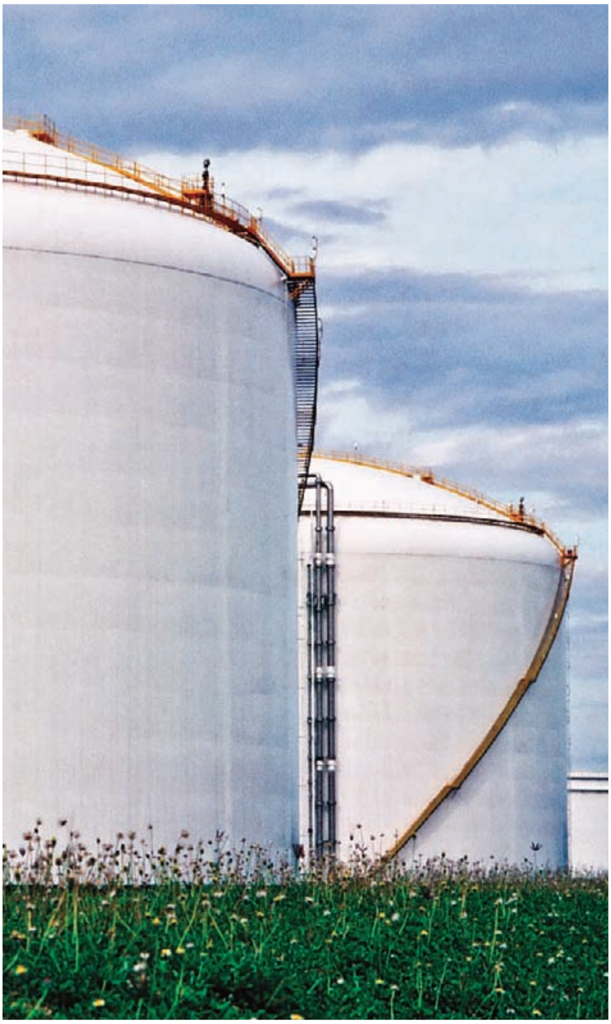
Tank Linings for Chemical Process Industries



V.C. Chandrasekaran

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Tank Linings for Chemical Process Industries

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Dedication

This book is dedicated to my granddaughters:

Esther Shine Peter,

Jessica Peter,

Abigail Arun,

Christa Victor

and

Arputham, my wife

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Preface

This book does not deal with the fundamental chemistry of rubber and its reaction mechanisms with acids, alkalies, fumes and gases prevalent in, and handled in, process industries. Such a treatise can undoubtedly be found in research work, papers and books published, which are rich resources enabling corrosion engineers to correlate science with facts and to act accordingly to solve problems of corrosion. Instead, this book deals with the specialty subject of protective rubber lining and its applications in various industries, highlighting technological aspects of manufacture and application.

This book is considered to be a unique addition to the world of technical literature, due to its thorough exposition of case histories and industrial practice. It is the product of a very long process to present an informative book on this subject in a concise form which should be useful to user industries and practising engineers in their respective industrial environments. This work is the author's sincere and humble wish to draw the attention of the concerned, serious, worried and interested readers and students to the technological aspects of protective rubber lining and its vast potential as a technically viable, and commercially important, material of construction for the process industries to combat corrosion.

The various corrosion challenges which the industries are facing undoubtedly and frustratingly make them look for materials to protect their plant and equipment from the attacks due to corrosive media. While they search, rubber comes in to the forefront offering to face their corrosion challenges, in preference to costly metallic alternatives like titanium, manganese, stainless steel, etc. Non-metallics, such as fibre-reinforced plastics and specialty plastics, have limited application in critical areas.

The author has been involved with the rubber industry for almost forty five years in the non-tyre sector, in production, manufacture and research and development and has aimed to focus throughout the chapters on the most important aspects covering the nature and use of various rubbers in anticorrosive application.

This book should be of immense help to chemical engineers, materials managers, maintenance engineers and practitioners in rubber and students alike. Moreover this will be a reference book for workers in fertilisers, caustic soda and other chemical and process industries. The clear and primarily non-technical style of writing for a technical subject such as this, which the author intended as far as possible, will also attract general readers with a more limited knowledge of rubber.

Acknowledgments

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Vast and resourceful information in the form of abstract papers and actual papers by leading scientists were provided to me as references by Smithers RAPRA, UK, the global authentic consultant on rubber and plastics, whom I thank with immense gratitude.

Lastly Vankatakrishnan Ranganathan who spent all days with me in front of the computer during the preparation of the manuscript is in my mind as usual and my thanks go to him too.

V.C. Chandrasekaran

1 Introduction

About two years ago a co-passenger from Paris who befriended me in Frankfurt Airport (since we mutually discovered a common interest and common destination, Chicago) and we spent a few minutes discussing an interesting article published in the US a few years ago, which he recently read and which I felt to be quite relevant to the subject matter which you are going to read in the forthcoming pages of this book.

