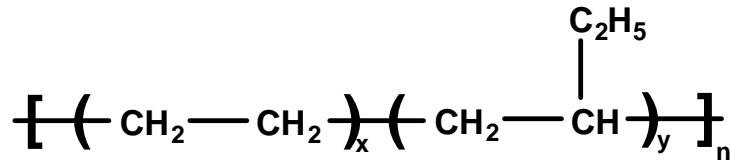
Shoe soles, adhesives, plastics modification, bitumen modification, miscellaneous moulded items, e.g., swim fins, black window glazing gaskets (UK -30 °C to +55 °C).

Not used in wire and cable.

3.25 Styrenic Block Copolymers: SEBS

Designation in ISO 1629 - N/A

In this type of styrenic TPE the polybutadiene mid-block used in the SBS types is replaced with ethylene-butylene which is saturated:



Ethylene butylene

As expected, the materials exhibit the same morphology as the SBS types but the saturated mid-block confers resistance to oxygen, ozone and UV light. Although it is said that improved phase separation gives improved stability to above ambient temperatures, the T_g of the polystyrene domains still restricts their use at high temperatures.

The SEBS types are again fully compoundable, and the following provides a brief summary of this type. The properties exhibited by the SEBS compounds are also representative of those of the SBS based compounds.

Typical properties

Hardness (Shore)	45A	55A	66A	95A
Tensile strength (MPa)	6.5	7.5	10.3	11.0
Elongation @ break (%)	800	700	700	425
Tear strength (kN/m)	28	21	48	78.8
Compression set (%)				
24hrs @ 23 °C		45		
24 hrs @ 70 °C		65		

Summary

Hardness range (Shore)	35A to 40D
Maximum temperature (°C)	65 to 80
Minimum temperature (°C)	-70

Advantages

- Fully compoundable, especially for tack
- Ability to be solution processed
- Good electrical characteristics
- Resistant to UV light, oxygen and ozone

Disadvantages

- Low maximum service temperature
- Not oil or solvent resistant

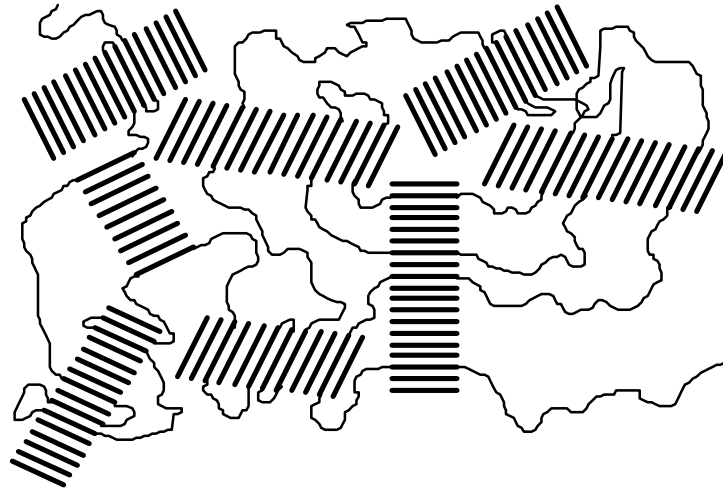
Uses

Wire and cable (US automotive, but not UK), adhesives, light-coloured window glazing strips (UK -30 °C to +55 °C).

3.26 Copolyether Ester TPE

Designation in ISO 1629 - N/A

These materials are segmented copolyether esters formed by the melt transesterification of dimethyl terephthalate, poly(tetramethylene ether) glycol and 1,4-butane diol. As with the thermoplastic polyurethanes, one can describe a hard segment and a soft segment, the hard segments forming crystalline areas which act as 'pseudocrosslinks'.



Typical morphology showing hard and soft segments showing one chain only for simplicity

These materials are again strong, tough and oil resistant, but are only available in a limited hardness range. Their hydrolytic stability is superior to the polyester thermoplastic polyurethanes, but they do require additional protection in applications where this could be a problem.

The following gives representative properties of the copolyether esters:

Hardness (Shore)	40D (92A)	55D	72D
Tensile strength (MPa)	25.0	38.0	38.0
Elongation @ break (%)	450	450	350
Tear strength (kN/m)	122	154	--
Compression set (%) 70 hrs @ 100 °C	60	56	--

Hardness range (Shore):85A to 75D

Service temperature: -50 °C to +150 °C

Advantages

- Resistant to oxygen and ozone
- Oil resistant
- Strong/tough

Disadvantages

- Limited hardness range
- Hydrolytic stability
- UV stability
- Electrical properties not adequate for primary insulation
- Cost

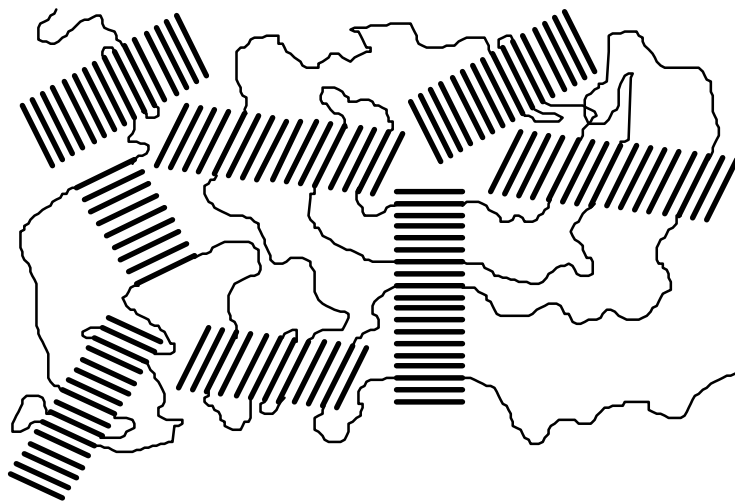
Uses

Cable jackets, hose jackets, tubing, seals, automotive bellows, mechanical parts, gear wheels, business machine parts.

3.27 Polyester Amide TPE

Designation in ISO 1629 - N/A

These materials exhibit the same type of morphology as the copolyether esters, the polyamide providing the hard segment, and the polyester the soft elastomeric phase. The service temperature is lower than that of the copolyether esters, but apart from this difference they exhibit similar properties.



Typical morphology showing hard and soft segments showing one chain only for simplicity

The following gives representative properties of the polyester amides:

Hardness (Shore)	40D (92A)	55D	72D
Tensile strength (MPa)	25.0	38.0	38.0
Elongation @ break (%)	450	450	350
Tear strength (kN/m)	122	154	--
Compression set (%)			
70 hrs @ 100 °C	60	56	--

Hardness range (Shore): 85A to 75D
 Service temperature: -40 °C to +80 °C

Advantages

- Resistant to oxygen and ozone
- Oil resistant
- Strong/tough

Disadvantages

- Limited hardness range
- Hydrolytic stability

UV stability

Electrical properties not adequate for primary insulation

Cost

Uses

Cable jackets, hose jackets, tubing, seals, automotive bellows, mechanical parts, gear wheels, business machine parts.

Section 4

Rubber Compounding Ingredients

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4.1 Accelerators

The rate of vulcanisation of a rubber compound is controllable by the choice of accelerator. The range of products offered to the rubber industry has been categorised historically into recognised classes. New developments have resulted in products that improve compound performance and which overcome dermatological problems, and do not generate nitrosamines and other extractable or volatile decomposition products.

Much of the accelerator volume used by the rubber industry is now supplied in treated forms to facilitate automatic weighing and reduce health contact problems.

4.1.1 Amines

Most of the materials in this category can be described as slow in character in their effect on vulcanisation. In most cases, they are seldom used on their own, only in combination with other accelerators being used as boosters.

4.1.2 Dithiocarbamates

Dithiocarbamates are generally classed as 'ultra' accelerators. When used alone they suffer from poor processing safety, due to a very rapid vulcanisation speed. They are usually used in combination with slower acting accelerators, except in the latex industry where elevated processing temperatures are not encountered.

Dithiocarbamates are polar in nature and thus will have a tendency to bloom when used in non-polar rubbers. The worst bloom problems will be encountered with the dimethyl derivatives; higher alkyl chain types have better solubility in non-polar rubbers. Some dithiocarbamates also confer antioxidant protection.

4.1.3 Dithiophosphates

Used in combination with other accelerators, the dithiophosphates reduce the risk of bloom and the formation of nitrosamines. Generally reversion stability is improved. The copper dithiophosphate will cause discolouration and contact staining.

4.1.4 Guanidines

Guanidines, when used alone, have a long scorch time and a long vulcanisation time requirement. Generally, when used as the sole accelerator, the properties of the compound, especially resistance to ageing, are poor. However, in combination with accelerators such as mercapto accelerators, they have a significant effect on the behaviour of the secondary accelerator increasing crosslink density and vulcanisation rate. They behave synergistically with thiurams, dithiocarbamates and to a lesser extent with sulphenamides giving considerable activation effects. Di-*o*-tolylguanidine can be used as a plasticiser for polychloroprene. The particle size of the guanidines can be critical; above 200 mesh they will not disperse readily.

4.1.5 Thiazoles

Thiazoles are classed as 'semi-ultra' accelerators. It is generally recognised that thiazole-type structures give better reversion resistance than the dithiocarbamates and thiurams. The term 'sulphur donor' was evolved to recognise that this type of sulphur containing accelerator could contribute to the chemical crosslinking process itself, by directly linking into the main polymer chain structure. It is also known that they confer some degree of antioxidant protection.

4.1.6 Mercapto Types

The mercapto accelerators are used in many rubber types and are very efficient. They confer good processing safety to the compounds, with intermediate vulcanisation rates, a broad vulcanisation plateau and very good ageing resistance. Used alone they give a relatively low crosslink density. In combination with other accelerators they often act synergistically giving faster vulcanisation and a considerably higher crosslink density. They do not usually confer optimum heat stability to products. In low sulphur compounds (semi-efficient) the mercapto accelerators are not very effective alone. In semi-efficient vulcanising systems in combination with bases they do, however, become very effective. However, such basic activation systems can have a detrimental effect on reversion stability in reversion prone compounds.

4.1.7 Benzothiazole Sulphenamide Types

The accelerators in this class become active as the amine groups are split off during vulcanisation. This accelerator type produces delayed commencement of vulcanisation, thus improving the compound's processing character. Their thermal stability depends on the substituents on the nitrogen atom, giving various degrees of retardation. Vulcanisation with these accelerators allows for good compound flow time, with a rapid crosslink density increase after the initial delay. Problems can arise when compounds are stored for long periods as the chemical structure of these accelerator types can alter depending on their history, giving reduced processing safety and loss of the expected vulcanisation start delay. Secondary accelerators, such as thiurams and dithiocarbamates, synergistically increase the vulcanisation speed.

Benzothiazole sulphenamide accelerators are suitable for semi-efficient and efficient vulcanisation systems.

4.1.8 Thioureas

Thioureas mainly find use for the vulcanisation of CR, epichlorohydrin (ECO) and some ethylene propylene diene terpolymer (EPDM) compounds. They show high crosslinking activity, with usually adequate compound flow time before onset of the crosslinking. In EPDMs, the thioureas are used as activators for low activity third monomer types and, in the presence of calcium oxide desiccants, in free state vulcanisation of extrudates, etc. The use of thioureas can overcome the retardation caused by the desiccant. In this case some care must be taken otherwise overcompensation may occur. Thioureas are not used in food product applications and are a known health hazard, particularly for pregnant women.

4.1.9 Thiurams

Thiuram accelerators break down into the corresponding dithiocarbamate before becoming active. There is thus a delay in the onset of vulcanisation. Thiurams can be used over a wide range of sulphur systems. They can behave as system activators when used in combination with thiazoles, whilst acting as retarders for dithiocarbamate and xanthate systems.

A drawback for this class of accelerators is that secondary amines can split off, which may possibly then form nitrosamines.

In low or sulphurless systems, thiurams containing more than one sulphur atom act as sulphur donors. They also confer low tendency to reversion, and good heat stability.

4.10 Xanthates

Classed as ultra accelerators, xanthates are among the fastest of accelerators available to the rubber compounder. Their speed is such that they find only limited application in solid rubber product manufacture but they are used in low temperature curing of latex articles.

4.1.11 Miscellaneous Accelerators

A number of chemicals are used which do not fall into the general categories of the conventional accelerator types used by the rubber industry.

Chemicals such as magnesium and lead oxides, calcium hydroxide, antimony tri- and pentasulphide can be used as boosters for organic accelerators for some products, such as thick walled large volume articles, e.g., rollers.

4.1.12 Mixed Accelerator Packages

A number of accelerator systems used specifically for known processes are provided in blends often with an added processing additive.

4.2 Activators

4.2.1 Metallic Oxides

Iron Oxide

Iron oxide is used for compounding silicone rubbers where it is used to improve heat stability. Iron oxide, mainly ferric oxide, also finds application as a pigment.

Lead Oxide

Lead monoxide or litharge is mainly used as an accelerator activator, and acid acceptor, and is especially useful in water resistant compounding. Litharge can also be used in long slow cures for such articles as ship's fenders, bridge bearings, etc., where it enables the inside of the product to fully cure before the outside becomes overcured with the possibility of degradation or reversion of the outer layer of the product.

Litharge can also be used to provide compounds with high specific gravity and provides low permeability to, and protection from, radiation.

Magnesium Oxide

Magnesium oxide is used as a compounding ingredient for a number of purposes. Light magnesium oxide is used as an acid acceptor in the vulcanisation of halogen containing rubbers; heavy magnesium oxide, which has a larger particle size than the light grade, is less active as an acid acceptor. It is, however, used in heat resistant seal compounds. Magnesium oxide is also used as a cure modifier in halogenated butyl rubbers.

If stored for too long, magnesium oxide can convert to magnesium carbonate or hydroxide with resultant loss of activity as an acid acceptor. Magnesium oxide supplied in stick form overcomes this problem. Some forms of pelletised magnesium oxides can be too hard to break down in soft compounds and problems can arise from hard undispersed 'ceramic'-like particles.

Some proprietary blends of magnesium oxide and zinc in the desired proportions for CR compounds are available with the addition of some processing additives to ensure the best dispersion characteristics.

Zinc Oxide

Zinc oxide plays a multi-functional role in rubber technology. Its main use is as an activator of the sulphur crosslinking reaction. Zinc oxide has been used as a pigmentation ingredient where it is particularly effective in absorbing ultraviolet rays. With high thermal conductivity and heat capacity in comparison to other compounding materials, zinc oxide can be used in some bulky product applications as an aid to heat conduction through a rubber mass to shorten cure times. It can, at reasonable addition levels, also assist with reduction of mould shrinkage values.

Zinc oxides are prepared from zinc metal by two main processes:

- the 'direct' or American process in which zinc containing ores are calcined in reducing conditions with subsequent burning of the resultant zinc in air,
- the 'indirect' or French process wherein purified zinc is sublimed and burnt in air to form the oxide; this method gives zinc oxides of the highest purity.

Both these methods give zinc oxides of low activity. Zinc oxide from the American process can have a varying sulphur content, dependant upon the ore's source, and unless known and allowed for, this can affect the compound vulcanisation rate.

French process material, in general, tends to have a blockier particle shape with a relatively narrow particle size range in comparison with the American process product. The French process oxides also exhibit a finer particle size and hence have a higher surface area.

Zinc oxides from wet chemical routes can be prepared to fineness values which control and enhance their reactivity in the rubber compound, with consequent higher activity rating. This route involves the initial precipitation of zinc carbonate followed by drying and calcination to remove water and carbon dioxide. The resultant zinc oxide is often characterised by having a high specific area. These grades do have a high tendency to agglomerate together and thus are often supplied in dispersed form for rapid and adequate dispersion in the rubber.

Zinc oxides can be prepared from chemical industry by-product sources and from zinc soaps from a variety of industrial processes. These grades are generally off-coloured and consequently considered of lower grade and offered at lower cost and are confined to use in black compounds. These grades can also vary in consistency, batch to batch, causing cure variation in compounds containing them.

According to the source of the zinc oxide there can be a problem with the inclusion of a small percentage of lead. Zinc and lead are found in the same ores in nature and unless correctly refined there can be some lead as a contaminant in the zinc oxide. Even 1% of lead in a zinc oxide is sufficient to cause discolouration of light coloured compounds.

Zinc oxide in storage will slowly absorb carbon dioxide and therefore cannot be regarded as an inert material. Old material may show different reactivity if the storage time exceeds 12 months, thus affecting cure characteristics of compounds.

Compounds containing fine particle zinc oxides can show increased viscosity. When an increased dosage of these fine particle materials is required there can be considerable stiffening of the compound, which can be used to advantage to give good dimensional stability to extrudates such as profiles and hoses and to stabilise open steam cured goods in general.

Extremely fine particle size zinc oxides, are easily incorporated into the rubber and have little pigmenting power and thus can be used in transparent vulcanisates without creating opaqueness. These grades can be used at as low a dosage as 0.8 phr giving the required degree of activation. Due to the ease of dispersion and high specific surface in contact with the rubber, the dosage level required for these grades is significantly lower than with conventional materials. This type of zinc oxide can also be used in the range of 20-50 phr as a reinforcing agent for products requiring high resilience for use in engineering products such as springs, etc., and for the production of food quality compounds.

Zinc Peroxide

Zinc peroxide is used as the curative for carboxylated acrylonitrile-butadiene rubber (XNBR) compounds. It confers better scorch safety than does zinc oxide. It is usually added in a masterbatch form.

4.2.2 Organic Crosslinking Activators

The crosslinking efficiency of many peroxide-initiated free radicals is low. These labile radicals can be converted to more stable radicals by contact *in situ* with polyfunctional monomers to form a three-dimensional network. Crosslinking efficiency is thus increased by some 20%. In addition, these materials act as plasticisers during processing and in some cases also act as hardening agents.

4.2.3 Silane Coupling Agents

Silane coupling agents improve properties of compounds containing silica and silicate fillers by forming chemical bonds across the filler and the rubber interface. They can also give improved properties with other materials, such as carbon blacks. They can be used with clays which do not form strong chemical bonds with the polymer, thus bringing them into the general category of useful processing additives. The improved compound properties result from a better compatibility and linkage of the rubber and filler. The coupling agent can be added direct to the mixer with the filler, or may be purchased already in place on the intended filler.

The silane coupling agents which are frequently used are bis-(3-triethoxysilylpropyl)tetrasulphane and 3-thio-cyanatopropyl triethoxy silane.

The effect of coupling agents on the physical properties of the compound is to:

- lower compression set,
- reduce heat build-up under dynamic conditions,
- reduce tan delta,
- improve crosslink stability,
- improve tear related characteristics, and
- improve resistance to swelling by water.

The addition of a coupling agent can dramatically improve the abrasion resistance of compounds containing silica reinforcement. The effect is dependant on the surface area of the silica.

4.2.4 Titanate and Zirconate Coupling Agents

Organometallic titanate and zirconate coupling agents form monomolecular layers on most materials, such as metals, metal oxides, carbonates, sulphides, sulphates, siliceous materials, carbon black, some synthetic fibres, dispersed dyes and organic pigments. They render the substrate hydrophobic (moisture free), organophilic (rubber compatible and reactive), organofunctional (e.g., phosphato flame retardant functionality to provide controlled intumesence) and catalytically reactive with the polymer phase.

They may also act as reactive super plasticisers to increase rubber flow while increasing the mechanical properties of the rubber. Viscosity reduction or polymer solvation and higher filler loading can be accomplished with less plasticiser. Flow is achieved through molecular rearrangement and not average molecular weight reduction of the rubber.

Titanates can, in contact with ingredients containing phenolic functionality, produce colouration. Zirconates generally do not produce colour when in contact with phenols.

Neoalkoxy zirconates also provide novel opportunities for the adhesion of fluorinated polymers to metal substrates because the introduction of a zirconate at the interface results in a metal oxygen zirconium VI organo fluoride.

4.3 Antidegradants

The unsaturated structure of the diene hydrocarbon rubbers makes them susceptible to attack by both oxygen and ozone. Oxidative degradation of all rubbers, irrespective of their structures, is inevitable as the energy associated with incident natural light is approximately three times that of a typical carbon-carbon or carbon-hydrogen bond.

Retardation of oxidative degeneration and the effects of ozone attack can be mitigated but not totally overcome by the use of chemicals which, unfortunately, in the case of the most effective types, carry the penalty of causing staining of the rubber compound or surfaces with which it comes into contact.

4.3.1 Antioxidants

Oxidative ageing of rubbers is limited by the rate of diffusion of oxygen into the rubber product and is usually confined to the outer 3 mm. Antioxidants are used to protect rubbers from the effects of thermal oxidation and the vast majority of compounds will contain one or more. Peroxide vulcanisates are usually protected with dihydroquinolines. Other antioxidants react adversely with the peroxide inhibiting the crosslinking reaction.

The durability of the antioxidant can be affected by a number of factors, the most important being the amount present in the compound. The process of vulcanisation can result in the loss of migratory or volatile antioxidants. Over long periods of service, the antioxidant will decrease in concentration at ambient temperatures due to reaction with oxygen. Loss by volatility is usually only a problem with antioxidants such as the mono-phenolics.

The most effective antioxidants for light coloured rubber compounds are the hindered bisphenols, but these offer little ozone and flex cracking resistance.

Strongly Staining Antioxidants

Aryl naphthylamine derivatives are good general antioxidants with moderate volatility and negligible effect on cure. These give a small degree of fatigue protection in natural and polyisoprene rubbers, but little in styrene-butadiene and butadiene vulcanisates.

Diphenylamine derivatives are very good antioxidants and provide fatigue activity and good metal poison protection.

Moderately Staining Antioxidants

Dihydroquinoline derivatives offer moderate antioxidant and flex cracking activity with excellent metal poison protection.

Non-Staining Antioxidants

Benzimidazole derivatives are excellent antioxidants, with limited fatigue activity. They offer excellent metal poison protection.

Bisphenol derivatives show very good antioxidant activity and are the best materials for light coloured articles. Selected materials are FDA approved. These derivatives have low volatility and no effect on cure rate and do not give a bloom. A slight pink discoloration can occur after prolonged exposure to light in white or light coloured products.

Hydroquinones show very good antioxidant activity, but offer limited fatigue and metal poison protection.

Alkylphenol derivatives show medium antioxidant activity, but provide limited fatigue and metal poison activity.

4.3.2 Antiozonants

Ozone attack on rubbers takes the form of cracking which takes place perpendicular to the direction of the strain.

Ozone attack occurs mainly at the olefinic double bond of a diene rubber and, if not protected against, will result in loss of physical integrity for thin sectioned articles and surface cracking on larger mass products.

Too high a dosage of antiozonant can result in the formation of unsightly blooms on the rubber surface. Too little antiozonant can lead to worse attack than when none is present.

Strongly Staining Antiozonants

Dialkyl-*p*-phenylenediamine derivatives show good antioxidant activity with very good antiozonant characteristics, with low volatility and at normal dosage levels give no visible bloom to the rubber surface. They give good to moderate flex cracking resistance and increase the critical stress required to promote cracking. The dialkyl-*p*-phenylenediamines are liquids; their use reduces compound scorch time and they can have a relatively short durability due to their high reactivity. Alkyl carbon contents of less than 7 are not used as they can induce dermatitis.

Aryl-alkyl-phenylenediamines have very good antioxidant activity with very good antiozonant characteristics, with low to moderate volatility and no visible bloom to the rubber surface. They give very good flex cracking resistance and have no effect on critical stress but reduce the rate of cut-growth. These are the most widely used antiozonants as they have high activity, with minimal effect on scorch time, are resistant to leaching and are highly persistent in product service. This class are more soluble in rubber compound than other types.

Diaryl-phenylenediamines have very good antioxidant activity with good to moderate antiozonant characteristics, with low volatility but will possibly bloom to the rubber surface. They give very good flex cracking resistance.

Non-Staining Antiozonants

Benzofuran derivatives and enolethers are offered as chemical antiozonants for light coloured rubber compounds. Benzofuran derivatives are used in CR and its blends with other rubbers and give ageing protection in addition to ozone protection.

The enolethers give ozone protection but not ageing protection with natural rubber (NR) and polyisoprene (IR), styrene-butadiene rubber (SBR) and butadiene rubbers (BR), but are less

effective in acrylonitrile-butadiene rubber (NBR). Enolethers act synergistically with microcrystalline waxes.

4.4 Antireversion Agents

In many sulphur vulcanisation systems there is an optimum peak for physical properties. Continuing the vulcanisation past this optimum condition results in loss of crosslinks and thus reduction in properties. A number of methods for reducing this property loss are now available.

1. Addition of bis-(3-triethoxysilylpropyl)-tetrasulphide plus accelerator and sulphur can counter loss of crosslinking. Accelerator systems which respond to this antireversion agent are the thiazoles and the sulphenamides. Thiurams do not respond. For cure state equilibrium to be maintained the proportions of the three constituents (sulphur, accelerator and antireversion agent) are adjusted to give a constant modulus.
2. The presence of sodium hexamethylene bis-thiosulphate results in the formation of hybrid polysulphidic/hexamethylene bonds. The polysulphidic portion of these hybrid bonds reverts to monosulphidic during reversion but stability is achieved by the presence of the hexamethylene.
3. Mono- or di-sulphenamides of pentachlorothiophenol are claimed to provide reversion resistance.
4. Dithiophosphates such as zinc dibutyl dithiophosphate used with a sulphenamide can give improved reversion resistance.
5. Mixtures of zinc salts of aliphatic and aromatic carboxylic acids confer antireversion characteristics with improvements in dynamic properties. Their efficiency is dependent upon the fatty acid chain length and structure.

4.5 Antistatic Agents

The production of light coloured products with a requirement for low build-up of static electricity requires the addition of an ingredient which is capable of providing the rubber with a low electrical resistance. Quarternary ammonium salts and ethylene oxide condensates provide one route. Of the common plasticisers, phosphate types have the lowest electrical resistance conferring properties in rubbers. Special 'antistatic' plasticisers, such as polyethylene glycol fatty alcohol ethers, are designed to give rubbers with low surface resistivity.

Surface bleeding and migration into other adjacent non-conductive compounds can be a problem with some antistatic plasticisers. Migration of plasticiser to bonding agent interfaces can also be the cause of product failures during service life.

4.6 Biocides and Fungicides

Residues of fatty acids from emulsion polymerisation and from cure activation provide sites for bacterial attack when the rubber product is exposed to warm moist conditions. The addition of a biocide/fungicide will give excellent fungal growth protection.

4.7 Blowing Agents

Physical blowing agents are generally low boiling point organic compounds, which volatilise during processing to create a cellular structure, e.g., pentane and dichloromethane. However, the most widely used agents in rubber are chemical blowing agents.

Chemical blowing agents used by the rubber industry are materials which are capable of evolving relatively high volumes of gas when heated to a prescribed moulding temperature. They are of two main types: inorganic and organic. The inorganic blowing agents, usually ammonium carbonate or sodium bicarbonate, evolve carbon dioxide on decomposition. The organic agents mainly evolve nitrogen, but may also give off carbon dioxide, carbon monoxide, ammonia and water according to their chemical composition.

There are four basic types of expanded rubber:

- **Foam Rubber:** A product produced exclusively from a liquid base, e.g., latex. Latex foam has an interconnecting cell structure and is most commonly used for cushioning applications.
- **Sponge Rubber:** Sponge rubber is made from solid starting materials and has an essentially interconnecting cell structure. The rubber compound for this product has to be of low viscosity to allow the generated gas to expand rapidly as it is formed. Inorganic blowing agents are normally used for this type of product with often a small additional amount of organic blowing agent to regularise the size of the cells being formed.
- **Expanded Rubber:** This class of product has an essentially closed cell structure. These products are most usually formed by moulding or extrusion processes and have a solid outer skin around the cell structure. Organic blowing agents are used for this type of process.
- **Microcellular Rubber:** A product usually used for shoe soling application produced by the incorporation of a blowing agent into the high styrene resin soling compound.

The choice of the type of blowing agent to be used to manufacture the cellular product depends upon the service application of the product. Where rapid recovery from compressive forces are required then an open-cell product is necessary to allow rapid passage of air back into the deflated cell structure.

Closed-cell sponge is used in a number of articles such as insulation and shock absorbing media and in seals of various types.

In order to be a good blowing agent, useful quantities of gas must be generated when heated to the temperature of rubber vulcanisation. The blowing agent must ideally be cheap, stable in storage, non-toxic, odourless, non-staining, easy to disperse and have no influence on the progress of vulcanisation.

4.7.1 Inorganic Blowing Agents

Inorganic blowing agents are cheap materials which are not totally stable in storage and this can affect the quality of the cellular product. The choice of particle size of the inorganic blowing agent dictates to a large extent the size of the pores of the resulting sponge, the larger particle types giving larger, more irregularly sized and shaped cell geometry.

Whilst sodium bicarbonate is the primary blowing agent, it is common compounding practice to use it in conjunction with a proportion of a weak acid, such as stearic or oleic acid, whose function is to trigger the reaction and assist in the uniform decomposition of the bicarbonate. The higher than normal fatty acid level will also act as a process aid, facilitating the bubble expansion process.

To achieve a fine dispersion within the rubber, an oil dispersion or paste of the bicarbonate can be used and this will result in a much finer and more uniform cell structure.

Other inorganic blowing agents used are ammonium carbonate and ammonium bicarbonate which produce mostly carbon dioxide with a small amount of ammonia.

4.7.2 Organic Blowing Agents

Azodicarbonamide (ADCA)

ADCA is a yellow crystalline solid which decomposes to produce a high yield of gas (220-240 cm³/g at standard temperature and pressure (STP)). The gas to which it decomposes consists of 62% nitrogen, 35% carbon monoxide and 3% ammonia and carbon dioxide. Moisture can affect the blowing characteristics of ADCA.

ADCA is activated by zinc oxide, zinc stearate (strongly) and urea (slowly). Barium stearate, calcium stearate and triethanolamine, when added at 10 phr, moderately activate gas evolution from ADCA. They do not have very much effect on decomposition rate when the cure temperature is at 170 °C, but a marked effect above 180 °C. The rate of decomposition of ADCA is significantly influenced by the particle size of the additive. Effective dispersion and heat transfer through the particle can be a means of controlling the cell quality and the manufacturing method for the product. The correct particle size is selected to achieve the optimum balance between cure and cell development.

ADCA has been marketed in blends with a variety of activators. These systems can be used to give better cell uniformity, better uniformity of colour and more uniform product hardness. The different activators also influence the temperature at which the effective decomposition of the blowing agent takes place.

p,p'-Oxybis(benzenesulphonyl hydrazide) (OBSh)

OBSh is a white crystalline solid that melts with decomposition at 164 °C (*in vitro*) to give 125 cm³ nitrogen per gram at STP. Gas generation can occur at as low a temperature as 120 °C, but at this temperature the generation rate is slow. Best gas generation occurs between 145 °C and 160 °C. The product is odourless, non toxic and does not cause discoloration.

Triethanolamine and urea are very strong activators of decomposition of OBSh. The activator reduces the temperature at which optimum gas generation occurs. DPG is also a strong activator of decomposition of OBSh. Stearic acid and calcium oxide are also moderate activators of OBSh.

Unlike ADCA, which is affected by moisture, OBSh can be used in alkaline latex conditions. In these conditions it generates nitrogen and forms acidic decomposition products which coagulate or gel the latex compound thus producing an expanded rubber product.

Dinitroso pentamethylene tetramine (DNPT)

DNPT is a free flowing light yellow powder. Alone DNPT decomposes at approximately 190 °C and produces 265 cm³ of gas per gram at STP. Nitrogen, nitrous oxide, various amines and water are produced. In a rubber environment the gas generation takes place within a range of 130-190 °C. A characteristic amine 'fishy' odour is quite pronounced and can be offensive for some applications. DNPT is non-staining.

DNPT is flammable, so it must be stored carefully to avoid contact with heat sources. It must also be kept dry as moisture reduces its activity. It is activated by peptisers and curing agents and therefore care must be taken at the weighing out stage of mixing.

DNPT is particularly active in full cavity moulded, precured closed-cell applications with CR, NBR, EPDM and SBR. It is efficient in an extrusion environment.

4.8 Bonding Additives

4.8.1 Rubber to Fabric Bonding Additives

Resorcinol formaldehyde latex (RFL) cord dips have only a limited application within the general rubber goods industry and for adhesion to be achieved with synthetic fibres it is necessary to use the systems developed by Bayer and Degussa. These systems are based upon a combination of resorcinol, a formaldehyde donor and a hydrated silica filler (commonly called the RFK system). This system is incorporated as dry ingredients into the rubber compound and is activated by the application of heat.

Hexamethylolmelamine ethyl ether or hexamethylene tetramine are used as the formaldehyde (methylene) donors and these combine with the resorcinol to give a resin which migrates through the compound to the rubber-fabric interface. In the presence of the silica, a reaction takes place forming a bond between the materials at the interface. The reaction of the resorcinol resin and the silica are vital constituents of the combination. The true role of the hydrated silica is not fully understood. The moisture content of the silica molecule appears to have a significant role in the effective promotion of the adhesion. It is also necessary that care be taken in the design of the rubber compound, to prevent reaction between the compounding ingredients and the resin/silica complex. As the action of the resin is at the interface there must be sufficient resin forming ingredients in the compound for migration to take place effectively. Too thin a layer of compound in contact with the fabric will mean that there is insufficient resin concentration to allow a high enough level for adhesion to be effected at the interface.

The RFK mechanism can be used with loomstate nylon and rayon fabrics, but polyesters will require a pre-treatment to achieve good adhesion. Hexamethylene tetramine should be avoided as the methylene donor when polyester fabrics are being used, as aminolysis of the ester linkages in the polyester can occur, which would cause significant degradation of fabric and adhesion to take place under severe service conditions. Hexamethylolmelamine ethyl ether should be used as the methylene donor in this case.

Using a pre-treatment of RFL with the fabric will also significantly improve the adhesion with most materials.

Reduction of the adhesion level will occur if certain compounding ingredients are not avoided. The acceleration system has a direct effect on the adhesion level; dibenzothiazole disulphide (MBTS) gives the highest adhesion levels. If a second accelerator is used, e.g., tetramethyl thiuram disulphide (TMTD) or diphenyl guanidine (DPG), then the adhesion is significantly affected. Other ingredients which cause problems are plasticisers and process oils.

If accelerators which leave amine residues in the rubber compound are used, then the above mentioned deterioration of a polyester fabric will occur. Thiurams and dithiocarbamates can also damage fabrics. These accelerator residues cause deterioration of both fabric and adhesion levels which usually occur under service conditions after long periods of exposure to high temperatures.

4.8.2 Rubber to Metal Bonding Additives

Adhesion promoters are used to achieve the optimum bond adhesion level. The basic unpromoted adhesion system is the RFK system. Addition of cobalt as a promoter to the resin system considerably boosts the adhesion level achieved. The type of salt used determines the cobalt level

and the quality of the adhesion. The cobalt salts used include: cobalt stearate, cobalt naphthenate and cobalt neodecanoate. Proprietary preparations consisting of organometallic compounds are also used.

The resin system has a number of practical drawbacks:

- Resorcinol fumes generated at high mixing temperatures.
- At least two stage mixing is necessary.
- If added at too high a temperature, scorching of compound will result.

A number of systems are being evaluated to reduce levels of cobalt in the complexes with resins. Organic borates and post vulcanisation stabilisers are being examined. Chlorotriazine-based bonding systems can reduce the adhesion system from three components to one.

4.9 Deodorants and Reodorants

This class of compounding ingredient was much more common in the days when natural rubber was the main rubber for production of a wide range of products. The early forms of natural rubber, produced by smoking with aromatic woods and with some degree of putrefaction possible in low grade materials, gave products with a distinct aroma. This aroma was pleasant to some people but distinctly obnoxious to others. To overcome this odour as far as possible, a wide range of products was offered. Many of the synthetic rubbers have their own distinct aroma and often this must be masked to make the final product acceptable to the general public. Odourants include vanilla, rose and lilac perfumes, at a low level of addition odour neutralisation occurs, at a higher level of addition perfumed rubber can be produced.

4.10 Desiccants

For a number of applications within the rubber industry it is necessary to add a desiccant to the compound to remove traces of water present in fillers or derived from chemical reactions taking place during vulcanisation. Failure to remove this water results in uncontrolled porosity in the product, especially in atmospheric cure conditions.

The usual agent used for the purpose is calcium oxide (quicklime). In its dry powder form dispersion in the rubber compound is a serious problem. Thus, the chemical is offered in a variety of carrying media to ensure adequate dispersion and, in most cases, to prevent moisture uptake by the calcium oxide after preparation and prior to incorporation in the rubber compound.

4.11 Dusting and Anti-Tack Agents

Dusting and anti-tack agents are applied either directly as powders or from water suspension or solution. Their prime objective is to prevent sheets of rubber compound sticking together, or blocking, into an unmanageable mass. The choice of the agent to be used will depend on the subsequent processing steps which the treated rubber is to follow.

Traditional, dry dusting agents can be rubber insoluble materials such as talc, starch or whiting, or rubber soluble materials such as zinc stearate. A number of dry dusting agents are recognised health hazards and must be handled with care.

Wet anti-tack agents can be soap or detergent solutions or suspensions of the dry agents in water. For example, dissolved polymers with non-ionic surface active agents which form a thin layer of polymer on unvulcanised rubber sheets; magnesium stearate in water; zinc stearate dispersion; and aqueous dispersions of fatty acid salts.

4.12 Factice

Factice is vulcanised oil used as a processing aid.

The oils from which factices are manufactured are unsaturated vegetable and animal oils, which react with sulphur. Fatty oils with iodine number greater than 80 (iodine number is defined as the number of grammes of iodine absorbed by 100 g of fat/oil) are generally used, i.e., oils with three or more double bonds per triglyceride molecule. Rapeseed oil is the most common oil used for general purpose grades and castor oil is used for oil resistant factice. Other oils are used in preference by other countries due to local availability and cost.

Factice has a number of uses in rubber compounds where it can stabilise dimensions of products such as hoses and tubing during the early stages of heating of the vulcanisation cycle. It imparts stability to extruded products, a silkiness to calendered products, gives good dimensional stability and overcomes many of the problems of 'crows feet' and blistering.

The addition level for the different applications varies from 5-10 phr for moulded articles to 15-30 phr for extrusions. Roller coverings, dependant upon hardness, are often made using factices to facilitate grinding operations. Special products such as erasers use factice, usually white factice, at levels between 200-400 phr.

In general terms, factice gives benefits to rubber processing without causing any undue effects on physical properties.

4.12.1 Dark and Golden Factice

These are made by crosslinking unsaturated oils with sulphur (and an amine catalyst, usually triethanolamine) at 140-160 °C. These products will give dark coloured vulcanisates which have poor contact stain properties when in contact with painted surfaces.

4.12.2 White Factice

Clear unsaturated oils are vulcanised at room temperature with sulphur monochloride to give a white, friable solid which is nonstaining and suitable for use in coloured compounds. Crosslinking using sulphur monochloride produces a white factice, but care had to be taken in its use, for if not used when fresh it develops a high level of acidity which affects compound cures severely. The acidity can be removed by steaming the factice just prior to use. Modern white factices contain a small addition of alkali to counteract any developed acidity.

Alternative crosslinking systems used to produce the wide variety of factices offered include:

- hydrogen sulphide
- diisocyanates
- peroxides (after suitable pre-treatment).

4.13 Fillers

The amount of reinforcement which a filler provides for a rubber is dependant upon a number of variables. The most important is the development of a large filler-rubber interface. This type of interface contact can only be provided by filler particles which are of colloidal dimensions. Spherical particles 1.0 μm in diameter provide a specific area of $6 \text{ m}^2/\text{cm}^3$. Such particles are representative of the lower limit of significant reinforcement. The upper limit of useful specific surface area is in the region of $300\text{-}400 \text{ m}^2/\text{cm}^3$. Fillers with particles sizes outside these arbitrary limits generally cause problems of dispersability, processability of the unvulcanised compound, and of serious loss of rubbery characteristics. In many cases, some of the white fillers can have particle sizes varying over a wide range even when sold to specific maximum sieve mesh size. In the case of the cheaper fillers, quite large 'grits' can also be present which will detract from the final physical properties of the rubber vulcanisate. The presence of certain metal ions, such as iron, copper and manganese, can have serious catalytic effects on oxidative processes for diene rubbers.

Some classification terms which may be encountered in some texts discussing reinforcement by fillers include:

- The extensivity factor - the surface area of a filler per cubic centimetre coming into interfacial contact with the rubber.
- The intensity factor - the specific activity of the filler at its interface with the rubber. This is dependant upon the filler's physical structure and the chemical nature of its surface. Different rubbers will behave differently to the same filler.
- Geometrical factors - structure, void volume and porosity will affect the filler's ability to be 'wetted' by the rubber into which it is incorporated. The shape of the particle will depend on the crystal structure of the mineral being used.

Carbon black is the most widely used filler for rubber compounds but a wide variety of white fillers is used by the rubber industry, ranging from highly reinforcing silicas to diluent ground whittings and limestones. Some of these fillers have an influence on the rate of crosslink generation due to their acidity or alkalinity. Silica and silicates are somewhat anomalous in their effects on cure systems for although one would expect them to behave as alkaline in nature and thus accelerate sulphur vulcanisation, in fact they contain substantial amounts of combined oxygen which represses or retards the reaction.

Various treatments can be carried out to alter the surface characteristics of white fillers, such as calcination, precipitation, and coating of the particles with various materials to improve their rubber compatibility and hence their reinforcement capabilities. The coating materials can be fatty acids, amines and silanes. The addition of silane coupling agents can be carried out during the mixing of rubbers with the fillers, but this technique does not always produce the desired effects due to interfering reactions between the filler surface and other additives, and the difficulty of ensuring adequate distribution of the coupling agent.

4.13.1 Carbon Black

Carbon blacks are principally made by the chemical decomposition of natural gas or oil. Two classes predominate: the furnace blacks (95% of black usage) which are active, and thermal blacks (5% of usage) which are inactive. There are a substantial number of blacks for special applications such as electrically conducting and printing ink blacks. The latter are of too fine a particle size for rubber use. The nomenclature used for carbon blacks includes the ASTM designation and the industry type as illustrated in the next table.

Nomenclature for carbon blacks (ASTM standard D-1765)			
ASTM Classification	Industry Type	ASTM Classification	Industry Type
N110	SAF	N347	HAF-HS
N220	ISAF	N351	
N234	ISAF-HS	N375	
N242	ISAF-HS	N550	FEF
N285		N650	GPF-HS
N299		N765	SRF-HS
N327	HAF-LS	N770	SRF
N339	HAF-HS	N787	SRF-HM
SAF – Super abrasion furnace, ISAF – Intermediate super abrasion HAF – High abrasion furnace, FEF – Fast extrusion furnace SRF – Semi reinforcing furnace HS – High structure, LS – low structure, HM – High modulus			

Carbon blacks are 90-99% elemental carbon with combined hydrogen and oxygen. Typical functional groups which are located on the surface of blacks are phenol, carboxyl, lactol, quinone, ketone, pyrone and lactone. There may also be traces of chemically combined sulphur present associated with the source of some feedstocks. There is no evidence that this combined sulphur has any influence on rubber crosslinking. The surface of the black particle is not smooth, and internal porosity of the particle may be caused by oxidation during the high temperature manufacturing process. In terms of rubber reinforcement, the surface activity of the black may be defined as the capacity for restricting the mobility of the rubber in contact with its surface. Strongly adsorbed rubber at the surface of the carbon black reduces the rubber's mobility and becomes bound rubber. Bound rubber is a strong function of the specific surface area of the carbon black and shows significant dependence on the degree of structure development, increasing with both variables.

The surface area of blacks ranges from 20 m²/cm³ (N990 - Medium thermal black) to 225 m²/cm³ (N110 - Super abrasion furnace black).

The finest particle of carbon black produced is basically spheroidal consisting of concentric layers of carbon atoms. These particles do not remain as individuals but aggregate together during manufacture forming grapelike and tangled three dimensional structures. These primary aggregates can become associated with others to form 'secondary' structures. This structure is weak in nature and can be partially destroyed during pelletisation. The remainder of the black's 'structure' becomes broken down during the mixing of the black into rubber.

The structure of a carbon black depends on the original nature of the oil/gas feedstock. Thermal blacks have little or no structure. Highly aromatic raw feedstocks give furnace blacks of high structure. Flame additives and furnace type and design also modify the black's structure. The higher the structure of the carbon black, the more irregular is the shape of the aggregate. The aggregates cling together to form agglomerates. In this form, carbon black is a fluffy, difficult-to-handle product, unsuitable for automatic weighing. Pelletisation produces a roughly spheroidal, easily broken pellet which will contain a large number of aggregates.

The size of the carbon black particle has a profound influence on its dispersion characteristics within a rubber matrix and determines the final vulcanisate properties of the rubber compound. Blacks of very fine particle size are difficult to disperse adequately and when dispersion is achieved give a high reinforcement. Large particle size blacks are easily completely dispersed, but do not give reinforcement. The structure of the black affects the processing properties of the rubber compound, but generally does not have great significance in the reinforcement.

Mixing of carbon black into rubber consists essentially of two phases:

- Incorporation - the carbon black is distributed into the rubber matrix but not into the desired state for complete reinforcement. At this stage of mixing the rubber penetrates the voids in the large agglomerates of carbon black. It is also at this stage that strong interaction between the rubber and black surface occurs in the case of small particle sized blacks with low structure, which makes the next step of dispersion difficult to achieve.
- Dispersion - the large carbon black agglomerates become broken down and 'wetted out' under the influence of the mixing shear forces into discretely dispersed small aggregates/particles. The rubber becomes occluded into the remaining small aggregates, penetrates the voids within and between the aggregates and enters any cavities, resulting in an increase in viscosity as the available free volume of rubber is diminished. The result of the rubber occlusion is an effective increase in black loading. High surface area, low structure blacks are difficult to disperse as their dense packing and low void volume gives them the ability to rapidly interact with the rubber. As a result of the strong adhesion between the black and rubber, good random spatial dispersion is difficult to achieve.

4.13.2 Clays

Clays are manufactured from naturally occurring hydrated aluminium silicates. The particles of clays are hexagonal shaped platelets. The particle diameter quoted for these materials is not a 'true' diameter, but only an estimate derived from sedimentation analysis.