The article was about coating a fuel rocket meant for launching a Titan rocket. The engines of the Titan rocket were extremely powerful ones, having a diameter of about 3 m and length of about 2 m, weighing approximately 250 tons and developing a thrust of more than half a million kilograms. Two such engines fitted on Titan containing combustible liquid fuels were capable of pushing into orbit a load of 2.5 tons or more. The rubber lining which protected the steel casing of the rockets against temperatures exceeding 3000 °C and containing highly corrosive gases was a nitrile rubber compound with silica and asbestos dust. During the commissioning of the launch, the rubber sheet became combustible, decomposed once and for all, and was burnt into ashes thus sacrificing itself in protecting the steel casings of the rocket against the attack of highly eroding gases at a temperature of 3000 °C. If the rubber lining was not able to resist high temperature and gases during even fractions of minutes during commissioning of the engine the steel casing would have burnt and launching would have failed. The thickness of the lining at the various regions of the rocket ranged from 20 mm to 250 mm. After lining the rocket was vulcanised in a 3.6 mm diameter autoclave.

And how was the lining applied? After the steel internal surface was well prepared by scraping and using highly abrading grinding stones, two coats of primer adhesive were given followed by laying on of the prepared rubber sheets (approximately 1.5 mm in thickness) by hand, which were rolled with a knurled tool in order to eliminate trapped air from between the sheet and the metal. The sheets were joined perfectly with taper-cut edges overlapping with each other. The number of desired sheets were applied thereafter one above the other, after roughening and cleaning the surface with solvent, until the required thickness was reached. After inspection, the product was vulcanised.

The article mentions strict control at every stage of manufacture to obtain fault-free lining thus ensuring maximum safety to the steel casing of the rocket. The control parameters started from checking the quality of raw materials, through surface preparation of the metal, to verification of the physical and chemical parameters of the lining sheets during their manufacture and application, as well as after vulcanisation.

This brilliant description of rubber lining and of its failure after providing the required performance of protection during even the shortest duration in the space industry is also relevant today for the application of rubber lining in chemical and other process industries; the choice of materials, techniques and controls should be put into practice.

Rubber linings are passive protection against corrosion of plant and equipment in chemical process industries. Rubbers act as sacrificial materials reacting or un-reacting with the corrosive media, diffusing the liquids or not diffusing, swelling by itself or not swelling, permeating or not permeating gases or fumes, abrading or wearing by the slurry particles, getting ozonised or oxidised; but still protecting the metal surface beneath it, during its considerable lifecycle under severe and stressed conditions. Rubber linings are applied in sheet form intimately adhering to the base metal, wood or concrete surface. They are not coatings but are solid flexible foils or membranes usually of 3 mm or 6 mm thickness, or more in certain instances.

The raw material bases are natural or synthetic rubbers. Rubber is used for corrosion/abrasion proof linings more than any other material because of its proven superiority in this service at a relatively low cost. Fertiliser, electroplating, ore-refining, petrochemicals, chlor-alkali and paper industries invariably turn to rubber linings, in preference to other types of linings, for their high resistance to corrosion and abrasion. Moreover, the variety of rubbers, both natural and synthetic, available and the flexibility to serve under wide temperature and pressure ranges, made rubber linings the worldwide accepted anticorrosive and antiabrasive media.

According to the National Association of Corrosion Engineers-International (NACE) nearly $10 billion is being lost each year through corrosion in the industries in the developing countries. This loss erodes into a substantial percentage of the Gross Domestic Product (GDP) of these nations. Preventing this industrial corrosion reduces the loss and damage to plant and equipment considerably on one side and offers a very huge potential for the anticorrosive rubber lining industry on the other.

During the presynthetic rubber period only natural rubber compounds, either soft or hard (ebonite), were used for lining the cast iron or riveted structures. Natural rubber by itself is resistant to many corrosive chemicals. In the presynthetic rubber era low-swelling compounded natural rubber was in use for oil resistance in ‘O’ rings and oil seal and packing manufacture. The riveted construction of the equipment was later complemented by gas-welded constructions. When electrically welded construction was becoming popular in the chemical industry rubber lining became increasingly popular too. It found a wide area of application as anticorrosive rubber lining and for acid resistant special products of all kinds such as calendered sheets, extruded profiles, moulded goods, hand built items such as expansion joints, customised sheets and foils and flexible covers, or in solution form for exterior coatings for atmospheric protection. The advent of synthetic rubber served to increase its potential applications.

Though for a number of years the application of rubber lining was limited to small fabricated tanks, vessels and pipes (which could be dealt with in a factory setting) the necessity arose to rubber line large storage tanks, ducts and vessels at clients' sites and other outdoor installations due to the rapid growth, upgrading and modernisation of the chemical process industries.