The type of clays used by the rubber industry are known to the clay industry as kaolin produced from deposits of a hydrous aluminium silicate, known as kaolinite.

They are classified by the effects that their addition has on the compound behaviour and properties:

- Soft clays,
- Hard clays,
- Calcined clays, and
- Treated clays.

Soft Clays

Soft clays are semi-reinforcing fillers and are used in high volumes for cost purposes. They give a soft pliable product for further processing. Soft clays have lower modulus, tensile strength and abrasion resistance than hard clays. They are usually lighter in colour than the hard clays and good enough for the production of brightly coloured products. Large volume loading up to 300 phr gives low shrinkage compounds with good extrudability and flow. Soft clays can show a higher water pickup on immersion than hard clays.

Hard Clays

The median particle size of 0.3 μm for hard clays gives an expected higher level of reinforcement than that found for the soft clays. Rubber compounds containing hard clays are stiff in nature. Hard clays absorb accelerators to a greater degree than soft clays and usually will require accelerator content modification or the use of triethanolamine, diethylene glycol or polyethylene glycols. Hard clays are a light creamy buff colour and will affect the colours of white and brightly coloured stocks. Some rubbers, such as SBR, will benefit by the careful selection of softener when using the 'hard' clays.

Calcined Clays

Calcined clays are hard clays which have been heat treated to remove the combined water. The removal of any surface bound entity from the clay particles improves the capacity to improve the electrical resistance of rubber compounds. Calcinated clays also reduce compound water

absorption. Calcined clays tend to find application mainly in cable and wire applications. They also find application where bright colours are required, as they have a good white colour. Calcined clays find some application in silicone rubber formulations.

Treated Clays

Treatment of water-washed hard china clays with silanes with pendant amino or mercapto groups enables them to give improved reinforcement to rubber compounds. Silane-treated clays give compounds with lower viscosity, considerably higher modulus and tensile strength and lower compression set than compounds containing untreated clays.

4.13.3 Silica

Silica fillers offered to the rubber industry are of three specific types

- ground mineral silica,
- precipitated silica, and
- fumed or pyrogenic silica.

Ground Mineral Silica

Ground silica, generally available below 300 mesh in size ($5 \text{ m}^2/\text{g}$), is used as a cheap heat resistant filler for a variety of compounds. There is no effect on the rate or state of cure.

Hydrated Precipitated Silica

Silica used as a filler for rubbers is silicon dioxide, with particle sizes in the range of 10-40 nm. The silica has a chemically bound water content of 25% with an additional level of 4-6% of adsorbed water. The surface of silica is strongly polar in nature, centring around the hydroxyl groups bound to the surface of the silica particles. In a similar fashion, other chemical groups can be adsorbed onto the filler surface. This adsorption strongly influences silica's behaviour within rubber compounds. The groups found on the surface of silicas are principally siloxanes, silanol and reaction products of the latter with various hydrous oxides. It is possible to modify the surface of the silica to improve its compatibility with a variety of rubbers.

The retention of water on the silica filler surface has significant effects on the processing of the compound and vulcanisation reactions. Despite rigorous drying procedures there is always a monomolecular layer of water retained on the surface of the filler. Silica fillers are sold with a known level of water content, generally 3-6%, but this can change markedly with changes in ambient humidity. Silicas with less than 3% water content do not achieve adequate dispersion in the rubber. Conversely, dispersion of the silica during mixing becomes progressively worse with rising moisture content. Similarly, vulcanisation rates are affected by increased moisture. Failure to control the humidity of the storage area for the silica will obviously result in variable compound behaviour. This phenomenon is not observed with thiuram disulphide and peroxide cures.

Silica fillers also react with the rubber causing an increase in viscosity and 'dry' and unmanageable processing behaviour. Filler activators need to be added to silica-reinforced compounds to overcome these problems. The usual filler activators used are diethylene glycol, polyethylene glycol and amines such as triethanolamine. Some of these activators not only overcome the problems of processing and accelerator absorption, but depending on the cure system used, will also act as vulcanisation activators.

Other additives such as silanes, titanates and zirconates are also used to overcome the processing characteristics of silica fillers. Silanes not only give improved processability of silica-filled compounds, but also provide improved 'crosslinks' between the silica particle surface and the rubber molecular chains giving increased physical properties. The use of silane coupling agents at a

2-5% level will improve the reinforcing performance of the silica to that of a similar size carbon black.

Fumed Silica

Fumed silica is prepared by burning volatile silicon compounds such as silicon tetrachloride. This type of silica contains less than 2% combined water and generally no free water. It reacts readily with hydroxyl groups. The particle size is in the region 5-10 nm. Fumed silicas are not generally used in conventional rubber compounding but find application with silicone rubber. The recognised surface area values for best reinforcement of silicone rubber by an amorphous silica lies between 150-400 m²/g.

Particle size of the silica and tight control of its size distribution decides the ability of the compounded silicone rubber to be optically clear, even at quite high levels of addition. This feature can be used to advantage in a number of medical applications such as intraocular and contact lenses, medical tubing, flexible lights and a number of other industrial applications where sustained clarity of transparency is important.

Isolated hydroxyl groups on the silica surface lead to hydrogen bonding between the silicone rubber and the filler surface. This bonding produces strong elastic rubbers. During storage, the rubber/filler bonds continue to form and the compound stiffens giving the effect known as 'crepe hardening'. This is a similar effect to that seen with other rubbers containing carbon black fillers, in which a 'structure' forms during storage. Before further processing, the structure will need to be broken down by milling to ensure good flow in down-line processes.

The degree of moisture present affects the properties of the silicone rubber vulcanisate. Moisture levels also determine the ease with which the filler is incorporated into the silicone rubber. Low moisture levels improve the final physical properties but definitely detract from the incorporation speed of the silica filler.

A silicone oil plasticiser is desirable to facilitate dispersion and to prevent undesirable polymer-filler interaction prior to vulcanisation.

4.13.4 Silicates

Silicates are semi-active fillers which, even at high loading, give soft and elastic vulcanisates.

Aluminium Silicate (Sodium Aluminium Silicate)

Aluminium silicate is obtained from a precipitation process and is a fine-particle, reinforcing filler. Except when used at high loading, it has only a small effect on the vulcanisation reaction. At high loading, there is a degree of accelerator absorption and thus the use of diethylene glycol or a similar activator is required. Aluminium silicate finds application in a wide range of products and is especially useful in high electrical resistivity applications. Aluminium silicate does not have the processing problems associated with silicas, giving easy to process compounds. Aluminium silicates are less reactive than the calcium silicates.

Aluminium Potassium Silicate (Mica)

Mica is available in a variety of grades and finds application as a semi-reinforcing filler and more often as a processing dry lubricant owing to its flake-like structure. It is also used as a dusting agent.

Calcium Silicate

Calcium silicate produced by precipitation is a fine powder with particle sizes down to 1µm. It is a reinforcing filler with a reactivity greater than aluminium silicate. It requires the use of additional accelerator as it slightly retards the vulcanisation reaction.

Calcium silicate also finds application in the formation of 'dry liquids' to convert liquids and low viscosity resinous materials to a free flowing powder to enable these to be handled by automatic weighing systems.

Magnesium Silicate (Talc)

Magnesium silicates, or talcs, have a different manufacturing process than the other silicates, being prepared by grinding of naturally occurring deposits. Depending upon the degree of 'fineness' of the particles, it can have a number of different applications in a rubber factory. Very finely ground materials are used as reinforcing fillers. 'Platy' talc, with crystals flat and plate-like in form, packs together in the rubber compound and improves impermeability to gas characteristics for a number of products. Larger particle size products are used in antistick applications, either by dusting or from a water suspension.

Grades of magnesium silicate are available which have been treated with zinc stearate or silanes to improve compound processability for extrusion and calendering.

4.13.5 Calcium Carbonate

Ground Limestone

This filler is mined, ground and sieved to a particle size less than 100 mesh and used as an inert diluent and cheapening filler for rubber compounds. It is usually off-white to cream in colour. Depending upon source, the filler can be contaminated with metal ions, e.g., iron, copper, manganese, which can catalyse oxidation. It can be used in very high loadings with great effect on compound hardness.

Ground Chalk, Whiting

Whiting is produced in a similar manner to ground limestone. It is a white powder produced in particle sizes down to 30 nm. More expensive than limestone, it is used as a diluent filler giving moderate hardness and a reasonably high resilience at high loadings. It detracts from tensile and tear strength. Whiting improves the appearance of extruded and calendered products.

Precipitated Whiting

Precipitated whiting is produced from solutions of calcium salts, or as a by-product from water softening processes. A range of particle sizes is available, from 20 µm to 50 nm. Precipitated whittings are semi-reinforcing resulting in compounds with better physical properties than with use of ground whiting. It is used in high loadings in mechanical and proofed goods. White in colour, precipitated whiting forms a good base for coloured products.

Treated Whittings

Precipitated whiting can be treated with up to 3% of a stearate to coat the particles. When thus treated, dispersion is readily achieved without particle agglomeration. Treated whittings give good product appearance and reasonably high physical properties.

4.13.6 Miscellaneous White Fillers

Barium Sulphate

Barium sulphate can be supplied ground directly from the mineral, or from the precipitation of barium salts. The ground material is used to give 'drape' to a product such as hospital sheeting, or to increase weight if the product is sold by weight, e.g., printing gums. The precipitation product is used as an inert filler for pharmaceutical products. Barium sulphate confers X-ray opaqueness to products. Products are of a high specific gravity.

Calcium Sulphate

Produced by grinding from gypsum, or hydrated plaster of Paris, calcium sulphate is inert. It is whiter in colour and of a lower density than barium sulphate.

Magnesium Carbonate

Two grades of magnesium carbonate are used in the rubber industry. Light magnesium carbonate is a fine reinforcing powder, giving good physical properties. It can also be used to stabilise products for steam cures, stiffening the unvulcanised product and preventing collapse. If properly formulated compounds containing magnesium carbonate can be translucent. The heavy grade is coarser, but is still a semi-reinforcing filler, with low colouring powers.

Mica Powder

Washed and ground, natural mica of 200-300 mesh acts as a laminar filler, giving good heat resistance and low gas permeability

Titanium Dioxide

Although, because of its cost, titanium dioxide is usually only used as a whitening agent for rubber compounds, it is in fact a reinforcing agent comparable on a volume basis with the reinforcement found with zinc oxide.

Zinc Oxide

Although now not used for the purpose, due to cost, zinc oxide is a reinforcing filler which gives high tensile strength and resilience, with only moderate hardness. When used as a filler the unvulcanised compound is quite plastic in nature, but has a marked tendency to stick to processing equipment. For good colour only low lead grades of zinc oxide should be used as fillers or activators.

4.13.7 Miscellaneous Fillers

Fibres

Fibres are added to rubbers for a number of reasons. Asbestos fibres were used in such products as brake linings, but their use has been discontinued in the rubber industry due to health and safety considerations.

Cellulose Fibres

Cellulose fibres produced from hardwoods, with various chemical surface treatments to ensure that they are compatible with rubbers, can be used to produce high modulus vulcanisates. The bond between rubber and fibres is created during vulcanisation. These fibres can be used to reinforce extruded hoses gaining orientation in the direction of flow. There is a range of fibres available which are compatible with different rubber types.

Flocks

A variety of flocks, produced from cotton, rayon or nylon, stiffen rubber compounds and improve abrasion and tear resistance whilst increasing tensile modulus.

Wood Flours

Finely ground wood flours, produced from hardwoods, are incorporated into rubber to produce products such as flooring.

Cork

Finely ground cork gives compounds with a high degree of resilience for products such as flooring and gasketing.

Ebonite Dusts

Ebonite dusts are used in the production of ebonite compounds to minimise and control the exothermic reaction of the crosslinking of large volumes of sulphur with diene rubbers.

4.14 Fire Retardants

The majority of rubbers support combustion. The by-products of the combustion can be lethal to life. In order to improve the resistance of the rubbers which support combustion, a number of products may be added to the rubber compound. These may be inorganic or organic in nature.

Antimony trioxide and chlorinated paraffinic derivatives are common materials used as fire retardants, as are intumescent zinc (or calcium) borate, aluminium hydroxide and magnesium hydroxide. These inorganic materials, used as bulk fillers, act to reduce the fire hazard. Halogenated materials release chlorine, which then combines with the antimony trioxide to form the trichloride, which is a flame suppressant.

During the combustion of rubbers it is usual to find carbon, carbon monoxide, carbon dioxide and water being evolved. In the presence of halogen-containing fire retardants, hydrogen chloride and hydrogen bromide can be evolved, which react with antimony trioxide to form SbOCl and SbOCl_3 . Hydrogen cyanide (HCN) is produced from nitrogen-containing flame retardants.

The carbon black generated by a fire from a rubber source increases the smoke density; other products are highly toxic and often corrosive. The halogens, phosphates, borates, and their acids evolved during a fire corrode metals and electrical and electronic equipment. Hence many of the fire retardants described below cannot be used in situations where the toxic gases evolved will create their own hazards. In these cases inorganic hydroxides are used, at filler-type addition levels. Aluminium hydroxide and magnesium hydroxide are used as non-toxic fire retardant systems.

Carbon black should only be used as a colourant in flame resistant compounds, as carbon black supports combustion, burning readily in the presence of oxygen.

4.14.1 Aluminium Hydroxide

Aluminium hydroxide is essentially non-toxic, but does require high addition levels to be effective. As a result, the physical properties of the compound usually suffer. Its fire retardancy action results from the endothermic reaction which releases water under fire conditions and produces a protective 'char'. The endothermic reaction draws heat from the rubber/filler mass and thus reduces the thermal decomposition rate. The water release dilutes the available fuel supply, cooling the rubber surface and mass.

4.14.2 Antimony Trioxide

Antimony trioxide reacts with chlorine, either in the rubber or present due to the addition of chlorinated waxes, to give gases which function by reducing the oxygen supply. The reaction produces dense white fumes that exclude air and extinguish flames.

4.14.3 Halogen Sources

The addition of chlorinated waxes will trap free radicals formed during the basic combustion process, by combination with a hydrogen halide, usually HCl.

4.14.4 Phosphate Plasticisers

Non-flammable plasticisers, such as tri-tolyl phosphate, tri-xylene phosphate, or a number of different brominated plasticisers, produce a dense hard brittle carbon 'char' after initial combustion which then acts as a barrier to exclude oxygen.

4.14.5 Zinc Borate

Zinc borate can be used alone or synergistically with antimony trioxide, aluminium hydroxide and halogen-containing additives. Zinc borate suppresses afterglow, forms a 'char', and can significantly reduce the smoke volume produced. It can also be used as the sole flame retardant or as a partial replacement for antimony trioxide. Zinc borate has a low toxicity rating. The hard exterior coating formed on the outer surface of the rubber is known as an intumescent foam; it excludes air, and, being inorganic in nature, forms a barrier to further attack by the fire.

4.14.6 Zinc Hydroxystannate

The performance of aluminium hydroxide/magnesium hydroxide-filled systems can be enhanced by incorporation of zinc hydroxystannate in halogen-free rubbers giving reduced smoke and toxic gas emission, coupled with higher flame retardancy. This action will be complimentary to the water release and endothermic effects of aluminium hydroxide/magnesium hydroxide filler systems.

In halogen-containing rubbers, zinc hydroxystannate can be substituted as a non toxic replacement for antimony trioxide to reduce smoke and toxic gas emission. Zinc hydroxystannate does not pigment the rubber and can be used to produce clear or translucent products.

4.15 Peroxides

The peroxide crosslinking of elastomers was discovered almost 80 years ago. It was found that natural rubber could be converted into a crosslinked state through a reaction with dibenzoyl peroxide. Development of silicone rubbers also required the use of peroxides to achieve a crosslinking mechanism and a number of types were developed for this purpose. The development of unsaturated ethylene-propylene copolymers in the early 1970s meant that many peroxides were developed which overcame the original shortcomings with regard to the thermal stability, crosslinking effectiveness, handling and safety aspects.

Only a limited number of peroxides are suitable for crosslinking purposes. The most suitable are those which form radicals through homolytic decomposition. These radicals are so aggressive that they can split hydrogen atoms from the polymer chain, producing stable peroxide decomposition products and polymer radicals. These polymer radicals can then be recombined, producing stable C-C crosslink bonds.

Crosslinking time is directly dependent on the rate of decomposition of the peroxide. The effectiveness of the overall crosslinking reaction is thus dependent on the type of peroxide and polymer radicals produced during the process. Cure time and temperature can, in a peroxide cure system, be determined solely from knowledge of the rate of peroxide thermal decomposition.

Crosslinking systems based on peroxides are usually simple. Unlike with sulphur vulcanisation systems, the addition of ZnO and stearic acid is not necessary, so crosslinking is achieved in many cases simply using a crosslinking peroxide. However, the addition of a coagent may be useful (see below). In some other cases, a combination of various types of crosslinking peroxides may be suitable.

The following rubbers can be peroxide crosslinked:

- Acrylic rubber
- Chlorinated polyethylene
- Chlorosulphonated polyethylene
- Ethylene-propylene copolymer
- Ethylene-propylene terpolymer
- Fluorocarbon rubbers (certain grades)
- Natural rubber
- Nitrile rubber
- Polybutadiene rubber
- Polychloroprene
- Polyester polyurethane
- Polyisoprene rubber
- Polysulphide rubber
- Silicone rubber
- Styrene-butadiene rubber
- Tetrafluoroethylene propylene copolymer

However, butyl rubber and epichlorohydrin rubber cannot be peroxide-crosslinked.

4.15.1 Compounding Considerations

Considering that the radicals formed by the decomposition of the crosslinking peroxide are very reactive, it is desirable that only reactions leading to crosslinking of the polymer occur, while undesirable side reactions are suppressed as far as possible. Compounding ingredients which are known to react with peroxide radicals are certain antidegradants, some types of filler and oil extenders. Ingredients which have a favourable effect on the degree of crosslinking are known as coagents.

Antidegradants

The use of antidegradants with a peroxide crosslinking system requires particular care since the main function of antidegradants is to deactivate the radicals. In these cases, reactions are to be expected between the antidegradant and the peroxides or polymer radicals, resulting in a reduction in the crosslinking density and suppression of the activity of the antidegradant. Optimum crosslinking and stability requires correct balancing of the dosages of the antidegradant and the crosslinking peroxide used.

Antidegradants known to be suitable for use in combination with peroxide crosslinking systems are thiophosphates, *p*-phenylenediamines and modified triazines.

Fillers

The rubber industry usually uses carbon black, silica, silicates and clays as fillers. Many of these undergo interference reactions with peroxide crosslinking systems. As a result there are fewer or no peroxide radicals available during crosslinking leading to a reduction in the crosslinking effectiveness. Depending on the quantity and type of filler, peroxide crosslinking may be completely suppressed.

If such fillers are to be used, they should have a neutral or slightly alkaline pH, otherwise additives such as ethylene glycol and triethanolamine, which are preferentially adsorbed on the surface of the filler, should be used, preventing any undesirable interference reactions between the filler and the crosslinking peroxide. These additives must, however, always be added to the mix before the peroxide. With some mineral fillers, such as some types of clay, the polymer may be bound to the filler by means of silane treatment, and the surface of the filler becomes completely non-polar. Consequently, the interaction with the polymer matrix increases, while the adsorption of the crosslinking peroxide by the filler is severely suppressed.

Extending Oils/Plasticisers

Extending oils for compounds crosslinked with peroxides have to be carefully selected. Synthetic ester plasticisers such as phthalates, sebacates and oleates may be used in combination with crosslinking peroxides without affecting the crosslinking reaction. Some derivatives of alkylated benzenes are also known for their very low consumption of free radicals, which is clearly desirable. Mineral oil with double bonds, tertiary carbon atoms or containing heterocyclic aromatic structure may react with radicals; paraffinic mineral oils are more effective than naphthenic types, which usually require extra treatment in order to guarantee optimum results when used in peroxide crosslinked blends.

Coagents

Coagents are reactive substances which improve the effectiveness of peroxide crosslinking. Most of them belong to the group of methacrylates or derivatives containing allyls, but polymeric materials with a high content of vinyl groups are also known to react in a similar way. Sulphur and sulphur donors can also be used. The improvement in the effectiveness of peroxide crosslinking may be explained by the favourable effect produced by the coagent suppressing undesirable side reactions between the polymer radicals. Most of the usual side reactions which may be anticipated involve the disproportionation and cleavage of the polymer radicals.

4.16 Petroleum Oils

Petroleum oils are offered to the rubber industry to meet two basic processing and compound requirements: to act as a processing additive, or to act as a rubber extender and softener. The classification depends upon the oil volume added to the rubber compound. As processing additives, the oil addition level is usually no more than 5-10 phr; for additions in excess of this the oils are regarded as extenders.

An ASTM Extender Oil Classification is published in ASTM D 2226. This table quotes constituents of extender and processing oils under three headings:

		Asphaltenes % max	Polar Compounds % max	Saturates %
Type I	Highly Aromatic	0.75	25	20 max.
Type II	Aromatic	0.5	12	20.1-35 max
Type III	Naphthenic	0.3	6	35.1-65 max
Type IV	Paraffinic	0.1	1	65 min.

All process oils used by the rubber industry are in practice mixtures of all classes of the three components, the mixtures deriving their classification from the preponderance of the main constituent type.

Aromatic - major portion $\geq 35\%$ C_a

Paraffinic - major portion $\geq 50\%$ C_p

Naphthenic - major portion $\geq 30-40\%$ C_n

If the oil is not compatible with the rubber in which it is being used, then it will exude at some time, either during compound storage, whilst awaiting subsequent product processing, or during service. Depending upon the loading of oil, this exudation can occur shortly after cure or after extended periods of service. This effect can be influenced by external conditions of temperature, etc.

In general terms, oils of an aromatic preponderance give best processability in general purpose rubbers, such as NR and SBR, but are prone to causing stains, can give poor odour and may contribute to poor ageing resistance. There is a growing awareness that continuous contact with aromatic oils can represent a health hazard. Paraffinic oils are less effective as processing additives, but also have less effect upon ageing, giving good colour and contact staining behaviour. Paraffinic oils are the most compatible oils for use with EPDM rubbers and can be used at high addition levels without causing exudation problems. Naphthenic oils give characteristics midway between the other two types.

Oils of the three types are offered in a range of viscosities and this will influence their processing character to some extent, although there is little evidence that it will have much influence on the ultimate compound physical properties, at least in natural rubber compounds. The small additions of oil to a compound help with filler dispersion by lubricating the polymer molecular chains and thus increasing their mobility. There will also be some 'wetting out' of the filler particles which enables them to achieve earlier compatibility with the rubber and improve their distribution and dispersion speed.

Process oils are controlled and marketed, within a molecular type, by viscosity which is influenced by the molecular weight and degree of branching of the molecular chains and the degree of cyclisation and aromaticity. The temperature influenced rate of change of viscosity is much greater for the aromatic oils than for the paraffinics. The viscosity of many aromatic oils can be too great for mobility in processing equipment fitted with oil metering devices when stored at low ambient temperatures and will require heated storage and heater traced pipelines.

Viscosity Gravity Constant

It is now common to use Viscosity Gravity Constant (VGC) as the criterion for choice of a processing oil. The VGC represents the overall average aromaticity of an oil independent of its molecular weight.

Rubber process oils can be classified using the VGC classification:

Aromatic - VGC < 0.950

Paraffinic - VGC < 0.850

Naphthenic - VGC $< 0.850 - 0.900$

4.16.1 Effects of Oil Type on Properties of Compound

In addition to the effect of viscosity on some physical properties, the oil's composition can also determine the level of some physical properties. In normal length mixing cycles, the tensile

strength of the compound increases with the aromaticity of an oil. Use of extended mixing cycles can also result in better dispersions with more saturated oils, but this is usually not economical. Highly aromatic oil containing compounds also have superior tear resistance, presumably because of superior filler dispersion. Paraffinic oils give the best resilience and dynamic heat build-up properties.

Care must be taken when choosing an oil for rubber processing to ensure that its content of polar fractions is low. These polar fractions contain some of the most chemically active compounds in the oil. Polar materials are thought to interfere with cure characteristics and play a part in polymer degradation. These effects will also be accompanied by a drastic reduction in weather resistance, although usually heat resistance is not affected.

The oil companies supplying the rubber industry claim that there is no effect on ageing properties when sulphur is present in an oil (up to 6% is possible). They claim that the refining removes the active mercaptans and sulphides and the remainder of the sulphur is complexed into polycyclic compounds and there is no evidence that this type of sulphur has any effect on cure. This claim may be true in some circumstances. However, it is known from practical experience that with certain polymers and compounds the claim is incorrect, especially when the high sulphur oils are used as test media. Oils supplied to the same oil specification from oil fields in different parts of the world, and meeting all the requirements of the specification may, because of widely different sulphur levels, have serious effects on high temperature ageing.

The most stable oils are the paraffinics because of their ability to resist oxidative attack. The oxidative instability of an oil is related to the presence or otherwise of polar structures, such as nitrogen and sulphur heterocyclic structures. The higher the aromaticity of an oil, the worse will be its resistance to oxidation.

In summary, the best oils for good stability in severe ageing environments, with good light stability and non-stain characteristics, are the paraffinics. The aromatics should only be used where the aforementioned requirements do not have to be met; the naphthenics fall between the two in terms of properties.

4.16.2 Suggested Oils for some Common Rubbers

NR

Aromatic oils are the most compatible with NR and give improved dispersion of fillers. If staining is a problem then a naphthenic oil with known low- or non-staining character should be used.

SBR

Aromatic or high aromatic oils give the best properties in compounds of SBR and black fillers.

EPM and EPDM

For EPDM, best compatibility, heat and environmental resistance is achieved with paraffinic oils of high weight and viscosity. In EPM compounds, the use of oil types other than paraffinics will lead to peroxide scavenging and poor resultant vulcanisation, unless compensation is carried out by increasing the peroxide level.

CR

Very high oil loadings of aromatic oils can be compatible with some grades of CR. However, the level of the oil's aromaticity must be carefully considered, for although compatible with loadings of up to about 100 phr of oil, stickiness of the vulcanised surface can result in highly filler loaded compounds. This has been found to be overcome by the use of oils with lower compatibility, i.e., less aromaticity, and by the incorporation of small amounts of factice or SBR to assist

compatibility. Aromatic oils can volatilise at the temperatures in which some CR vulcanisates are used. The higher the viscosity, the better the resistance to volatility but the viscosity of aromatic oils is affected greatly by temperature, falling rapidly as the temperature rises.

Naphthenic oils are compatible with CR in levels of up to 15-20 phr. They disperse in the compound rapidly. Paraffinic oils, unless used below the 5 phr addition level, will tend to bloom. At 1-3 phr dosage however, they can be useful in improving processability of compounds containing them.

IIR

High viscosity paraffinic oils are the preferred petroleum plasticisers for IIR, due to their compatibility and high viscosity index.

NBR

Little petroleum oil is used in plasticisation of NBR compounds, but generally the aromatic grades are the most compatible.

4.17 Pigments

A relatively small proportion of coloured rubber products are produced. In order to establish a good, permanent colour for the compound it is necessary to use the correct 'white' filler, and to establish a good base white pigmentation as a foundation for the colour of the product. Correct colour matching is a skill, and needs consideration of the effects of the ingredients of the compound on the final colour of the vulcanised compound. Simply matching the colour of the unvulcanised compound to a given standard colour may not be sufficient. Pigments do change colour to a minor or major extent when subjected to heat and to protective and vulcanisation ingredients in the compound. Many pigment suppliers offer a colour matching service.

4.17.1 White Pigments

Titanium Dioxide

Although, because of its cost, titanium dioxide is usually only used as a whitening agent for rubber compounds, it is in fact a reinforcing agent comparable on a volume basis with the reinforcement found with zinc oxide. There are two forms: anatase, which has the greatest whitening power, and rutile, which is somewhat creamier in colour. The rutile form is more thermally stable.

Lithopone

Lithopone is a mixture of zinc sulphide and barium sulphate in equimolecular proportions. It is used to establish a white base for coloured compounds.

Zinc Oxide

Although more usually recognised as a component of compound activation systems, zinc oxide (lead free) can be used as a whitening agent, or as a base for pigmentation by inorganic or organic pigments.

4.17.2 Coloured Pigments

Examples of colourants include:

Black – iron oxide

Blue – cobalt blue, indanthrone, α -copper phthalocyanine

Green – chrome oxide, cobalt green, polychloro copper phthalocyanine

Orange – cadmium sulphide/selenide

Red – iron oxide

Yellow – chrome rutile yellow, cadmium sulphide/zinc sulphide

Inorganic Pigments

Inorganic pigments usually are less intense in their colouring ability than organic colours, and give rather dull colouration. The colourations obtained from inorganic pigments are very stable and have outstanding weather and chemical resistance. Care should be exercised to ensure that there are no deleterious inclusions in the pigment, such as free metallic ions which will catalyse oxidation. Copper, cobalt and iron ions are the main problem in this area.

Organic Pigments

Synthetic organic pigments give bright colouration to rubber compounds at relatively low dosage levels. Many of these pigments are supplied as pastes, which greatly improves the dispersion in the rubber compound. Some dyestuffs which are soluble in rubber can be used to give delicate colours in translucent compounds.

4.18 Plasticisers for Polar Synthetic Rubbers

The term plasticiser is most commonly reserved for the synthetic liquids added for the purpose of depressing the T_g . A variety of plasticisers with molecular structures containing polar groups are used, most of these being esters.

The important criteria for a plasticiser is that it must be compatible with the elastomer for which it is used, otherwise bleeding will occur. Exudation of plasticiser in this way can be a problem in subsequent manufacture and a disaster if it occurs at a rubber/metal interface during service.

The majority of plasticiser consumption is in CR and NBR. Plasticisers are also technically important in chlorosulphonated polyethylene, hydrogenated nitrile, ethyl acrylate copolymer, epichlorohydrin copolymer and ethylene-acrylic terpolymer. At around 10 kt/annum (Europe), total consumption of plasticisers is on a much smaller scale than the process oils used in hydrocarbon rubbers. Typical addition levels are below 20 phr.

As well as aiding processing, a major function of plasticisers is to extend the operating temperature range by improving low temperature flexibility. The majority of demand in CR and NBR is satisfied by general purpose phthalate plasticisers: di-2-ethylhexyl phthalate (DEHP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP). However, a wide variety of speciality plasticisers, mainly esters, are marketed within the rubber industry. The majority of these have linear molecular structures giving them better low temperature performance than the phthalates. Examples of such plasticisers are di-2-ethylhexyl adipate (DOA), butyl carbitol adipate, di(butoxyethoxyethyl) adipate (BCA), and di-2-ethylhexyl sebacate (DOS).

The range of speciality rubber plasticisers on the market includes proprietary products whose compositions are not fully disclosed. In practice, there is considerable overlap in performance between different plasticisers, and for many compounders the use of a particular plasticiser may be related more to continuity of historically proven formulations than to current cost/performance optimisation.

When two extreme temperature conditions require compliance in a specification a compromise often has to be made. Good low temperature plasticisers can often be volatile at higher

temperatures and good plasticisers for high temperature conditions are not effective at very low temperatures.

Some of the linear plasticisers used in rubbers have a sufficiently high molecular weight to be relatively non-volatile at high service temperatures and are suitable for meeting moderately severe heat ageing specifications. For resistance to more extreme heat ageing, trimellitates are used, for example, in heat, oil and fire resistant chlorosulphonated polyethylene-covered cables. In some applications requiring fire resistance, phosphate plasticisers are used, e.g., in foamed NBR pipe insulation. In formulating oil resistant rubber compositions plasticisers are usually chosen so that the effects of swelling by oil absorption are balanced by extraction of plasticiser by the oil.

4.19 Pre Vulcanisation Inhibitors

Sulphur vulcanisation of rubber is catalysed by the presence of alkali materials. This activation of the vulcanisation system can result in unwanted short scorch times. The addition of weak acids to the rubber compound results in retardation of the crosslinking mechanism. The common materials used for retardation are

- salicylic acid,
- benzoic acid, and
- phthalic anhydride.

These materials are crystalline solids with high melting points which result in their poor dispersing qualities. Their addition also results in reduction of the cure state and lowering of compound modulus.

N-Cyclohexylthiophthalimide (CTP) functions as an effective retarder of vulcanisation for accelerators in the sulphenamide classes. It produces scorch retardation without effect on compound modulus. It is not effective, however, in other classes of vulcanisation systems, notably those based on thiazoles, thiurams and dithiocarbamates.

More recently, pre vulcanisation inhibitors based on thioketals have been introduced:

- (bis-isopropylthio)acetoacetanilide: an effective retarder for mercaptobenzothiazole (MBT) but less effective for *n*-cyclohexyl-2-benzothiazole sulphenamide (CBS) and dibenzothiazole disulphide (MBTS).
- *N*-isopropylthio-*N*-cyclohexylbenzothiazyl-2-sulphenamide (iso-PCBS) which is an alternative to CTP for the control of sulphur/sulphenamide vulcanisation reactions. Its ability to react with the amines liberated by the accelerator dissociation during the cure reaction and the autocatalyst MBT (also liberated) gives iso-PCBS a strong retardation capability. By-products are thioamines and isopropylthiobenzthiazole (iso-PBDT), the latter being a powerful retarder in its own right.

Other materials with similar or greater cure retardation than CTP are tri(dioctylpyrophosphato) titanate and thio substituted di- or tri- amino 1,3,5-triazines.

4.20 Process Additives

Rubbers, especially some of the newer synthetics, are difficult to process at some stage during their manufacture. Some rubbers are tough, somewhat intractable materials which are difficult to mix

with the compounding ingredients. Other rubbers have a great affinity for the metal of the mixer chamber and rotors and are difficult to remove after being compounded. Poor release from, and fouling of, mould cavities is a characteristic of some rubbers.

With applied technical experience and the correct process additive, some of the problems of rubber processing may be solved or at least alleviated.

A process additive is an ingredient which is added in a small dosage to a rubber compound solely to influence the performance of the compound in factory processes, or to enhance physical properties by aiding filler dispersion.

The process additive should ideally:

- aid dispersion,
- reduce polymer nerve,
- promote compound flow characteristics,
- act at a low dosage level,
- not adversely affect the finished product,
- reduce power consumption.

Processing additives exist in a variety of types and can be classified generally as:

	Example
Physical peptisers/lubricants	Zinc fatty acid salts/soaps
Lubricants	Fatty acid esters
Silicone modified processing additives	
Antistick agents	Amides Pentaerithrityl stearate Calcium fatty acid amides Zinc stearate

4.20.1 Stearic Acid

Stearic acid, as used by the rubber industry, can be a variable product. It is naturally occurring, derived from residues from animal product processing. Stearic acid is sold on a 'you get what you pay for' principle, i.e., a range of materials is available from cheap products with a range of low molecular weight fatty acids other than stearic acid present to more expensive further processed products. At the more expensive end of the market are products which have been pressed a number of times to expel the lower molecular weight fractions from the mass. A product from this type of process gives much more reproducibility for activation purposes and tends to be less prone to blooming from the surface of the finished rubber product.

Stearic acid is normally added to a rubber compound at a 2 phr level. Reduction of the stearic acid level can cause problems from the naturally occurring constituents of NR which include fatty acids, as these can vary depending on the supply source. If the total fatty acid level is too low then the cure system can become too sensitive to other inherent materials.

The use of soluble zinc soap activators such as zinc 2-ethyl hexanoate instead of conventional stearic acid gives efficiency of vulcanisation and ensures that stress relaxation and creep properties are optimised. Zinc soaps, including the new high efficiency activating types, do not bloom from the compound, either during processing or subsequently during service.

Zinc stearate is formed during the vulcanisation process with sulphur accelerated compounds, but the addition of zinc stearate alone as replacement for stearic acid and zinc oxide does not produce

the efficiency of activation found when the two materials are added separately. Zinc stearate is used by the rubber industry as a dusting agent because of its ability to dissolve into the rubber stock on the application of heat. There is the possibility, however, that the absorption of the zinc stearate into the rubber surface may well mean that there is a considerably higher level of cure activation at the interface of two connecting zinc stearate-coated rubber sheets. This may cause variation in properties in the rubber mass leading to built-in stresses which may develop into product service problems.

4.21 Release Agents

Many rubber compounds have a tendency to stick in the mould cavity after vulcanisation and require some type of mould release agent. The substances used are surface-active materials such as detergents, soaps, wetting agents, silicone emulsions, aqueous dispersions of talc, mica and fatty acids, applied by spray or brush. Alternatively, 'dry' types based on polytetrafluoroethylene or polyethylene, usually carried in a solvent, can be aerosol applied. An alternative is the addition of an incompatible material to the rubber compound which will bleed to the rubber surface during vulcanisation.

Many release agents build up on the metal mould surface and can form hard deposits combined with compound degradation products. This leads to the need for frequent mould cleaning.

Application of any mould release agent should use the minimum amount required to effect release.

4.21.1 Non-Silicone Release Agents

These products are applied to the mould cavities and do not cause product faults and generally do not cause bond problems.

4.21.2 Silicone Release Agents

Liquid Types

Silicone-based release agents, although extremely effective in their designed function, can be a real hazard if used incorrectly. Through-transfer to rubber surfaces during cavity loading will destroy any attempt at bonding to other substrates. The liquid silicones are often supplied as water emulsions.

Resin Types

Silicone resins, which after being sprayed onto the mould surface form a resin under the influence of the heat of the metal mould, are effective and relatively long lasting release agents. A single application of the resin will remain viable for a number of products 'lifts' before requiring re-application.

4.22 Resins

Resins from natural sources, and a number derived from a petroleum base, have been used for many years. These are normally added to the rubber compound in small dosages to confer some processing or property advantage.

The solubility of any resin in the rubber system is an important factor in determining the effect upon the properties of the rubber compound. Much depends upon the polarity of both the resin and

the polymer in the degree of compatibility they achieve. Mixtures of unspecified resins of different polarity and therefore different compatibility are blended together and marketed as processing additives designed to assist with the blending of normally incompatible elastomers (homogenising resins).

4.22.1 Coumarone and Coumarone-Indene Resins

Generally used as tackifiers and plasticisers, these resins are added to rubber compounds at dosages from 1-5 phr. Although used to some extent in NR which inherently has good tack, these resins are used in many synthetic rubbers which are very deficient, or totally lacking in building tack. The coumarone/indene resins are used alone or in combination with other tack imparting materials. Liquid grades, though difficult to handle unless converted to dry powder form, give greater tack than the solid grades. Non-black SBR compounds require addition of these resins if optimum properties are to be obtained, but care must be taken in choosing the grade if compound colour is important.

4.22.2 Petroleum Resins

Petroleum resins of both aromatic and non aromatic types are a large, continually growing, family of materials which find considerable use within the rubber industry. The earlier resins were highly unsaturated, dark-coloured materials originating from treatment of oils in the production of petrol. As the petroleum industry's by-products have become progressively exploited, many more resins have become available with good colour and melting points up to about 130 °C. The resin types range from low unsaturation content to highly aromatic materials. The type of resin produced depends upon the source of the oil and the types of olefin present in the feedstock. Petroleum resins are usually copolymers, often with segments from a wide range of different monomers. The colour and softening point of the resin can be controlled by the manufacturing processability

The highly aromatic resins are often used as coumarone/indene resin substitutes. A range of soft aromatic resins is available, produced from the alkylation of xylene and other aromatic hydrocarbons with dicyclopentadiene. These are excellent softeners for a wide range of rubbers. In common with other aromatic materials derived from petroleum sources, some of the resins used within the rubber industry are deemed to be carcinogenic.

4.22.3 Terpene Resins

Terpene resins are most commonly used in adhesive production, where they confer very strong tackifying properties. The terpene resins improve the resistance of adhesives to oxidative degradation. These resins are normally produced from β -pinene and are light yellow in colour. Polymers of dipentene and limonene are also available as resins.

4.22.4 Vegetable Resins

Many types, such as pine tar, are distillates from pine tree farming in Scandinavia. Pine tar is a dark viscous liquid used at about 3-7 phr dosage level. It does not affect hardness levels to the same extent as the equal amount of petroleum oil. From the nature of its sources it can vary in acidity and thus has tended to be replaced by cheaper more predictable alternatives which are available from the residues of petroleum distillation. Tack improvement of rubber compounds is derived from the presence of colophony resin derivatives.

4.22.5 Natural Rosins

Naturally occurring rosins are derived from vegetable sources in the forms of exudates, i.e., gums. Rosin and rosin esters have found a number of applications within the rubber industry. Rosin acids are easily oxidised and thus it is more usual to find rosin presented to the rubber industry in a

hydrogenated or disproportionated form. Disproportionated rosin soaps find wide application in the polymerisation processes of SBR.

4.22.6 Phenol Formaldehyde Resins

Both thermoplastic and thermoset phenol formaldehyde resins find application in rubber compounds. The thermoplastic resins act as excellent tackifiers whilst the thermoset resins act as plasticisers during processing then crosslink to give a reinforcement structure to the compound. Suitable resins for many applications can be tailored by variation in the type of phenol and the ratio of formaldehyde. Lower levels of formaldehyde produce tackifying properties whilst the higher formaldehyde levels contribute, in the presence of hexamethylene tetramine during the rubber cure, to a greater degree of resin polymerisation within the rubber network creating a crosslinked structure which contributes to the hardness and abrasion properties of the compound.

The various types of resin have been discussed above. However, the listings for these materials have been categorised to indicate their prime usage in the industry and have been assigned according to the manufacturers classification:

- homogenising resins
- petroleum resins and proprietary blends
- reinforcing/bonding resins
- resins for adhesives
- tackifier and dispersing resins
- vulcanising resins.

4.23 Vulcanising Agents

4.23.1 Sulphur

There are two basic crystallisation forms for sulphur - monoclinic and rhombic. Rhombic is the most stable form, at least up to 96 °C; the other types revert to this stable form at a rate dependant upon temperature. When sulphur solidifies from the molten state (melting point 114 °C) the crystalline form which occurs is monoclinic (needle-like crystal structure). Below 96 °C, the monoclinic form becomes metastable and changes into the rhombic form.

Normal rhombic sulphur has differing degrees of solubility in the different rubber types. In NR and SBR the required proportion for crosslinking dissolves relatively rapidly at room temperature. In stereospecific rubbers such as polybutadiene and nitrile it does not solubilise so readily. As one would expect, the solubility of the sulphur within the rubber increases with temperature increase.

If the level of sulphur in a compound is higher than that necessary for the required degree of crosslinking, problems of bloom will occur. As the temperature during compound mixing rises, the amount of sulphur becoming soluble within the rubber greatly exceeds the solubility level of the sulphur within the rubber at room temperature. Sulphur not dissolving into the rubber will remain within the rubber matrix and will not bloom to either the unvulcanised or vulcanised surfaces. Sulphur dissolved into the rubber in excess of its solubility level (i.e., a super saturated solution) at an elevated temperature will form an unwanted bloom on the rubber compound surface at ambient temperatures. The rate of crystallisation of the excess sulphur from the super saturated solution will depend on the rubber type, ambient temperatures and such factors as fingerprints on the rubber surface.

A further complicating factor with rubber compounds is that some compounding ingredients, e.g., 2-mercaptobenzothiazole, will accelerate and increase the sulphur blooming.

4.23.2 'Insoluble' (Amorphous) Sulphur

Sulphur in its amorphous form is known in the rubber industry as 'insoluble sulphur'. Insoluble sulphur is used by the rubber industry as, if not converted to the rhombic form by excessive processing heat, it will remain undissolved in the rubber and thus cannot bloom to the surface of the unvulcanised rubber compound. This is a factor which is very important for products which require a number of processing assembly steps in their manufacture.

Amorphous sulphur is a metastable variety and is insoluble in carbon disulphide. Its change to the stable rhombic form is temperature dependant. At normal ambient temperatures, the amorphous form is virtually stable requiring many years to convert. At 100 °C, the change occurs in about one hour. At about 110 °C the change will occur in about 20 minutes. Care must be taken to ensure that processing temperatures do not exceed 100 °C otherwise the advantages of its use will be quickly lost.

Various attempts have been made to improve the stability of amorphous sulphur. Addition of small amounts of halogens, i.e., chlorine, bromine, iodine, treatment with sulphur monochloride or the addition of a terpene have some effect on the rate of conversion. As far as is known, none of the modified materials are commercially available.

Dispersion of soluble rhombic sulphur does not usually create problems in most polymers, but addition of the insoluble form can create problems of incorporation into the rubber compound due to insolubility in the rubber. The insoluble sulphur particles tend to agglomerate into small lumps, which cannot then be dispersed effectively. Various treated insoluble sulphur products are available which aid incorporation.

When properly dispersed there will be no difference in the effects of the two sulphur types on the course of the vulcanisation reaction.

Insoluble sulphur, if handled incorrectly, can generate a high degree of static charge on its particles and has been the cause of a number of explosions whilst being discharged into storage hoppers and silos.

4.24 Waxes

The amount of wax addition to a rubber compound will depend upon a number of factors:

- the type of rubber being protected
- the required appearance of the rubber product
- the temperature of service for the component
- the type of service - static or dynamic
- the effect of filler type
- the effect of process oils
- the rate of wax migration to rubber surface
- the type of wax being used.

The solubility of wax in vulcanised rubbers is low (of the order of 0.5% for NR) but enough wax has to be added to a rubber compound to ensure that once the compound has been vulcanised and the rubber cools, the rate of migrational movement of the wax from the rubber mass to the surface of the rubber is rapid. Dependant upon the application, the addition level of wax can be up to about 10 phr. Migration of the wax to the rubber surface will also carry other ingredients such as antioxidants, antiozonants and other materials (e.g., vulcanisation residuals), to enhance the surface protection.

4.24.1 Paraffin Waxes

Essentially these waxes contain straight unbranched alkane chains of from 17 to 50 carbon atoms in length which can pack together to form crystal structures. These types of waxes give bloom films which can be brittle, uneven and which may, because of poor adhesion, flake off from the rubber surface during its movement, especially if lower melting point waxes are being used. Any cracks in the wax surface continuity result in a higher gas permeability and thus enable ozone to attack these areas. Ozone attack on rubber surfaces exposed by wax cracking is usually more severe than occurs in unprotected rubber surfaces.

4.24.2 Microcrystalline Waxes

Non Linear Paraffin Waxes

These waxes have branched structures of higher molecular weight (40-70 carbon atoms) than paraffin waxes and form a quite different crystalline structure on the surface of the rubber when emerging from solution from within the vulcanised rubber. Microcrystalline waxes form smaller crystals, which pack tighter together to form a more coherent, much more flexible film on the rubber surface which is more resistant to ozone penetration.

Ceresine Wax

There are three sources of ceresine waxes: natural mineral (ozocerite), petroleum refining (petroleum ceresin) and lignite refining (cerasin).

The waxes consist of both cyclic and paraffin hydrocarbons. At similar melting points, the waxes have a much higher molecular weight than paraffin waxes and are less stable. Ceresine waxes have a very delicate crystalline structure, with fine needle or short plate crystals. Properly constituted blends of ceresine and paraffin waxes have a dense microcrystalline structure.

4.24.3 Polyethylene Waxes

Polyethylene waxes of low molecular weight have been used as processing additives for many years. These waxes assist with compound viscosity reduction and flow in moulding applications, and can be used to assist in wetting out fillers. They can also provide some degree of antidegradation protection under static conditions. Polyethylene waxes give good mould release, impart a gloss to vulcanisates and improve the slip properties of products. Modified polyethylene waxes are also used to improve adhesion of EPDM to metals for application such as tyre valve stems.

Section 5

Rubber Processing Equipment

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5.1 Autoclaves

Autoclaves for rubber product vulcanisation are available in a wide range of sizes to suit the product type. The main use for autoclaves is in the production of extrusions, sheeting and components which are of unsuitable size or construction for conventional mould vulcanisation. Examples of this type of product can range from roller coverings to hand-built products such as footwear.

There are two main types of autoclave available. Steam curing is still the more widely used method and involves the use of a gas or electric boiler supplying steam to a single-cased autoclave. Increasing in popularity is the use of hot atmosphere curing in autoclaves, where the internal pressurising medium (either air or nitrogen) is heated by electric heater elements. This method has the advantage of providing independent control of pressure and temperature, unlike with steam, and eliminating the detrimental effects of condensation. Use of nitrogen also eliminates surface deterioration of the product from oxidation.

An advantage of the autoclave for smaller components, is that a large volume of the same or different products can be vulcanised at the same time, provided that the curative systems in use do not interact between the different compounds. It is usual to support extrusions and low hardness products in talc. Products formed on mandrels and sheeting, for example, are cloth wrapped to prevent distortion.

The temperature is raised using a number of steps to achieve uniformity of temperature throughout the product mass, before the final vulcanisation stage is reached.

It may be necessary to use a gas or steam circulatory system to ensure uniformity of temperature throughout the whole of the autoclave and its contents.

5.2 Cable Manufacturing

Cables with elastomeric covers are manufactured by extrusion of the compound around a metallic conductor. The compound must be prepared in a manner to ensure that there are no residual conglomerations of ingredients, which could act as a source of electrical failure. In smaller diameter cables extrusion of the compound to cover the conductor is usually by a crosshead die system, which can apply one or two compound layers to give the required insulation properties. It is usual to use duplex extruders applying insulation and sheath compound at one pass, directly before the covered cable enters the curing tube system. The construction of the die head is designed to apply the compound co-axially to ensure correct dimensional concentricity. The metal conductor/cable is controlled both before and after the extruder/vulcanising system by capstans which are co-ordinated so that the correct tension can be maintained on the cable throughout the process.

Cables which are of larger dimensions can be manufactured by the older batch process. The conductor covering portion of the process is similar to that for small cables, but the covered cable does not enter a vulcanising tube. Large diameter cables, with multi-conductor construction, can be covered by using a compound tape lapping system. The individual conductors are covered with insulation by passing the conductor with two flat tapes applied through grooved rollers to nip the tapes together to form a seam. The combination of conductors bunched together are then lapped using a continuous compound tape. The lapping method can also be used to apply the initial insulation layer. Cables manufactured by this method require a cotton support tape application prior to being wound on to large drums and vulcanised in an autoclave. An alternative method is to apply a lead sheath, for cable consolidation, using a lead press. After vulcanisation the cotton tape or lead sheath is stripped from the cable.

5.2.1 Continuous Vulcanisation Tubes

Steam tube vulcanisation of cables is a common method used by the cable industry. The cable after covering is passed through a steam tube connected to the extruder crosshead. The end of the tube connected to the extruder is fitted with a seal system. After traverse of the steam tube the cable with its now vulcanised sheath emerges through a sealing system, is cooled and then coiled. There are three tube systems used, horizontal, catenary and vertical. The catenary is shaped to follow the natural drape of the covered cable as it passes through the steam tube, thus eliminating contact with the walls of the curing vessel, especially in the case of large diameter cables. The length of the steam tube depends on the size of cable to be vulcanised, as it is necessary for full cure to be achieved before the cable emerges from the end distant from the extruder. Gas tubes are also available for dry curing.

5.2.2 Fluid Bed Systems

Although to some extent fluid beds have diminished in popularity for vulcanisation, this method can be used in cable vulcanisation. The heating medium is a bed of tiny glass spheres fluidised by steam or hot air.

5.2.3 Hot Air/Infrared Tunnels

Hot air tunnels are often used for vulcanisation of cable covered with rubbers such as silicone. These systems may also incorporate infrared radiation as a means of boosting heat transfer to the product.

5.2.4 Lead Presses

Large diameter cables can also be vulcanised in 'short' lengths using a lead cover. This method can be a problem for coloured cables coated with rubbers with sulphur content, which can form a lead sulphide stain on the surface of the rubber in contact with the lead sheath. It is necessary to use very large drums to support the cable during vulcanisation in an autoclave, and it may also be necessary to rotate the drum to offset any eccentricity of the cable cover which may occur, due to gravity causing compound movement, owing to the reduction of compound viscosity with temperature rise.

5.2.5 Salt Bath Systems

Systems are available which use molten salt as the curing medium. These systems can be either unpressurised or pressurised, and can have a salt recirculation system fitted. The advantage of this method of vulcanisation is the high temperatures which can be achieved with consequent greater product throughput rates.

5.3 Calenders

A rubber calender in basic form consists of two or more hardened and accurately machined metal rollers known as 'bowls' rotating in bearing journal boxes which are set in rugged iron frames. One bowl in each pair is equipped with nip adjustment to control the thickness of processed material. Adjacent pairs of bowls rotating in the same or opposing directions form a 'nip' where the material being processed is squeezed into sheets or is laminated to form the desired product. The drives for the bowls include constant or variable speed motors and reduction gearing, to achieve the bowl surface speeds specified by the processing requirements of the materials. Modern calenders are usually fitted with individual DC motors via double universal joints, or directly fitted hydraulic

drives to each bowl. A calender, depending on the number and the design of its bowls, is capable of sheeting, frictioning, coating, profiling and embossing.

Calenders for processing rubbers are made in a number of bowl configurations, horizontal and vertical, and in sizes ranging from laboratory units to giants weighing many tons. The three-bowl vertical calender with 24 in ((60.96 cm) diameter) x 68 in ((172.72 cm) face length) bowls and the four-bowl 'Z' and 'L' with 28 in (71.12 cm) x 78 in (198.12 cm) bowls are typical of the machines used for mass production of tyres, belting, sheeting and the like. Three-bowl calenders have been widely used for processing of mechanical rubber goods. The four-bowl calenders are popular in tyre plants. The four bowls permit simultaneous application of rubber compound to both sides of tyre cord fabrics and steel cords. Two-bowl calenders are used to produce strips and profiles, often in combination with extruder feeding, in which case they are commonly referred to as 'Roller Dies'.

5.3.1 Sheeting

This basic operation utilises a two-bowl calender in horizontal or vertical configuration. The feed material, either in strip or 'pig' form, is fed into one side of the nip and is squeezed by the bowls, thereby emerging as a sheet which is pulled from the bowl by some manual or mechanical means or supported by a 'liner' cloth. Because of their versatility, three-bowl calenders are now more widely used for sheeting as well as other basic calendaring operations. Thickness control is accomplished by use of the adjustable nips and may be further refined by automatic control systems using thickness sensors. It should be noted here that the force required in the nip to flatten the feed material causes deflection of the bowls, however slight. If some corrective steps are not taken, the product thickness will vary across the sheet, resulting in excessive variations of the product and possibly excessive use of expensive materials. In order to overcome these problems, three basic techniques are used to achieve uniform product thickness:

1. Grinding or 'crowning' of the bowl faces to compensate for deflection. The bowls are mechanically ground so that the diameter at the centre is larger than that at the ends of the bowl face. Under load the 'crowned' bowls deflect so that the gap between them is more uniform. Grinding and regrinding after service wear must be carried out at normal running temperature if the 'crowning' is to be correct.
2. Bowl 'crossing' whereby the bowl axis can be mechanically deflected from a planar relationship. This effect will create a progressively greater gap between the bowls from centre to ends. Because bowl crossing is a deliberate misalignment of the horizontal axis of the bowls, it is also known as 'axis skewing'.
3. Bowl 'bending' whereby the bowl is physically bent by the application of force to the outside of each bowl journal bearing. Positive bending causes an increase in bowl convexity while negative bending causes an increase in concavity.

In order to minimise air entrapment and blistering, the thickness of each sheet is generally limited. To build up the required thickness of the final sheet, two or more plies of calendered sheet are usually laminated on the bottom bowl of a three-bowl calender.

5.3.2 Frictioning

Frictioning involves rubbing or wiping an elastomeric compound into a substrate of textile or metallic cords, which may or may not be held together by 'pick' threads or fill yarns, or the substrate may consist of a 'square woven' fabric like 'hose ducks' or 'belt ducks'.

Usually a three-bowl calender is employed wherein the rubber sheet is formed between the upper and middle bowls while the resulting sheet is simultaneously being frictioned into the substrate

between the middle and bottom bowls. In this operation the upper and middle bowls may be moving with either 'friction' or 'even' surface speed, but the middle and bottom bowls will only be run with 'friction' or unequal surface speeds so that the rubber is effectively wiped into the substrate being carried on the bottom bowl.

5.3.3 Coating

A coating or skim-coating operation is similar to that described for frictioning except that the middle and bottom bowls will run at 'even' surface speed so that the rubber sheet is merely laid and pressed against the substrate. This is particularly true of a multi-pass operation where the substrate will have previously been frictioned. The coating operation may produce a heavy deposit or merely a thin 'skim' coat depending upon the product requirement. Generally, multi-purpose calenders such as a three-bowl unit, are equipped with 'even' and 'friction' gearing arrangements so that a number of combinations of bowl speed ratios are possible.

A more complex form of coating calender is the four-bowl 'Z' or 'L' arrangement. A four-bowl calender can simultaneously apply a rubber coating onto both sides of a fabric. In effect, the No. 1 and 2 bowls and the No. 3 and 4 bowls form pairs where two rubber sheets are produced. The sheets are then laminated to a substrate between the No. 2 and 3 bowls. Very sophisticated devices are usually incorporated into the calender design to control thickness and width of the individual sheets and the resulting laminate.

5.3.4 Profiling

Many rubber products require uncured components which are not rectangular in cross-section. In such cases, at least one calender bowl may have a peripheral design cut into its surface to produce the desired cross section. This method is particularly useful for long production runs, but becomes expensive in terms of bowl change and bowl inventory necessary when many different sections are required. For shorter run working, the calender bowl may consist of a heavy basic mandrel onto which may be clamped solid cylindrical or split cylindrical steel 'shells' into which the appropriate profile design has been cut. Such calenders often have the bowls outside the frames to improve access and facilitate bowl changing. Consequently the bowls are comparatively short.

5.3.5 Embossing

Some rubber products are made from uncured components which must have a surface design that cannot be economically formed by subsequent moulding. One such example is the cover strip around the sole of canvas shoes. The method of producing such strips is similar to 'Profiling' in that the required design is engraved into the calender bowl or 'shell' as a mirror image of the design itself.

5.4 Compound Drying/Cooling

Rubber compounds after dropping from the mixer and being sheeted off from the dump mill need an anti-tack treatment, which normally involves the sheets or hides being passed through a tank of the treatment, or by spray in water. Before the rubber compound can be passed into storage it is necessary to remove all the water from the surface of the compound.

A variety of compound processing units are available which automatically treat, dry and often stack the compound into pallets for storage. These machines can be of the type which handle individual sheets of rubber compound, or can pass a continuous sheet, or strips through the system and then 'wig-wag' it into the storage units.

5.5 Compression Moulding Presses

Compression moulding, the oldest and still most universally used technique, is in many respects and for many products the cheapest process because of its suitability for short runs and because of the low mould costs.

The press used for compression moulding is substantially constructed and has two or more platens which are heated either electrically or by saturated steam under pressure. The platens are brought together by pressure applied hydraulically, either by water or oil, to give a loading of from 75 kgf/cm² to 150 kgf/cm² on the projected mould cavity area. Mould designs are generally based upon the availability of such pressures, which are necessary to achieve closure with acceptably thin flash. The wide range of platen sizes offered usually ensures that there is a suitable press available for the manufacture of most products.

Many types of component are produced by this method with little difficulty, but, unless very extreme measures of mould design are employed, some components of an intricate nature defy moulding by compression techniques. The reasons are usually the difficulty or cost of preparing a suitable blank shape, the impossibility of ensuring flow of the required amount of rubber into the cavity, or the inability to retain loose metal inserts for bonding in their correct positions.

Compression moulding is a relatively slow process and, therefore, attention has been directed to means of increasing cure rates. Limited success can be achieved by compounding techniques and/or increasing curing temperatures, but difficulties arise from prevulcanisation or scorch and from the low thermal conductivity of rubbers creating uneven cure, the outside of the component being degraded whilst the centre remains incompletely cured.

In some sections of the industry, it is still common practice to use the hydraulic press only to close the mould, which is fitted with clamps while it is under pressure and is then removed from the press; vulcanisation is carried out in an autoclave. This technique is often used for bulky components requiring long low-temperature cures.

5.5.1 Presses with Vacuum Chamber Extraction

Presses with vacuum extraction fitted to extract gases from moulding cavities eliminate moulding faults arising from air entrapment, or gases generated during vulcanisation. These presses are particularly useful when products are being produced from complex cavity configurations. Presses can either be fitted to a vacuum line or fitted with individual extraction units.

5.6 Continuous Vulcanisation

Continuous vulcanisation units are of a number of types. See also the section on Cable Manufacturing.

5.6.1 Hot Air Systems

Vulcanisation using hot air systems remains the most important production system for profile production. Hot air can be used alone but can also be supplemented by the addition of infrared heaters. The systems usually consist of modular units which can be built up into the required length. Air speed can usually be controlled and the compound throughput can be adjusted from speeds of 2.5 m/sec up to 20 m/sec. These systems are sufficient for thin section profiles, but thicker articles will require slower transport speeds. Addition of microwave systems to these units

will overcome the slow heat transfer problem. Although air travels in many of these units in a laminar movement, ideally a turbulent flow would be more efficient enabling heat transfer to the centre of the product to be improved, with a consequent reduction in heat input requirements.

5.6.2 Infrared Systems

Infrared heating systems are used for crosslinking during the application of surface finishes to profiles, such as flock finishes. Silicone profiles are also produced using high temperature infrared systems.

5.6.3 Liquid Cure Medium (Salt Bath)

The LCM or salt bath is the most common type of system in use. Commonly, salt baths comprise a stainless steel trough or tank and a hold-down device which also acts as a conveyor. The pressure exerted by the difference in specific gravity of the rubber compound and the salt medium create an upward pressure forcing the extrudate against the steel conveyor. This pressure can cause severe product distortion in soft and sponged products. Single tank length or multi-unit short length stainless steel belts are used, the latter being easier to adjust for metal expansion caused by the high vulcanisation temperatures used. The baths may be heated directly by electric heater rods.

Spray/cascade units are available in which the hot salt is sprayed over the surface of the product. This type of system can lose a lot of heat during the spraying operation.

This method is the only anaerobic non-pressurised system which is suitable for vulcanisation of peroxide crosslinked systems.

The LCM baths use a mixture of nitrate/nitrite eutectic salts. As it contains up to 40% sodium nitrite the salt system is toxic and can cause water pollution, and also cause nitrosation of volatile secondary amines.

After passage through the salt mixture the products require washing, with subsequent treatment being required to purify the water prior to discharge to the drain, or recycling.

5.6.4 Microwave (Ultra High Frequency, UHF) Systems

The most important feature of a microwave system is the radio wave generator. Magnetrons of up to 6 kW have been used and their life expectancy is in the region of several thousand hours. The actual lifetime depends upon the dielectric characteristics of the compounds being processed, i.e., the more polar the compound, the longer the life of the magnetron. Non-polar rubbers do not absorb as much energy as polar rubbers and consequently unused energy gets reflected back. Some of the reflected energy is captured by special absorbers but some still reaches the magnetrons. This reflected energy reduces the life-time of the magnetron. Additionally, because of the reduced energy absorption the magnetrons are required to operate continually at their maximum output, which also affects their life-span.

Many versions of this type of equipment are available and manufacturers should be consulted to ascertain the best system for the proposed application.

The integrated hot air/UHF units, at present in the development stage, will help to overcome some of the problems associated with vulcanisation of complex profiles with irregular wall thickness or asymmetrical geometries.

5.6.5 Fluid Bed System

This system, developed by Rapra during the period 1959 to 1974 uses the principle of fluidisation of particles by the passage of air through the mass. In its simplest form the powder, usually glass

beads (ballotini), is held in a metal trough in the lower portion of which lies a layer of porous ceramic tiles, above the air pipes and heating means. Passage of the heated air through the ballotini causes fluidisation. There is some degree of loss of fluidisation immediately above the profile being vulcanised if the fluidisation is from below, but this can be improved by using side entry for some of the air.

After removal of the vulcanised product it is necessary to remove the glass beads from the product surface. Ultrasonic cleaning units can be used for this purpose. It is also necessary to clean the glass beads from time to time to remove vulcanisation products from their surface.

5.6.6 Gamma Irradiation Systems

Gamma ray emitter units are available which can be located between a UHF system and a hot air oven. It may be necessary to adapt the rubber compound for use with this system.

5.7 Conveyors, Material/Haul-Off

Conveyor systems are applied in a number of areas in the rubber industry. The types used can range from simple canvas belt conveyors used for haul-off from conventional extruders, to systems used for transport and cooling of profile products, both in and emerging from continuous vulcanisation units. The latter types have to be resistant to the temperatures used in such systems and are variously constructed from glass fibre-reinforced polytetrafluoroethylene or a silicone rubber covered belt.

Steel belts are used to transport rubber profiles through the liquid salt medium in the LCM (liquid cure medium) baths. These belts, either used singly or in multiples are often used in conjunction with chain driven roller systems. Steel belts, in the high temperatures of a LCM medium expand considerably, and the multiple belt system helps to overcome this problem to some degree, by allowing easy adjustment for overall length. The belts used in these systems are customised to the particular equipment and normally can only be sourced from the original equipment manufacturer.

Other areas of use of conveyor systems are for transport of rubbers and chemicals to mixers, for carrying product from various sources to further processing and packaging.

5.7.1 Flat Belt

Flat conveyors can be constructed from fabric or rubber/fabric with or without a rubber surface layer. For some applications it may be desirable to use a metal mesh or chain construction.

5.7.2 Screw Conveyor

Screw conveyors are used to transport particulate materials within a stores or ingredient weighing area.

5.8 Cutting Equipment

5.8.1 Bale Cutters/Guillotines

The ideal bale cutter for most rubbers consists of a guillotine where slices can be cut off the presented bale. The older star shaped bale cutter dealt with the two hundredweight bale of natural

rubber in smoked sheet or creped form, but these lumps can be a considerable feed problem tending to stick in the throat of the internal mixer.

5.8.2 Clicker Presses

Clicker presses are required for bulk cutting of components used in the manufacture of a number of hand-built products such as footwear.

5.8.3 Gasket Cutting Lathes

Specialised lathes designed for the parting off of rubber sections from vulcanised rubber extrusions to form seals. These are designed for a variety of purposes.

5.8.4 Laser and Water Jet Cutters

Both systems are designed to cut rubber efficiently from sheeting to form a variety of finished rubber and foam/sponge products.

5.8.5 Automatic Cutting Machines

This type of machine can be programmed to efficiently produce such items as gaskets from rubber and fabric insert sheeting.

5.9 Deflashing

Many moulded products can be separated from their excess moulding scrap by use of scissors, cryogenic deflashing or buffing. The latter process has to be carried out with caution for those products which are bonded to metal substrates, because excessive generation of heat will result in loss of the bond integrity and product failure.

5.9.1 Buffing Machines

These units can vary from simple wire brushes rotating at high speed to carborundum belts. Heat generation in the rubber product is the main problem with these units.

5.9.2 Cryogenic Deflashing Units

Cryogenic deflashing of rubber is commonly carried out using liquid nitrogen as the temperature depressant, although some smaller units can be operated using solid carbon dioxide as the low temperature medium.

Correct determination of the required time in the deflashing unit is necessary otherwise the bulk of the product can become brittle with fractures occurring in the mass of the product.

5.10 Dipping

The dipping process, as the name implies, involves the immersion of a former into either a latex, or a rubber solution, and then its slow withdrawal to leave a uniform deposit on the former. Subsequent processes involve, amongst others, drying the deposit, and curing it, if this is required.

Latex dipping is far more common than solution dipping, although for those polymers not available as a latex the latter is frequently the only option. If a latex is available then the product obtained from it is generally superior to that derived from solution dipping.

5.10.1 Latex Dipping, Principal Methods

Simple Dipping

This is dipping without the assistance of ancillary aids such as coacervants. Thin deposits are formed by viscous latex wetting the former. Single dips are prone to defects such as pinholes, whereas multi-dipping can build up thicknesses of 0.005 to 0.010 inches (127 to 254 μm) and prevent the occurrence of pinholes; the deposit is allowed to partially, or totally dry between dips. Condoms are an example of a product produced by simple dipping.

Coacervant Dipping

In wet coacervant dipping a liquid coacervant, e.g., acetic acid, is used to assist the build up of the deposit either by dipping the former into the coacervant and then the latex, or by dipping the former into the latex and then the coacervant. The latter is generally preferred to prevent slippage of the deposit.

In dry coacervant dipping, dry coacervants such as calcium chloride, calcium nitrate, cyclohexylammonium acetate and other salts are dissolved in a volatile solvent. The former is dipped into the coacervant solution, withdrawn, and the solvent allowed to evaporate, before dipping into the latex.

In both wet and dry coacervant dipping the thickness of the deposit depends on the dwell time in the latex and the stability of the latex to the coacervant. The initial rate of deposition is high, but slows down with time until a limiting thickness is obtained.

Heat Sensitised Dipping

Although not widely used, it is possible to produce a heat sensitive compounded latex and then to use a heated former to cause deposition. The thickness of the deposit depends on the heat sensitivity of the latex and the temperature and heat capacity of the former.

5.10.2 Latex Dipping, Ancillary Processes

Formers

A variety of materials have been used, e.g., glass, porcelain, aluminium, wood and plaster of Paris. Ease of cleaning is often the factor which governs the choice. Collapsible formers are also used for fabric supported films.

Dipping Tanks and Machines

A circulating tank is recommended, the motion being required to prevent skinning, creaming and sedimentation. Screening or filtration is also provided to retain air bubbles, and any coagulum. The tank contents need to be maintained at a constant temperature and the tank is equipped with a lid to prevent evaporation of water when not in use.

Dipping machines are generally of two types; either the formers are moved to the tanks or the tanks are moved up to the formers. Although the latter requires more energy, the motion tends to be more uniform and free of vibration.

Leaching and Drying

The order of these operations can vary - leaching with water is required to remove water soluble residues, residual coacervant and other surface active substances; the resistance to water absorption is improved as a result. Warm or hot water is normally used.

Drying may be carried out by direct gas heating, infrared, electric elements with forced air convection, hot air or live steam.

5.10.3 Solution Dipping

The thickness of the resultant deposit is mainly controlled by the viscosity and solids content of the solution.

The stability of the deposit after immersion will depend on the volatility of the solvent, amongst other factors.

5.10.4 Dip Coaters

An alternative method to that of using a spreading machine or a calender for the initial preparation of fabrics for application of rubber (for composite product assembly) can be by the use of dip coaters. Application of rubber compound by this method ensures a better penetration of the fabric interstices than can be achieved by conventional 'frictioning' techniques using calenders. More delicate fabrics which would not be strong enough for calender application can also be treated with rubber by this technique.

The method consist of passing dried fabric over a spreader roller to eliminate creases, then through a bath of the rubber solution/dough and then squeezing off excess material by passing the dipped fabric through a pair of squeeze rollers.

5.10.5 Cord Resorcinol Formaldehyde Latex (RFL) Dipping/Drying Lines

Cords used for reinforcement of such products as drive belts, V-belts and hose require treatment with RFL to achieve the ultimate adhesion to the rubber compound. Although many simple systems can be built in house it can often be preferable to purchase a custom built unit. The dipping and drying units are usually built in tandem, with let-off and wind-up units attached.

5.11 Dusting Devices

Application of talc or other dusting media can be made by the use of either a dip tank for hot unvulcanised compounds or by the use of automatic dusting machines for extrudates.

A number of the materials used in the rubber industry to prevent sticking of hot rubber compounds to themselves or machinery have a certain degree of environmental hazard associated with them and thus require controlled application. Machinery for this purpose is designed to minimise any atmospheric pollution.

5.12 Extruders, Cavity Transfer Mixer

The Cavity Transfer Mixer (CTM) is primarily designed as a distributive mixing device to be used as an add-on unit to existing extruders. The original concept of the Cavity Transfer Mixer was devised by Gale at Rapra. Both parts of the barrel and screw unit have hemispheres cut out of their

surfaces to provide an overlap by half a pitch. These displaced hemispheres force the material travelling along the extruder barrel towards the die to take a serpentine path, between the two sets of cavities. In addition, due to screw rotation the material is subjected to an alternate shearing and cutting action. The action of the CTM is much more intensive than that of the Transfermix.

The CTM is capable of reducing 'nerve' for problem compounds such as those based on natural rubber, by ironing out thermal inhomogeneities and overcoming elastic memory. However, it is not self-cleaning, it generates some additional heat, it does not have forward conveying ability and it can also create back pressure.

5.13 Extruders, Cold-Feed

Hot-feed extruders require the rubber being fed to them to be pre-processed to achieve the required degree of viscosity and temperature required for transportation, compaction and delivery through the die. Variations of temperature and viscosity of the rubber stock being fed to the extruder are consequently generally transmitted through to the product resulting in variability owing to the lack of control of the parameters which control swell and extrusion rate.

Owing to the intransigence of processing of a variety of rubber compounds using hot-feed extruders, the technology developed for the processing of polyvinyl chloride (PVC) compounds by the plastics industry was applied to the extrusion of rubbers. Early machines were basically modified hot-feed extruders, often incapable of dealing with the wide range of rubber compounds encountered.

In order to be successful the cold-feed extruder must bring its feedstock from ambient temperature to the required temperature for adequate quality extrusion, break down any filler-polymer interaction structure in the compound, and be capable of dispersing any excessively high heat generation to a circulating cooling medium. Thus it is necessary to use a higher power input to the extruder and fit a more adequate cooling/heating medium for heat control of the barrel. Scorch safety of the compound is also a vital factor in the use of these machines.

The feed characteristics of cold rubber compounds differ considerably from those of hot compound to the extruder and a number of devices were developed to overcome this problem. However, the productivity of the early machines was not as high as for the hot-feed machines.

Initially it was thought that to achieve the required uniform conditions in the compound before the die area had been reached was simply a matter of extending the barrel length/diameter ratio (L/D) from 4:1 to 10:1 or 12:1. In fact this was not the case and later machines were extended to 15:1 or 20:1.

Screw configurations to achieve greater working of the rubber compound, thus developing greater consistency and extension of barrel lengths were used initially to overcome some of the problems. These developments were still insufficient to overcome some consistency problems and thus research work concentrated on the production of mixing screws and pin barrel extruders. The latest cold-feed extruder designs have overcome most of the problems.

5.14 Extruders, Dump/Pelletiser/Strainer/Roller Die

5.14.1 Dump Extruders

Many extruder manufacturers now produce dump extruders which are fitted beneath the discharge door of an internal mixer and receive into their feed hopper the full charge of the mixer. The speed of extrusion of the machine is governed by a series of sensors in the feed-hopper, to ensure that the process is continuous and that the screw will not be starved of compound, thus ensuring a continuous production of the mixed rubber compound. Product from such a machine can be slab or pellets.

The screw design is a critical factor in the efficiency of the dump extruder in converting the mixer dump in the form of large lumps into uniform products. To achieve the required engulfing of the mixer charge the screw is made as deep as possible at the feed throat. It is normal practice to have a double diameter screw at the feed end to increase the capacity to take the volume of the rubber. Having engulfed the rubber, the screw narrows down to a smaller diameter to the delivery zone. The other feature commonly used is an oscillating ram that forces pieces of rubber into the screw.

The machines are generally short, with an enclosed barrel with an L/D ratio of around 6:1. This barrel length is normally sufficient to create enough pressure for the non-restrictive die heads that are generally used.

Reasonably constant throughput can be obtained from most dump extruders, as long as the extruder speed is set so that one batch is just running out as the next one is dropped from the mixer. The extrudate is not good enough to form an accurate finished product directly.

Twin screw versions of dump extruders are available which are claimed to overcome some of the problems of single screw machines, i.e., high energy input, sticking and accelerated wear.

Many manufacturers supply extruders with interchangeable heads, which can act as strainers, roller die devices or pelletisers.

5.14.2 Pelletisers

Pelletisers are designed to convert a Banbury mixer batch into free flowing pellets which can easily be conveyed to the next step in a process.

5.14.3 Strainers

Some processes and products require the compound to be strained to remove any extraneous material or undispersed agglomerates. A range of heavy duty extruders suitable for this purpose, together with the necessary fittings for changing of the strainer units are available.

5.14.4 Roller Die Systems

Roller die systems can combine a dump extruder with a two bowl calender to produce good quality sheet for application in such products as conveyor belting. Roller head extruders are more integrated with the calender bowls mounted at the front of the extruder cylinder.

Processing of rubber sheeting for products such as conveyor belting is best carried out using such a combination of extruder, often a pin barrel type, and a two bowl calender to control the emergent thickness of the sheet. Compound is often fed directly from the mixer into the extruder throat through a hydraulic ram actuated feed, being forced down into the screw flights. The compound emerges from the extruder through either a sheet die or a tube die, the tube being split to lay-flat prior to entry into the roller system.

The extruder is used in the dump position from the final stage mixer, to achieve the final blending of the rubber compound. This ensures an emergent sheet from the roller die which is very homogenous in nature. Any blisters or bubbles which occur in the relatively thick section from the extruder are eliminated by the subsequent passage through the even speed calender bowls, which are set at a very slight undersize to the emergent rubber sheet from the extruder die (without any rolling bank formation in the calender bowls). By use of the roller die system calendered sheet up to about 20 mm can be achieved with a great degree of accuracy and good quality finish.

5.15 Extruders, Gear Pump

The concept of gear pumps as a means of extrusion of rubber compounds has not, until recently, been one which has appealed to the rubber product manufacturer. The main problem has been with lubrication of the system which relies on the suitability of the material being processed for this purpose. Plastic materials in their molten state act as lubricants in a way that rubber compounds cannot.

Modified gear pumps are available for rubber processing and are fed by rubber strip directly into the pump which presses the compound first through a strainer unit. This unit is extremely short, thus minimising heat development, thereby reducing the risk of compound scorch. From the strainer unit a feeding strip enters the extruder with no cooling necessary. The energy requirement for the gear pump unit is claimed to be 75% less than for a conventional rubber extruder.

Modified gear pumps have the ability to provide surge-free flow of material to the die. The conveyance of the gear pump is largely independent of the die head pressure. The passage of the compound through the gear pump results in the following characteristics:

- Safe degassing of compounds, independent of the conveying behaviour of the compound, by avoiding problems caused by flooding of the vacuum zone of an extruder.
- Highest possible compound flow consistency, resulting in dimensional stability even in interrupted production runs (i.e., starting-up and shutting-down of the line).
- Low temperature generation due to friction independent pressure build-up, especially with high operating pressures.
- Lower consumption of energy due to reduced build-up of frictional heat.

5.15.1 Combined Extruder and Gear Pump

Fitted to an extruder a gear pump is particularly useful for difficult compounds and process conditions. The compound is softened and plasticised in the extruder and fed into the gear pump under low intake pressure. The gear pump intake pressure regulates the speed of the extruder so that the gear pump is always filled. The gear pump builds up the pressure required at the die. A screen can be fitted if desired.

The gear pump can be fitted to a normal cold-feed, pin or vacuum extruder and enhances the accuracy and quality of the product.

5.16 Extruders, Heads and Dies

Production of extruder dies for complex products, such as profiles, requires a method for accurately calculating the required shape of the die and the flow inlets.

Computer aided design (CAD)/computer-aided manufacture (CAM) programs have been developed to carry out the necessary calculations. One current system known as Polyflow is offered by a Belgian organisation (Polyflow SA). Polyflow can be used to calculate three-dimensional flow and die swell, using finite element analysis. Other systems are available.

Generally speaking these systems are suitable for die design, but the cost of their use may limit them at present to complex dies, not the general run of the mill types. The latter are best made using conventional trial and error methods.

5.17 Extruders, Hot-Feed

The hot-feed rubber extruder is usually characterised by a relatively large screw depth and a relatively short L/D ratio of the barrel of 3 to 8:1 with the greatest number of machines having a ratio of 4:1. The barrel comprises usually a cast iron outer with either a traditional replaceable nitride liner, or, in the case of one manufacturer, of a single piece construction with an integral cast liner which has a surface hardness of Rockwell C60-62 and a hardness depth of 1.5 mm. The functional life for the bimetallic barrels is longer than for conventional nitride liner systems.

As it is claimed that the bimetallic barrels mentioned above wear less than the nitrided barrels, the clearance between the barrel and the screw is maintained longer and hence the optimum performance of this type of system is considerably extended.

The compound being presented to the hot-feed extruder has already been worked on a mill to reduce its viscosity and thus has acquired a considerable amount of heat from shearing forces exerted between the rolls of the warm-up mill. Thus less heat will be generated in the passage of the rubber up the extruder barrel than in a cold-feed machine. Additional heating or cooling of the compound, to ensure temperature uniformity by the time the rubber compound reaches the die orifice, is supplied by enabling the barrel to be heated by steam, or water cooled, as required, from a surrounding jacket. This type of thermal control jacket suffers from the usual problems associated with hardness of the water supply.

Compression of the rubber compound as it travels up the barrel is developed in the extruder by either decreasing the thread pitch but maintaining a constant root diameter, or alternatively by increasing root diameter whilst maintaining constant thread pitch. Each of these situations increases the pressure as the rubber compound travels up the barrel. The last portion of the screw prior to the die entry, however, is maintained at a constant pitch or root diameter to enable stock to stabilise in characteristics just prior to entering the die head, to ensure uniformity for extrusion through the die. Conventional extruder screws achieve a compression ratio of 2.5:1.

In the simplest and most often used form, the screw has a free channel cross-section that diminishes at a steady rate from the feed to the delivery end. The ratio of the channel depths from feed to die region along the screw is usually referred to as the compression ratio, since it gives a crude indication of the relative conveying capacities at feed and discharge.

It is normal practice to have screws double flighted under the feed section. This is mainly because a single flight, working in conjunction with the feed roll, does not effectively pull in the feed strip in a consistent manner. In some extruder constructions the double flight continues down the length of

the screw, and in others the screw reverts to single flight after the feed section due to the theoretically better conveying action.

Assuming that compression is achieved by decreasing screw depth, then choice of screw thread does have some influence on screw behaviour, but the operating characteristics are mainly determined by average depth and compression ratio. The general rule is that low head pressure applications are best served by deep, higher compression screws, whereas high head pressures need shallower, low compression screws. The rubber compound in an extruder with a conventional screw is being worked in vastly different modes. Close to the barrel liner the compound is processed and worked effectively. But by far the largest proportion of the transporting compound is contained in the valleys between the screw flights and in this area there is virtually no work input, this situation is aggravated as the size of the machine increases.

Apart from improving the mixing effect in the deeper part of the screw the restriction that occurs towards the delivery end also helps to make sure that the screw runs full. If a screw does not have a diminishing channel depth along its length then it is difficult to feed rubber at a rate that will keep up with its unrestricted conveying capacity. The screw then runs partially filled after the feed opening and only becomes completely filled at a point that allows sufficient pressure to be developed to overcome the restriction at the die.

The main problem with a feed controlled condition is that throughput is determined entirely by what the feed end manages to pull in and this is very sensitive to the conditions in the feed area. For this reason it is better to keep the machine running full so that the conveying characteristics of the screw determine output rather than the combined characteristics of screw, feed roll, feed opening and feed strip. The compression designed into a screw should therefore be sufficient to achieve complete filling at the lowest likely head pressure.

Experience also shows that there is great variability in the amount of mixing (working) that different compounds need in order to give a smooth extrudate. Compounds with high loading of filler and oil tend to process easily, whereas some compounds with a preponderance of rubber (especially natural rubber) and low filler/oil content can be very problematic. For some difficult, nery compounds there is essentially no acceptable operating region and even cold-feed rubber extruders with conventional screws will not satisfactorily process these materials. Fortunately, not many compounds are of this type.

The extruder dies used in the early days were usually very carefully constructed with tapered entry from the barrel to the die orifice, ensuring smooth passage of flow for the compound through the die without any areas for compound stagnation and possible scorching or premature vulcanisation. The construction and tuning of these dies to produce the correct dimensional profile was a highly skilled operation. Dies used in these early machines were usually heated by externally applied batwing gas flame heaters impinging directly onto the die orifice and its immediate environs. The attainment of the correct temperature for smooth extrusion of the emerging stock was a skilled task usually only carried out by the leading hand or foreman. Modern machines are fitted with heaters and thermocouples in this area. Modern dies, for the sake of economy, are often simply plate dies made up of single or multi-stack plates depending on the quality of the product and the sensitivity to scorch of the compound being extruded.

5.18 Extruders, Mixers

Extruders with modified barrels and screws have been used to carry out the function of a continuous mixer of rubber compounds. The early machines of this type had both barrels and screws fluted, but at different parts of the chamber. One of these machines is the Transfermix. The rubber commences travel down the barrel of the machine in the flights of the screw, but transfers to

the flutes of the barrel as the path towards the die is taken, since there is decreasing screw flight height whilst the barrel has increasing flute depth. At the point of maximum depth of barrel flute the screw is at maximum flight height, so that all the compound has been transferred into the flutes of the barrel. As the material progresses further, the reverse is true until all the material is back in the flights of the screw. Each such transfer is a shear plane, and depending on its ultimate use the Transfermix can have two, four or more shear planes.

Second generation machines known as Multi-Cut Transfermix give a more concentrated mixing and plasticising of the compound in only one transfer zone, avoiding the lengthening of extruders in response to increasing demands of processing and overcoming the problems of scale-up in plasticising from cold-feed. This type of machine is particularly suitable for blending two dissimilar compounds, with the compounds being fed in as strip.

5.18.1 Powder Feed Extruder-Mixers

In the era of development of powdered rubbers, machines were developed which would carry out the function of continuously mixing rubbers and filler powders to produce a compound and give the product as an extrudate. These machines functioned adequately for their purpose, but other major problems associated with the concept of powdered rubbers meant that their uptake by industry was extremely limited.

5.19 Extruders, Piggy Back Systems

The concept of two or even three extruders in tandem, or 'piggy back', feeding to a common die to produce such items as tyre camelback are available from a number of producers. The machines are used to produce components having either different layers or sections consisting of a number of different compounds. Applications using this type of system are tyre components and automotive sealing profiles.

These complex systems demand strict screw speed control for all the individual machines in the setup, to balance the extrusion characteristics of the different rubber compounds forming the multi-unit component.

A similar principle is used for products that require a stripe of surface coating of a second compound or application of an alternative coloured compound. Sizes and positioning of the various machines in these systems can be tailored to suit the application.

See also extruders, pin barrel.

5.20 Extruders, Pin Barrel

Rotating laminar planes are generated around a simple conventional conveying screw in an extruder and little exchange of material takes place between the various travelling layers of compound. Additionally, because of the poor conductivity of rubber the cold rubber at the core of the travelling compound is insulated from the warm plasticised outer layers. This effect is present along the whole screw length.

Even higher shear rates in the extruder cannot prevent laminar flow in the screw flights and therefore resultant unmixed particles being carried over the shearing sections. Lengthening of the residence time in the barrel also has to be restricted to limit unacceptable temperature build-up, which would result in scorched compound. It is thus necessary to have an effective means of

interfering with the laminar streaming of the compound and this must be found outside the influence of the screw geometry.

A Uniroyal patent originated the principle of using pins protruding into the extruder barrel to disrupt the laminar flow of compound, and this principle was further developed by Troester in their QSM (cross-flow mixing) machines. The protrusion of pins into the barrel necessitated a modification to the screw design to accommodate them. Many papers can be found in the literature dealing with this type of pin extruder.

The screw/barrel/pin combination gives great flexibility due to very good mixing and dispersive action on the compound being transported down the extruder barrel. The arrangement of the pins in the barrel divides the material being transported in the rotary laminar flow along the screw flights. The material undergoes flow division and shifting with only a low shear rate, providing mixing and homogenising without excessive thermal overstressing. The repeated division and rejoining of the material streams constantly creates new surfaces, to give intensive mixing and break-up of the laminar flow, and provides heat interchange between the rubber particles. Energy absorption is claimed to be low and the machine is self-cleaning. If necessary a mixing zone portion can also be machined into the screw to improve the productivity when difficult natural rubber stocks are being processed.

Extruders with retractable pins (hydraulically inserted or withdrawn) can be used to vary the degree of mixing that takes place as the compound travels the length of the barrel.

5.20.1 Pinconvert

A further development is the combination of the pin barrel extruder system with that of the Transfermix (see under EXTRUDERS, MIXERS). The combined system is known as Pinconvert and is available with or without vacuum extraction.

5.21 Extruders, Ram

The ram extruder is a very old concept, being first used by Hancock in the rubber industry for extrusion of plasticised gutta percha. Ram extruders have been developed to give pre-forms for other processes. The machines use a roll of warmed rubber stock (either mill sheet warmed in a bath of hot water, or alternatively a roll of freshly milled compound). The pre-heated compound is then pushed into the cylinder of the machine; the die head is locked in place and the ram traverses forward, forcing material from the die orifice. On emerging the compound can be automatically cut to a predetermined volume by rotating knives. This type of machine is capable of handling very fast curing compounds.

Other versions of the machine are designed for specific purposes, e.g., a twin ram machine capable of producing a continuous extrusion, and versions capable of applying tread rubber directly to a buffed tyre carcass whilst simultaneously forming the tread pattern.

5.22 Extruders, Vacuum

The vacuum extruder was developed to eliminate unwanted gases from rubber compounds, so that the profiles produced from rubber stocks could be vulcanised at atmospheric pressure without problems of porosity occurring. Removal of the volatiles is achieved in principle by combining the actions of two individual machines in series, into one machine. The first part of the extruder screw

effectively functions as a cold feed extruder, passing the material to a vacuum zone. The second part then pumps the rubber to the die.

Provided that the vent zone does not become pressurised, the throughput is unaffected by what happens further downstream. Moving to the second stage, at low head pressure this will run with only a short length of the screw at the delivery end filled. As pressure in the barrel rises, more of the screw will run full and, even if the depth and helix angle of the screw are optimised for maximum pumping capacity, a point will be reached where the whole of the second stage is filled. Herein lies a problem with vacuum extruders. If open channel space for volatiles becomes eliminated then rubber will start to extrude through the vacuum vent.

Cutting back first stage throughput by a more restrictive barrier can help but also results in more heat being generated, so the extrudate temperature limitation is reached at low screw speed and output. The solution to the balance between the first and second stages has largely come from better proportioning of their lengths. For many purposes it appears that the second stage screw needs to be approximately the same length as the first. For high head pressure applications the second stage needs to be significantly longer than the first.

Manufacturers usually have to standardise on certain machine options but the barrel configuration clearly has to be such that the proportions are suitable for the highest head pressure that will be generated. To cover a range of requirements it is conventional to have two screws available; one for high pressure and one for low pressure applications. One is made fairly restrictive in the first stage so that the second stage can cope with the highest pressures that are encountered. The second screw is made to give a higher throughput per revolution, so that better productivity can be obtained when pressures are lower. It is also normal practice to have a vent plug and a single-stage screw available, so that the machine can be run non-vented and greater outputs obtained when the type of compound permits.

Apart from the two-stage screw, the only other distinctive features of a vented extruder are the vent port and the vacuum pump connected to it. The critical part of the vent port is the shape of the opening into the barrel. Rubber tends to come out of the screw channel as the flight passes the vent opening and the design of the vent opening must be such as to deflect it back into the extruder. The main requirement of the vacuum pump is that it should be capable of maintaining a high level of vacuum. Water ring pumps that are limited by the vapour pressure of water are not usually adequate.

Vacuum extruders can be single- or multi-vented. Versions also exist which have an added pin barrel processing extension.

5.23 Granulators/Shredders/Grinders

For some applications, such as when it is necessary to dissolve or solvate rubbers, or rubber compounds to form doughs and solutions it is desirable to use a machine in this category. Various types of machines can be used to produce the required form. Grinders are also used to reduce scrap vulcanisate to form a rubber crumb for purposes of working this waste product back into cheap compounds, or prior to reclaiming rubber by chemical processes.

These processes cause considerable wear on the machines. Heat generation, particularly when grinding vulcanisate, can be a fire hazard unless grinding and storage is controlled adequately.

5.24 Hose Machinery

A large variety of hose constructions are produced by the rubber industry for a wide range of applications. To contain transported liquids, usually under pressure, it is necessary to reinforce the hose construction with fabric, yarn or short fibres to constrain expansion of the rubber. Although hand-built construction using fabric still represents a proportion of the production, it is also very common to use yarns either braided or knitted directly onto the hose liner. For heavy duty purposes it is also necessary to use wire, in a braided form, to either reinforce or protect the hose from external damage. Use of short fibres as reinforcement represents a small proportion of hose production and requires specialised dies for extrusion to orientate the fibres circumferentially.

5.24.1 Braiding Machines

Braiding of rubber products, i.e., hoses, can be with either yarns produced from cotton or synthetic fibres, or metals, depending on the use of the hose. The principles of use of the braider are the same for both types of filaments. The yarns are laid down from the braiding machine in a similar manner to that of a maypole, the cross-over angle of the braid is critical to the stability of the hose in use. The correct angle of cross-over for the yarns, known as the Neutral Angle, is at 54 degrees to the axis. Angles greater than 54 degrees will cause the hose to grow longitudinally under pressure. A braiding angle of less than 54 degrees will cause the hose to grow in diameter.

Braiding hoses with wires to resist high burst pressures or for external protection is common, using a braiding machine. The wires used, usually of steel, will be either zinc- or brass-coated to achieve adhesion during vulcanisation. The gauge of the wire and its tensile properties will be matched to the expected service demands for the hose.

The bobbins of the braiding machine are loaded with the appropriate number of wire filaments to achieve the desired structure.

Braiding machines are of two basic types vertical and horizontal and both find application depending upon the type of hose being manufactured.

Wire/Bobbin Winders

As with reinforcing textile cords it may be necessary to rewind treated wire from production spools to smaller unit spools for specific machines, such as braiders.

5.24.2 Knitting Machines

There are two types of knitting used in rubber product construction, i.e., warp knitting and weft knitting.

Warp Knitting

The basic stitch produced in warp knitting is the chain stitch. The yarn is looped around the needle stem and another loop of the yarn is formed in the hook of the needle and is then pulled through the first loop, itself then becoming the loop held on the needle shaft, whilst another loop is formed in the hook. In this way a chain of interlaced loops is formed. By displacing every other loop onto the next needle, the chains of interlaced loops are linked together to form the simple knotted tricot structure. If one of the yarn loops become broken in this type of fabric then the whole fabric, in the line of the yarn, will 'unzip'. This problem can be overcome by displacing the throw of the stitches.

Weft Knitting

In this method the looping yarn runs transversely to the length of the fabric. Loops are formed on a row of needles and the next loops are caught in the hooks of the needles and then drawn through the first loops. Weft knitting machines normally give a circular product and can be used to form the

reinforcement continuously around an extruded hose liner. Weft knitted fabric is very flexible, having high tear resistance, and is used in many types of hose structures for vehicle applications.

These fabrics can be applied in the hand-built construction of hoses in a spiral form at an angle to the axis of the hose. The knitted fabric can also be produced directly onto the surface of the inner liner of a hose and subsequently be covered with the outer cover compound by a cross-head extruder.

5.24.3 Hose Builders

Hose may be hand built using a three roll wrapping machine. The centres of the three rolls form an equilateral triangle. The hose during construction sits on the junction between the two lower rollers and pressure is exerted to consolidate the composite by the upper movable roller. An extruded inner liner, after fitting to a solid inner mandrel, is placed into the machine between the rollers and then the various layers of rubber coated or resorcinol-formaldehyde-latex treated, fabric are applied in a spiral form, with overlap. Once the reinforcement layers have been added the cover rubber is applied and a cloth, usually nylon, is spirally wrapped around the constructed hose using the roller system. The hose is now ready for vulcanisation.

5.25 Hydraulic Drives

Hydraulic units can be fitted to mills, internal mixers, dough mixers, calenders and extruders.

The use of hydraulic units to drive rubber processing machinery has enabled the elimination of cumbersome gear boxes and their respective couplings. The hydraulic drive unit is fitted directly to the end of the shaft to be driven. It can be controlled fully across the entire speed range and provides full torque from rest, even under heavy load, up to the maximum rotational speed demanded. Shock loads do not affect performance and it has the ability to stop immediately on demand, due to its low inertia, unlike conventional drive systems. The unit requires little maintenance.

Advantages of the system also include improved operator safety due to the ability to stop immediately on demand. Full torque is available at all speeds. Change of mixing roll or rotor speeds can be carried out either by a pre-programmed method or operator choice, thus allowing change of friction ratio on demand. The units are totally enclosed and can be supplied so as to be explosion proof. Better energy efficiency is possible due to the improved management of shock loading which causes excess power demand. A further advantage over conventional gear box systems is the considerably smaller floor space required for this piece of equipment. The hydraulic pump unit sits on the floor in the locality of the machine being driven, but requires far less space than conventional motors and gear boxes.

5.26 Injection Moulding Machines

Injection moulding incorporates the automatic feeding, heating and plasticisation of a rubber mix and its subsequent injection into a mould at a temperature as close as possible to the vulcanisation temperature. A measured quantity of the mix is injected through a narrow orifice, by a high pressure ram into a tightly closed mould, in which vulcanisation takes place. The whole operation being carried out by a single machine specially designed for the purpose.

Injection moulding of silicone and polyurethane rubbers differs, because the material mixed and injected is usually liquid.

An injection machine and mould cost considerably more than a compression press and compression mould. The main economical advantages of injection moulding lie with long production runs and complicated mouldings. For short runs compression or transfer moulding may still be the most suitable process.

Some injection moulding machines are designed according to the First-In, First-Out (FIFO) principle. The material first plasticised is also the first material to be injected so that the thermal state of the entire shot volume is identical.

Injection moulding machines can be in a horizontal or vertical mode, with or without tiebars, or with a C frame structure for easy mould fitting and access. Machines are also available which can deal with two colour/compound injection into the same mould cavity.

Machines differ in their mode of heating, plasticisation of the mix and delivery of the mix to the mould cavity. This may be by simple ram (plunger or piston) or by screw.

Simple ram machines are cheaper than screw machines having equivalent shot volumes. Although the simple ram injection moulding machine was once quite widely used it was generally obsolescent by 1977. Plasticisation by screw is quicker and more controllable than by heat conduction in simple ram machines. A higher and more uniform compound temperature and thus a more uniform viscosity is achieved.

The advantage of screw machines is that work done by the screw heats and plasticises the mix, under conditions which can be carefully regulated by jacket temperature, screw speed and back pressure. A natural rubber mix leaves the extruder section of the machine 20-30 °C higher than the jacket control temperature.

Screw machines need to be subdivided and carefully defined because of some confusion in terminology. The simplest of the screw machines is the fixed screw machine which extrudes directly into the mould. More importantly screw machines can be subdivided into:

- (a) the reciprocating screw (screw-ram or screw-plunger) machine in which the screw itself acts as a ram and
- (b) the 'screw-machine-with-separate-ram' or 'pre-plasticising screw' or 'extruder-plunger' machine in which the screw extrudes into a separate chamber and a separate ram injects the rubber into the mould cavity.

5.26.1 Reciprocating Screw (Screw-Ram) Machines

In reciprocating screw (screw-ram) machines the mix is heated and plasticised as it progresses along a retractable screw. When the required shot volume has collected in a chamber (made by the retracting screw) in front of the screw, the mix is injected into the mould by the forward ramming action of the screw. The mix temperature which is already well above the screw jacket control temperature receives a further rise in temperature from the work done during high-pressure injection through the nozzle or gate into the mould.

A minor disadvantage of some of the earlier machines was that a screw fits its cylinder less tightly than a simple ram. A small quantity of compound may therefore flow back past the advancing flights of the screw, thus reducing the precision of the volume delivered by the ram and causing a wastage of the applied pressure. The effect is to limit the maximum pressure that can be applied by a screw-ram. This limit is usually around 140 MPa or a little higher, which is quite adequate for most purposes. In a new machine the recycling of material which flows back past the flights of the screw may be trivial. However, if a screw becomes worn, or if runners and gates into a mould are

too small, premature scorch may occur and may lead to regurgitation of feed in the throat of the extruder.

Modern designs fitted with non-return valves through which the plasticised rubber compound passes into the injection cylinder portion are capable of giving precise shot volume. The non-return valve is activated by the injection pressure. The injection ram/non-return valve unit ensures complete purging of the injection chamber.

5.26.2 Screw Machines With a Separate Ram

Screw machines with a separate ram combine the advantages of both screw and simple ram machines.

The rubber mix is extruded by a screw through a non-return valve into a separate chamber from which it is injected into a mould by a simple ram set at an angle to the screw. The tight fitting separate piston gives accurate delivery of the rubber mix allowing more efficient application of ram pressures up to 160 MPa. This pressure can inject even unusually high viscosity natural rubber mixes of Mooney viscosity (ML1+3, 120 °C) up to 100.

This type of machine separates the functions of plasticisation and injection for the better control of both. A “V” head design was first patented in 1960 and improved in 1961 with the extruder set at right angles to the injection chamber (this angle has not always been adhered to for new designs). An important feature of the design is that the temperature of the injection chamber can be set higher than that of the extruder to maintain the temperature of the rubber mix, which always leaves the extruder at a higher temperature than the set extruder jacket temperature. The design also lends itself to high shot volumes.

The principle of this type of machine has resulted in the manufacture of large machines capable of high volume shots of 8 litres or more.

5.26.3 Multi-Station Machines

In the 1960s multi-station machines played a very important part in the success of the injection moulding process and in the manufacture of unit soles, plimsolls, tennis shoes, casual shoes, bootees, wellington boots and mechanical goods. Significant reductions in the cure times and cost of these relatively thick products are possible using this type of machine.

The essence of the early 1960s process was that one injection unit fed 4, 6, 8, 10 or 12 vertical presses on a rotating mould carrier. Sometimes two injection units were used at different mould stations, one injecting a soft upper compound for a bootee and the other a harder sole compound. Sometimes two different coloured compounds were used.

Economies of production personnel can still be achieved today, and a unit cost reduction of 30-50% is possible. Physical properties of mouldings can be enhanced and the adhesion of the bond in a rubber-metal part is improved. Tool costs can be cheaper than for compression press methods because the throughput is greater.

All these rotary table machines are perfectly suited for automation using only one station each for unloading of products, cleaning and loading of inserts.

5.26.4 Shuttle Machines

An injection machine can be equipped with a two-sided shuttle table using either 1 or 2 complete moulds. Applications are in production using a common top mould plate and two identical lower plates. Products with metal inserts or which require unloading and mould cleaning times as long as cure times are best suited to this process.

Modern shuttle machines can be set up with two complete moulds so that approximately 2/3 of the cure time is under full clamp pressure in the main station. The clamp pressure is then reduced and the closed mould is shuttled out to continue the cure in the side station where it is opened for product removal, mould cleaning and insert loading. While one mould is in the side station the other is injected and receives the first part of its cure. With a special mould opening device on the shuttle table the machine becomes as effective as a two-station machine.

The system is most suitable for very high volume through-put which needs more than a single machine. The system can give 70-98% improvements in output in some applications. Capital cost is about 45% over that of a single station machine.

5.26.5 Machines and Moulds for Special Purposes

For applications requiring two different compounds, such as a double hardness sealing ring or a two colour rubber shoe sole, some machines have two injection units. One injects into the bottom/centre mould plate and the other into the parting line. Two injection units on a single-station vertical press are used in combination with twin rotating cavity plates.

5.26.6 Injection-Compression Moulding

The injection-compression process is an important variation in which rubber is injected into a partly closed mould under low pressure used for moulding-on of rubber soles to footwear uppers. Rubber is injected into a gap between the shoe upper and the sole plate, which is held 3-4 mm wider than it would be in its final position. After injection at the first mould station of a multi-station machine the sole plate is closed in the manner of compression moulding at the second mould station and rubber is pressed along the sole and over the toe cap. The importance of the process is that it becomes possible to mould without using normal high injection pressures which tear and distort canvas, leather or synthetic uppers.

5.26.7 Injection-Transfer Moulding

This process uses the plasticising and heat advantages of the injection unit to impart good flow properties to the rubber mix. It also offers the advantages of the flexibility of the transfer layout without the sprue and runners of the balanced runner system required by injection moulding. The space used by runners in other systems can be profitably used by more mould cavities.

After the mould has closed, but before final clamping, a measured quantity of rubber is injected into the transfer port. The rubber forces the transfer port open until it contains the required volume. With a top injection system the mould is forced downwards and the transfer piston remains stationary. With a bottom injection unit the mould is stationary and the transfer piston is raised. In both cases the effective volume of the port is increased by the filling action of the rubber.

The final clamping action forces rubber through the sprue holes leaving a thin (0.13-0.25 mm) transfer pad. The mould is designed with load springs to break open the plates and to help support the top plate and plunger when bottom injection is used.

5.27 Internal Mixers

Internal mixers of various types are produced in a range of sizes such that the appropriate capacity can be achieved for any size of production facility. There are a number of producers of the conventional types of mixer. Some mixers come with special modifications to improve mixing ability and quality.

Large amounts of energy are consumed during the mixing process and this gives rise to large temperature rises in the rubber batch. Internal mixers therefore have cooling channels in the chamber walls, rotors, and sometimes the ram head, to dissipate this heat. The inlet water temperature is controlled in most modern machines, but in many companies this is still not the case.

Rotor speed control is an integral part of the process of rate of temperature rise. The modern mixer is generally supplied with variable speed, constant torque electric motors driving via gear reducers or by a hydraulic drive system which has a motor shaft mounted tachometer to control rotor speed. Systems that can monitor, adjust and record the mixer rotor speed provide improvement in resultant compound uniformity. Changes in rotor speed within a cycle can be programmed.

The number of rotor revolutions per mix cycle relates directly to unit work input and to temperature rise. This variable can be employed when checking between mixed batches for changes in feeding operations, materials and mixer conditions. Power/work input measures the energy consumed by the mixer. A greater compensation for variations in feed stocks and mixer temperatures is provided by power control.

Ram pressure, however applied, either by hydraulic, pneumatic or mechanical means, can be varied to suit the needs of the mixing department. Modern mixer control systems can automatically alter the ram pressure between and even during individual mixing cycles. Monitoring the ram position enables the intake time of the raw materials to be deduced by measuring the time elapsed for the ram to reach the bottom of its travel limit. When the ram reaches the bottom of its travel, ingestion is complete. It is possible to monitor ram height throughout the mix cycle. Greater control of fill factors can be achieved with the aid of this feature.

The use of computers to control all of the variables during mixing can give greater batch consistency than the less sophisticated control strategies.

Effective mixing requires both dispersive and distributive processes to take place during the mixing cycle. Dispersive mixing takes place in a high shear zone. The manner in which both mixing processes are accomplished is dependent on the design of the mixing rotors, the basic types being tangential and intermeshing.

5.27.1 Intermeshing Rotor Machines

In the case of the intermeshing rotor machine the majority of the mixing action takes place between the rotors with the shearing action being created by the rotor design. Unlike the tangential mixers where the rotors revolve at different speeds, the rotors in intermeshing machines run at the same speed.

Variable Intermeshing Clearance (VIC) Rotor Internal Mixer

The variable intermeshing clearance rotor mixer is designed to allow a variable clearance between the intermeshing rotors of the mixer. This ability to adjust rotor separation distance achieves optimisation of the amount of energy being transferred to the compound. Initial intake of the raw polymer is also assisted by starting the mixing cycle with a wide gap between the rotors and then adjusting them, whilst the machine is running, as the raw materials are ingested.

The technical advantages of being able to vary the clearance between the mixing rotors include the possibility of taking up wear on the surface of the rotors by maintaining the clearance between the rotors constant, without having to carry out the time consuming task of providing welding of wear resistant material. Tests carried out have shown that the consequences of being able to vary and control the clearance between the rotors of the VIC are the same as those found in open mill mixing. Better dispersion, uniformity, control of temperature and higher productivity result.

Tangential Rotor Internal Mixer

The high shear forces required for dispersive mixing, in the case of the tangential designs (or Banbury-type mixer), are generated by passage of the mix between the rotor tip and the mixing chamber wall. The distributive mixing action is accomplished by transfer of material across the rotor and between rotors, the flow path being controlled by the angle and length of the wings. The flow of material around the mixing chamber is also dependent on the volume loading of the mixer, efficient mixing normally requires approximately 70% filling of the available chamber volume. The volume fill is also dependent upon the type of rubber being processed. Certain materials, e.g., EPDM, require a higher volume loading, typically 80%.

Monitoring and control of the metal temperature of the mixers results in faster, more accurate alteration of mixer temperatures being achieved. Tangential mixers have been shown by Elwood of Farrel to be very susceptible to changes in compound output with changes in mixer metal temperature. Such a trait can be advantageously exploited via the employment of a process control apparatus. This type of system would digitally monitor and control to the pre-specified temperature settings.

5.28 Laboratory Processing Equipment

The major manufacturers of factory size processing equipment for the rubber industry also offer a range of equipment of a suitable size for laboratory use. Specific requirements can usually be accommodated in addition to a range of standard equipment. Many of the items will be built to specific demand from the customer.

Laboratory presses are made by most moulding press manufacturers.

Laboratory mills are in general similar to factory equipment in construction but are generally better equipped to ensure operator safety.

5.29 Marking Devices

Marking crayons and inks/paints are some of the oldest methods of applying identification to slabs of rubber whilst being stored prior to incorporation into products or during factory operations. Care must be taken to ensure that the materials used for such identification are compatible with the rubbers on which they are being used. Coloured markers can also contain pigments which may contain active metal ions which could conceivably cause activation of oxidative degradation of the rubber if used extensively.

Marking devices are available which impress identification into the surface of the unvulcanised rubber slabs. Other devices can continuously apply an identification to extrudates on emergence from the die.

5.29.1 Printing Machines

Printing machines for the purpose of giving identification to rubber products, together with batch and quality related information can be used to apply the required information to the rubber product either continuously or individually, dependent upon the product type being manufactured.

5.30 Metal Preparation for Bonding

Metals must be pre-treated for satisfactory bonds to be achieved with elastomers.

Metals, especially the more common iron and steel types, come from the foundry coated with oil, grease and most often a generous layer of oxide formed on the exposed surfaces. All these materials must be removed from the surfaces and from the pores of the metal to ensure that the oils and greases cannot exude under the increased temperature of vulcanisation, when they become more mobile or volatile. Surface oxides also must be removed for they are often only loosely attached to the metal substrate and will detach themselves under duress in service, after bonding.

The scheme of work consists of:

1. Rough degrease to remove greases, oils, etc.
2. Degrease with suitable solvent or detergent systems
3. Blast cleaning
4. If necessary further degrease
5. Treat the cleaned metal with primer coat bonding agent.

5.30.1 Degreasing Systems

Solvent

The more usual method of grease and oil removal from the metal surface is by degreasing in the vapour of a chlorinated solvent such as trichloroethylene or perchloroethylene. Direct contact with the degreasing fluid is not an efficient way of removing greases from metal surfaces, always leaving a molecular layer, at least, still lying on the cleaned surface. The most common units consist of a tank with condensing coils around the upper edges to prevent the solvent vapour from escaping to the atmosphere of the preparation shop. Fitted to the tank unit will also be a means of lowering and subsequently raising the treated metal from the tank.

Detergent

The current trend and environmental pressure for the industry is to move towards the use of detergents to remove oils. The action of the detergent can be supplemented by the use of ultrasonic agitation to remove the oxide flakes. These systems are, of course, water-based and efficient drying of the metals is essential otherwise further oxidation will rapidly take place. Careful choice of the detergent is also necessary otherwise the residues can also detract from the bond strength achievable. Power washers, using suitable detergent systems, can be used for final cleaning and degreasing of metal parts for bonding purposes.

Ultrasonic Cleaners

Cleaning of metal components of a fragile nature can be achieved by the use of ultrasonic cleaning units. Under the influence of a detergent solution and the effects of the ultrasonic emission, detritus is lifted off the metal surface. After such treatment the metals will require thorough washing and drying before applying the bonding agent.

5.30.2 Blasting Systems

After degreasing, metals have to be blasted with a sufficiently abrasive material to remove the surface oxidation layer. Application of the abrasive to the metal surface to be cleaned depends very much on the dimensions and type of metal. Large dimensioned metals and interiors of such articles as tanks, will require application of the abrasive by means of air blasting techniques. Smaller metals of suitable strength can be treated in 'rumblers' machines where the metals are tumbled whilst being blasted by the abrasive carried in an airstream.

The usual medium used for steel substrates is iron grit. Alternatives to iron grits are alumina, quartz sands and carborundum. The choice of grit used must be coupled to the type of metal being treated. Incorrect grit/metal combinations can lead to formation of galvanic cells remaining on the surface of the blasted metals.

An alternative process to grit blasting uses a number of different chemical routes. It is sufficient to say here that these can be very efficient, but do occupy rather large factory floor areas and can, if not controlled correctly, give variable quality of prepared surface. The usual chemical pre-treatment systems consist of acid etching of the surface followed by several water dips and subsequent passivating (surface coating with oxides, phosphates, cadmium plating, etc.)

5.31 Microwave Heating

High frequency and microwave techniques are used in a number of applications within the rubber industry and, by exciting the molecules throughout the rubber mass, rapidly achieve uniform heating of the whole moulding blank or extrudate. The earlier high frequency methods suffered from the defect that inevitable variations in the uniformity of the black dispersion in the rubber led to hot spots being created by a greater degree of excitement for the poorly dispersed black agglomerates. The newer microwave techniques are not so sensitive to this variability and are more successful. Non-polar rubbers such as natural rubber do not readily absorb microwave energy, but this can be overcome by the addition of carbon black.

Microwave units are available for both continuous vulcanisation systems, for preheating of moulding blanks for compression and transfer moulding, and for heating large bales of frozen rubber prior to mixing.

5.32 Mills, Cracker

Mixed compounds, especially natural rubber based recipes containing fine particle fillers, such as carbon black will, during storage, form a rubber/filler structure that must be broken down before the compound can be further processed using preparation mills. Very robust mills constructed with very strong rolls having semi-spiral corrugated surfaces are required to deal with the high shear forces necessary to break the structure down. These cracker mills are also used in the production of crumb rubber.

Significant heat generation during the breakdown also means that cooling must be efficient if the mill is in constant use. Stronger than normal 'breaker' plates commensurate with the overall strength of the mill body will also need to be fitted, otherwise production will be frequently interrupted due to rupture of weaker breaker plate units.

5.33 Mills, Mixing

The two-roll mill represents the earliest form of rubber processing machine, used by the rubber manufacturer being developed from the masticator of Hancock. Over the years the emphasis of the role of the two-roll mill has moved from being that of the prime means of compound preparation for the majority of the rubber industry, to that of secondary usage. In the modern factory conventional two-roll mills are used for compound blending and for 'sheeting off' of compound mixed by other means. In addition they are used to warm-up compounds from store, and for a number of blending purposes to achieve compound uniformity for other processes.

In the early days of the rubber industry all mixing was carried out on two-roll mills. Now this situation only occurs occasionally, or when small or expensive batches of material are required, e.g., silicones or fluorocarbons. Mill mixing is an efficient method for breaking down agglomerates and, over a period of time, with good operatives, good homogeneity can be achieved. One batch, however, can take some 30-40 minutes to mix.

5.33.1 Influence of Mill Variables

For any given size of mill there is a minimum volume of polymer per unit width of roll, below which no dispersive mixing occurs. Increasing the amount of material above this minimum level increases the high shear zone in the polymer, increasing dispersive mixing. There is an upper limit however, above which a circulatory flow develops at the entrance to the nip region and no further improvement occurs.

The nip width (or gap between the rolls) is critical. Increasing the width decreases the shear stress developed and less dispersion occurs.

The friction ratio or speed differential between the rolls is another critical parameter, shear stresses increasing as the friction ratio is increased. Increasing the speed of both rolls also increases the shear stresses.

The viscosity of the polymer or mix also controls the level of the shear stresses developed in the nip region. The level of temperature in the rubber mass, by its effect on viscosity, will also influence the level of shear stresses developed.

The flow behaviour of rubber on a mill is dependent on the material, nip width, roll speed and temperature, and certain combinations can give flow instabilities, the worst case from the mixing point of view being 'bagging', i.e., loss of adhesion of the rubber compound to the mill rolls. A decrease in nip width, an increase in speed or temperature, can overcome this problem.

Modern two-roll mills are available in a range of sizes designed to suit specific applications. They can be made available with either mechanical or hydraulic drive systems and fitted with the required devices for operator safety.

5.33.2 Laboratory Mills

Laboratory mills are in general similar to factory equipment in construction but are usually better equipped to ensure operator safety.

5.34 Mills, Stock Blenders

The final quality and reproducibility of rubber compounds mixed 'from scratch' on a two-roll mill, or finalisation of compound batches mixed in an internal mixer, depend to a large degree on the skill of the mill operative. In order to overcome to some extent the reliance on operative skill and to ensure reproducible mix quality many mills are now fitted with 'stock blender' units. These consist of a driven twin roller system, of similar overall length to the mill rolls, fitted above the mill frame.

On achievement of a 'band' of compound running around the mill roll, the compound is cut off from the front of the mill and is fed up into a feeder unit which traverses back and forth before the two driven rollers of the blender. By this action the rubber is effectively randomly worked and blended as it passes from the blending unit back down into the nip of the mill.

5.35 Mixers for Rubber Cement/Dough and Solution

Rubber cement/dough and solutions are prepared for a variety of processes from adhesive manufacture, to hand-built products, to fabric coating. The rubber compounds to be used in the spreading process must have a sufficiently long pre-vulcanisation (scorch) life, so that they can withstand the cutting and dicing process preparatory to dough mixing.

Organic solvents are used to make the rubber dough. Natural rubbers are soluble in rubber solvent (a specific petroleum fraction) or naphtha. Nitrile and polychloroprene compounds require aromatic or chlorinated hydrocarbons as solvents. Often mixtures of solvents are used.

5.35.1 Z-Blade (Sigma-Blade) Dough Mixers

Rubber doughs required for the spreading process are traditionally prepared by milling the rubber compound into thin sheets, cutting these into strips from the mill and sometimes chopping into smaller pieces. The prepared compound is placed into a sealable tank containing the appropriate solvent for the compound and allowed to soak overnight. After about 12 hours soaking the mass is transferred to a Z-blade (Gallery- or Sigma-blade) mixer, where the dispersion of the rubber into the solvent is continued until a satisfactory dough consistency and correct viscosity has been reached. The temperature of the mixer chamber can be controlled by passing cooling/heating fluid through the passages in the mixer walls. After the required even consistency is achieved the dough can be sieved to remove foreign bodies or any undispersed lumps. Alternatively, after being mixed the dough can be ram strained through a suitable gauze. The dough must be quality and colour checked before use to ensure a consistent product, and the deposition of the required thickness of coating at each pass through the spreading machine.

There are alternative mixers which give quicker breakdown of the rubber/solvent mass to give a smooth dough. These are usually based upon a rotational principle with rotating and stationary paddles to break up the centrifugal movement of the dough and thus create turbulence within the material being mixed. Once mixed the dough must be stored in closed containers to prevent solvent loss and consequent change in viscosity. Use of zinc coated containers must also be avoided to prevent gelation occurring owing to the presence of zinc ions.

5.35.2 Paddle Stirrers

Normally only used for further dilution of previously prepared rubber solutions to ensure uniformity. Often used after storage periods for such products as bonding agents to lift deposits from the bottom of delivery and storage drums and to re-establish full dispersion of all the components of the system.

5.35.3 Planetary Mixers

The mixing mechanism of this mixer revolves around two axes. The mixing blades revolve around a common axis and also their own axis of rotation. This mixing action is particularly effective especially for less viscous solutions.

5.35.4 Rotational Mixers

A vertically arranged rotor system consisting of protruding arms revolves within a cylindrical chamber fitted with stationary deflector protrusions. The combination of the movable rotor and static protrusions effectively mix the diced rubber feed and solvent by turbulent flow. It is usual to have at least three speed possibilities and thus lump-free preparation of the product is possible in relatively short mixing times. Mixing times for these machines is considerably less than for the Z-blade mixer.

5.36 Mould Cleaning

Frequent mould cleaning is essential in long-run production to ensure good product appearance. The cleaning frequency is dependent on the application of the components being manufactured, the type of compound being processed and the temperature of vulcanisation.

The methods used are: manual scouring with steel wool and abrasives, wire brushing, grit blasting, vapour blasting, and chemical cleaning in salt, acid or alkali baths. The first two methods are suitable for simple moulds, while the remainder are applicable to any size or configuration of mould. The types of material used for grit blasting include ground vegetable matter, such as nut shells, of 10-30 mesh; the particles after use are cleaned and recycled. Frozen CO₂ pellets or beads can also be used for blast cleaning. Vapour blasting consists of high-pressure application of a detergent solution at high velocity to the mould surface. The latter two techniques can be used in conjunction in some mould cleaning systems. The abrasive and detergent action effectively removes the deposit.

Chemical cleaning baths are used in large-scale plants and are extremely efficient but are hazardous in use, requiring the usual safety precautions associated with caustic chemicals.

Ultrasonic baths can be used to remove detritus from delicate moulds. This method eliminates the possibility of damage by blasting techniques and does not present the health hazard of chemical methods.

Salt baths can also be applied to mould cleaning. They are efficient in use but have the hazards associated with high temperature caustic chemicals.

Rubber compounds containing amine generating chemicals are also available to strip the compound and release agent residues during a cleaning cure. The mould is either totally filled by the cleaning rubber compound, or in the case of larger moulds, such as tyre moulds, with a veneer over a conventional rubber stock. The detritus is then removed after the cleaning cure having become bonded into the rubber surface during the vulcanisation cycle. By use of these cleaning rubbers down-time for the mould is minimal as the mould does not have to be removed from the press.

5.37 Moulds

For the satisfactory large-scale production of components, it is necessary to use carefully designed and well-constructed steel moulds suitably hardened and finished, depending on the surface quality required in the product. Small runs can be achieved using moulds of cheaper materials such as aluminium alloys. These latter moulds may require the support of frames or bolsters to prevent spread under repeated operation.

With compression moulding, to ensure dimensional consistency, it is necessary to allow the excess material to move away from the edge of the cavity so that the 'lands' between the cavities can contact with minimum thickness of rubber (flash) between them. Spew grooves and channels are provided of sufficient dimensions to accommodate this excess, and also to allow the escape of air from the mould cavity. In some cases, where the shape is complex, it may be necessary to provide extra venting to allow air to escape from a blind area, where it is likely to be trapped.

Injection and transfer moulds do not require any provision for excess material flowing out of the mould, simply an escape route for the volume of air in the cavities, which the parting faces provide.

The mould is closed under pressure and held so while the rubber is forced into the cavities. These methods give parts which carry little or no flash adhering to them at the parting lines of the mould.

In moulds for complex product shapes it can be advantageous to provide vacuum extraction to the cavities so that air and evolved gases can be removed from the mould cavity, before and during vulcanisation to ensure complete cavity filling, and a product without air (gas) blemishes.

5.38 Ovens for Cure, Post-Cure and Ageing Applications

5.38.1 Cure/Post-Cure Ovens

Curing ovens can be of two types: long ovens with internal conveyors or cabinets. In the case of many heat-resistant rubbers, such as silicone and fluorocarbon rubbers it is necessary to supplement the press cure with an oven post-cure to eliminate residues from peroxides and to complete vulcanisation. Cabinet type ovens are generally used. The gases emanating from the components must be evacuated from the oven during the post-cure cycle. Accurate maintenance of the temperature over the extended post-cure cycle is vital and adequate internal air circulation amongst the component load is required. It is usually necessary to treat the evolved gases to prevent emission of noxious materials to the atmosphere.

5.38.2 Ageing Ovens

Ageing ovens are similar in nature to post-cure ovens requiring very accurate temperature control systems and monitoring for volume throughput of circulating air to ensure compliance with the requirements of specification testing.

5.39 Preheating Bales

5.39.1 Hot Room Equipment

Bales of natural rubber especially, and many synthetic rubbers benefit from storage in a 'hot room' prior to being prepared for the mixing department. Natural rubber in particular arrives in factories in a 'frozen' (hard) state due to crystallisation and will require a few days storage in warm conditions so that damage does not occur to the mixer from the hard rubber charge. Crystallisation occurs very rapidly at temperatures as low as $-26\text{ }^{\circ}\text{C}$ but the rate between 0 and $10\text{ }^{\circ}\text{C}$ is still appreciable. Crystallisation is a reversible physical change without detrimental effects.

5.40 Preheaters Other Than Microwave

Compound preheaters installed prior to entry into the vulcanisation unit can assist with the production of sponge profiles with improved 'skin' quality by the onset of vulcanisation. This helps to retain the profile of sponge, by increasing its green strength, prior to its passing through the following microwave unit. The preheater units can be either infrared or hot air.

5.41 Presses, Lead

Certain types of hose and cable are produced by a moulding method where the pressure exerted from the internal curing medium is restrained by an outer coating of lead which encases the hose. After the hose has been constructed with its various rubber layers and reinforcements, the unvulcanised hose is passed through a lead press or extruder and a casing of lead is formed surrounding it. The lead can be either fluted or smooth, depending upon the required finish. After covering with lead the hose is wound around a large diameter drum and then filled with water and/or air. The hose ends are clamped and then the hose is placed in an autoclave for vulcanisation. The water/air expands under the applied heat and the hose compaction takes place within the hose 'mould' before vulcanisation commences. After vulcanisation and cooling the water/air is released, the lead stripped from the outside of the hose by slitting and the lead is reprocessed for the next application.

Hoses produced by this method are generally used for comparatively low pressure applications, and are often produced in lengths of up to 500 metres, with a bore size of up to 40 mm.

5.42 Presses, Rotary Curing

Continuous vulcanisation of rubber based products such as thin conveyor belting, flooring and similar can be achieved using a large rotating heated drum. Pressure is exerted to the product by means of a continuous stainless steel belt which presses the sheet to the surface of the drum. The belt is also heated from its reverse side to give optimum heat transfer to the vulcanising rubber.

The pressure exerted by the steel belt is less than for other methods of vulcanisation, but is usually sufficient to ensure full compaction, zero porosity and a good surface finish. For flooring products a mesh belt can be used to give a rough surface to the underside of the flooring, to facilitate adhesion to the floor substrate by applied adhesive.

Special rotary curing units are designed for 'continuous' vulcanisation of V-belts. This method eliminates any areas of overcure and moulded in stresses, which result from methods using presses vulcanising belts in sections. Belt and tension roller pressure release mechanisms allow for easy unloading and loading of the belts.

5.43 Spreading/Coating Machines

The spreading machine used by the rubber industry consists of a means of applying a thin layer of rubber dough to a fabric, which then passes over a heated chest to remove solvent.

The dried fabric is presented to the machine by passing a leader cloth under the dough application blade.

The variety in the number of profiles of blade that have been used over the years for specific applications is legion, but fundamentally there are still only three basic types.

The spreader most commonly found in the rubber industry has a working width across the application roller/blade of 1.5 metres. Wider spreaders (up to 4 metres) exist for very wide cloth coating but they require special control of the bending of the doctor blade and have compensatory mechanisms to overcome this problem.

Bull nosed blades give little penetration of the fabric, with heavy coating weight. They are used when easily damaged fabrics are being processed.

Tapered or v-shaped blades give good penetration with lightweight coat application. If this type of blade is chamfered on both sides of the 'v' (which in fact effectively creates a rounding off), there is produced, in effect, a small diameter roller. This shape results in a high hydraulic force which enables the rubber compound to be forced further into the cloth structure than would be the case with the sharp tip of the conventional 'v' blade.

Flat, or square section blades usually have a lead-in chamfer on the feed-in side: fabric penetration depends on the width of the flat section and coating thickness on the angle and width of the chamfer. Generally this type of blade can be used to give the required coating thickness coupled with good penetration of the dough into the fabric.

With modern machines the various blades are carried on a knife support beam, which allows easy blade changing and enables the blade to be given a varied angle of set. This knife support beam is controlled by the use of two pneumatic cylinders which control the pressure at the ends. Correct operation of this system gives much better control of the process eliminating any knife rise and fall, which created flutter in older machines and hence variability of spread thickness. A digitally activated quick lift mechanism also allows quick blade movement to enable the passage of any cloth imperfections, such as yarn knots and cloth joins, which would otherwise foul the blade. Correct alignment of the blade to the roller gives correct thickness control across the width of the coated fabric.

Alternatively, the doctor blade can impinge onto a small conveyor belt system which supports the travelling fabric. This mechanism is less commonly used than the rigid roller as it leads to reduced control of the thickness of the spread. For precision work, using very consistent cloth, an accurately machined chromium plated steel roll can replace the rubber covered roller.

5.44 Temperature Control Units

Control of the temperature of rubber compound whilst being processed in extruders and injection moulding machines is vital if the product from these processes is to be uniform in quality. Failure to control temperatures in processing equipment can lead to scorching of the compound as it emerges from the extruder die or injection machine nozzle. Most modern items of processing equipment are fitted to a temperature control unit using either oil or water as the circulatory medium.

5.45 Thickness Gauges

Control of product gauge is of considerable importance for the majority of products produced from calenders and various means have been used to achieve this from the early days of the machine. Inaccuracies in gauge on calendered products can not only mean out of specification goods being produced, but also one can be giving away free of charge considerable quantities of expensive compounds (unless the product is sold by weight, of course).

Early thickness control systems relied on the calender operator setting up the machine correctly by the use of hand-held thickness gauges, with the consequent slowness of response time during set-up and running before any desired modification to gauge could be achieved. It was usual to run the calender at a low speed to set-up the required dimensions for the product and then to speed up the

machine to its full running speed after the operative was satisfied. Changes in speed will of course have some effect on the dimensions of the product.

Older beta gauge systems rely on mechanico-electrical systems, sensing the thickness by scanning above the calendered sheet as it passes over a precision measuring roller. An interim system used in the evolution of today's gauge controllers relied on reflection devices such as laser probes and pneumatic volume indicators. These devices had a high sensitivity, but were insufficiently accurate. Modern calenders are tending towards the use of transmission systems using isotopes. These systems require calibration with the type of rubber compound being used if they are to be utilised to their greatest degree of accuracy. Multiple fixed or single scanning heads are used to ensure that the whole of the product is examined for accuracy. This type of gauge can be accurately used for control of individual bowl adjustment, together with cross axis and bowl bending device adjustment, to ensure the highest degree of automation. Use can also be made of sensors scanning the compound on the individual calender bowls in addition to the final product.

Dimension measuring devices are also necessary to control width and thickness of extrudates for most applications. In many cases it is also necessary to check weigh cut to length rubber sections.

5.46 Transfer Moulding

Transfer moulding uses an additional pot/ram section built into the top of the mould. A pad of rubber compound sufficient to fill the cavities, plus an allowance for the 'transfer' pad remaining in the transfer pot, is put into the pot and the mass transferred into the individual cavities.

In addition to in-mould transfer pots, loose pots are also used which sit on top of a mould. These save on mould costs and weight but some excess compound can escape between pot and mould surface.

Two methods of introducing a heated mix to the cavity are common. The first involves the use of outside pre-heaters.

The other method is to use a transfer mould where the blank is placed in a 'pot' portion of the mould and then picks up further heat as it passes into the cavity. This method is frequently adopted for rubber-to-metal bonded, large and complex components.

The mould consists of 3 or more parts. The mould cavity is made in a conventional manner, but, mounted above and connected to it by a series of holes or transfer ports, is another cavity. The prepared rubber is placed in this upper chamber, and an integral ram is used to transfer the rubber into the mould cavities under pressure. The energy required to force the rubber into the cavities increases the temperature of the rubber mass as it flows through the connecting holes. As a result, curing times are significantly reduced.

In commercial use are a wide variety of machines which transfer fixed volumes of compound to clamped moulds, by the operation of a ram in a cylinder fed with pre-heated slugs. These machines are capable of high speed semi-automatic cycling and are a great advance over the use of loose transfer moulds in conventional presses. The components which are produced are to a large degree flash-free, it only being necessary, in the majority of cases, to remove the injection feed and runner system.

5.46.1 Presses with Vacuum Chamber Extraction

Presses with vacuum extraction fitted to extract gases from moulding cavities eliminate moulding faults arising from air entrapment, or gases generated during vulcanisation. These presses are

particularly useful when products are being produced from complex cavity configurations. Presses can either be fitted to a vacuum line or fitted with individual extraction units.

5.47 Tyre Building Equipment

Tyre building requires a number of specialised items of equipment, which are specific to this part of the rubber industry.

In all tyres there are three types of components, the reinforcement layer(s), the rubber parts and the steel bead wires which locate a tyre to the wheel, or 'rim' of a vehicle. Rubber is used in packing strips, inner lining, sidewalls and the abrasion-resistant tyre tread.

Until the 1970s in Europe and the 1980s elsewhere tyres were built in 'cross-ply' (diagonal ply) construction, with the reinforcement layer running at a bias to the direction of tyre rotation. Now the vast majority are radial ply with the carcass reinforcement layer placed radially, or at 90° to the direction of rotation. There is always an even number of 'plies' or reinforcement layers – generally car tyres have two and trucks around 6 or 8 plies. In addition, there are tread reinforcing (bracing) layers called belts, which run around the circumference under the tread.

5.47.1 Tyre Reinforcement

The reinforcement is usually of textile (rayon, nylon or polyester) or steel. It is made up into a fabric before incorporation into the tyre. Textile tyre cord is woven into a fabric with a very strong, close warp and a widely spaced weft, this is then impregnated with a sticky rubber compound breaking the weft strands, which gives a unidirectional series of cords held together with rubber. Passenger car tyres are generally built of textile casings with steel belts. In a steel 'fabric', standard steel cords are placed in parallel, close packed formation and rubberised to form a ply of reinforcement. Steel provides greater strength and stiffness, and is used for carcasses in larger tyres and belts for most tyres.

Creels are used to supply the wire to the coating calenders. The creels are carried by frames, in banks with sufficient locations to supply the necessary number of wires for the type of web necessary for the tyre to be produced.

Fabric Bias Cutters

Rubber coated fabric is cut to give a bias to the fabric on its application to the tyre carcass. The knife angle can be adjusted in the cutting machine.

5.47.2 Bead Forming Devices

Steel bead wires are used at the extremes of the reinforcing plies to ensure a complete seal to the rim. Many turns of small diameter wire are wrapped in a rubber-impregnated tape to form a flexible hoop of high strength.

The wire beads used are produced from a combination of multi-strand copper, zinc or brass coated high-tensile steel wires. The required number of wires are formed into the required shape and then passed through a cross-head extruder to be coated with rubber compound. The coated wire layers are then formed into a coiled ring and the free wire ends secured together. For certain heavy duty applications use is made of either a light weight rubberised fabric or a small fibre filled rubber sheet to cover the joint area. In some cases the bead construction is also partially vulcanised.

5.47.3 Extruder Dies for Tyre Profiles

A variety of extruder die heads are used to produce the different tread profiles required for the different tyre types.

5.47.4 Tyre Building Machines

The various tyre components are built together on the 'building drum' of a tyre-making machine. The builder applies strips at appropriate points to provide a gradual transition from one major component to the next. Many of the processes have been automated, but operator skill is still important. Air entrapment between layers must be avoided to prevent ply separation in service.

5.47.5 Tyre Moulds and Mould Containers

Tyre moulds and mould containers are made specifically for the tyre industry.

5.47.6 Tyre Vulcanising Presses

Vulcanising presses for the tyre industry are specific to that production. Older machines used an inserted bladder or airbag, whereas modern presses have a fitted diaphragm which is automatically inflated during the press closure and exerts pressure to the inside of the tyre, pressing it into contact with the tread forming pattern of the mould. The cure time is controlled to some extent by the heat transfer capabilities of the diaphragm which transmits heat to the inner layers of the tyre construction. Accurate control of the heating medium for the diaphragm and the high temperature obtainable allow cures in the region of 15 minutes or less to be achieved, dependent on the structure of the tyre being vulcanised. All phases of the cure cycle are automatically controlled.

5.47.7 Tyre Press Loading Equipment

Mechanical loading devices to load the tyre into the mould cavity.

5.47.8 Tyre Testing Equipment

This can include X-ray devices and drum wheel test rigs.

5.48 Tyre Retreading Equipment

Tread wear during the life of a tyre represents a loss of only 30-40% of the actual tread compound. For worn, undamaged tyres a fresh patterned tread may be fixed to the casing.

Retreading of tyres may be undertaken in a variety of ways. Unvulcanised material can be applied and then cured at 150-180 °C ('hot' retreading), or prevulcanised tread can be applied at temperatures of around 100 °C ('cold' retreading). Vulcanisation may take place with or without moulds, or in an autoclave.

5.48.1 Buffing Machines

The tyre is prepared for retreading by a buffing/grinding process. This provides a fresh uncontaminated surface for bonding to the new tread material and in addition rubber crumb/buffings. When only the tread is renewed the process is known as 'Top Capping'. In 'Recapping' the new material is extended over the shoulders of the tyre. 'Bead to Bead' remoulding also applies a thin veneer to the tyre sidewalls. The latter is the process most commonly applied to car tyres.

5.48.2 Retreading Using Unvulcanised Extrusions

The retreading compound is in the form of an extruded section. It can be supplied at a width to cover the whole area to be retreaded, when it is called 'Camelback', or it may be in a narrower strip for winding. The extruded material is then vulcanised to the casing in a patterned mould.

5.48.3 Retreading by Direct Extrusion

An extruder equipped with a reciprocating die forms the tread pattern directly onto the compound as it is applied to the casing. The casing is then vulcanised in an autoclave.

5.48.4 Retreading by Smooth Tread Extrusion and Pattern Cutting

A layer of retreaded rubber is formed on the casing and consolidated by pressure. The tread pattern is cut out of the applied rubber either in the same operation or subsequently. Vulcanisation takes place in an autoclave.

5.48.5 Prevulcanised Tread Replacement

A pre-cured tread with pattern is prepared by moulding. A thin strip of unvulcanised cushion rubber compound is inserted between the casing and the tread rubber to form the bonding agent between the new and old components. The tread is then applied to the casing and consolidated by pressure. The cushion rubber is then vulcanised. This is also known as 'cold retreading'.

5.48.6 Vulcanisation Autoclaves

Autoclaves can be specifically designed to accept moulds for tyre retreading.

5.48.7 Retread Testing

Drum wheel test rigs are available to check the performance of tyres with retreads.

5.49 Weighing Equipment

5.49.1 Weighing Units For Liquid Dispensing

Liquid ingredient weighing can be an area of considerable problem when accuracy of addition is vital and dispensing equipment, fitted with heaters where required are very necessary to reduce compound variability.

5.49.2 Weighing Rubber Chemicals

Advances in quality control requirements for rubber compounds have demanded that special care is exercised in the weighing of the various fillers and critical small volume powders necessary for the formulation. Ingredient weighing systems are available which can be tailored to the specific requirements of individual factories. Additional components can include conveyors, bagging units and pneumatic conveyance systems.

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