First, it was carried out by vulcanising the lining with saturated steam on site. Then rubber compounding and processing techniques were developed where the new compounds could be vulcanised at lower temperatures, i.e., at 100 °C using hot water. A few decades ago, rubber compounds and adhesive bond solutions were developed which were capable of self curing at ambient temperature, over a certain period of time such as 7 to 10 days. Thus it was possible to rubber line equipment of any size. Storage tanks of surface areas 2000 to 5000 m^2 were no longer rare. In Zambia a few decades ago, around 10,000 m^2 of lining was carried out for a thickener plant in a copper-refining project. The lining of unvulcanised sheets with chemical vulcanising processes, such as painting an accelerating solution on, had not been fully accepted by chemical engineers. Today all forms of vulcanisation are in use and each has special applications, advantages, disadvantages and limitations. For example, for vacuum environments an autoclave vulcanised lining is preferred over one cured by a self-curing method or an open steam curing method. For rubber lining on site the most suited method is cold bonding.

It is to be noted that there is no alternative material exacting the qualities of natural or synthetic rubbers for chemical resistance applications.

2

Rubber – An Overview

Natural rubber is obtained from the *Heavea brasiliensis* tree. This tree is found in abundance in areas with a tropical climate, such as Brazil, Venezuela, Malaysia, India and East Coast African countries. The traditional method of slitting the bark and letting the milk drip to form a solid mass called 'latex' continues to be the sole method of obtaining natural rubber.

Natural rubber was the only high polymeric material serving humanity until the advent of polymer technology. Hence the term 'rubber' until that point only referred to this natural substance. Since its discovery, the use of rubber has become widespread; when worldwide demand increased, the natural rubber available was inadequate. This made it necessary for scientists to obtain substitutes for natural rubber.

The traditional view that rubber properties are related to high unsaturation lead to numerous theories of the elastic behaviour of rubber based on geometric structures resulting from the unsaturated linkages [1]. The material's susceptibility to chemical action is attributed to the unsaturation of the natural rubber molecule. Physical properties that are not intrinsically dependent upon the carbon-carbon double bond configuration (C=C) are tensile strength, elasticity, rebound, elasticity recovery, mechanical orientation, electrical properties and solubility. These are primarily dependent on the molecular weight distribution, entanglement and coiling up of long chain molecules.

The chemical unsaturation, which is extremely important in allowing vulcanisation to take place, is the greatest weakness of the natural rubber molecule, since it allows the oxidation reaction. Therefore, in the case of soft rubber goods, moulds, extrusions or sheetings, only a fraction of the available double bonds are utilised in the vulcanisation process with sulfur. The large residual unsaturation is responsible for the pronounced chemical reactivity of the soft rubber. It is this unsaturated character which makes natural rubber very susceptible to oxidation by oxygen, ozone and other oxidising chemicals with consequent deterioration and disintegration on ageing. This also explains the material's lack of resistance to such chemical agents as strong mineral acids, and also its lack of heat stability.

It may be interesting to compare the saturation levels of both natural and butyl rubbers. Cured butyl rubber (IIR), with its predominant saturation, is resistant to many acids making it a viable protective lining while cured natural rubber (NR), with its predominant unsaturation, is used as a protective lining because it forms an acid resistant protective layer by reacting with acids, especially hydrochloric acid (HCl).

In appearance, IIR resembles natural crepe rubber, since it is an aliphatic, hydrocarbon polymer; the density being the minimum (0.91) attainable for elastic materials of this type. In IIR, the original unsaturation is very small, and even this low unsaturation is greatly reduced and may even be entirely eliminated during the compounding and curing process. The fact that once vulcanised it is extremely resistant to chemical attack is understandable because it becomes, after vulcanisation, not only a nonthermoplastic strong elastic material, but also essentially a chemically saturated product as well. This means that whilst physically vulcanised IIR resembles soft vulcanised natural rubber, chemically it may be considered most similar to ebonite; almost devoid of any unsaturation.

Butyl rubber is extremely resistant to acids and other deterioration influences. Like natural rubber, it is not resistant to aliphatic hydrocarbon but does show a surprising resistance to benzene, ethylene dichloride and oxygenated solvents. On the subject of resistance to ageing and chemicals, Staudinger states that 'Every reaction that shortens the length of molecules liquifies to mass, and conversely, every reaction that lengthens the atomic chain tends to solidify the mass. These two actions correspond exactly to the chief transformations which rubber undergoes, which are nothing more than changes in consistency namely a fluidising degradation and hardening degradation [2]. When both NR and IIR are compared after an accelerated ageing test, IIR, of low unsaturation, undergoes only the degradative softening type of deterioration under the severe influence of heat, light and air, and NR, predominantly of high unsaturation, undergoes hardening deterioration.

For the most effective development of rubber-like elasticity, permanent interlocking of the chain molecules at a few points along their length to form a three dimensional network is desirable. The crosslinks should be sufficient in number to ensure a permanence of structure that is a suppression of viscous flow and yet not so numerous as to seriously restrict the internal segment mobility of the polymer chain. A very convenient way of affecting this crosslink is to react natural rubber with sulfur. Sulfur linkages are formed between the chains with strength comparable to those linking the carbon atoms to the polyisoprene chains in the starting material. This process, known as vulcanisation, occurs as a consequence of the presence of highly reactive double bonds in the polyisoprene chains. The effect of vulcanisation is to raise the glass transition temperature of the amorphous polymer and to lower the melting point of the crystallites formed on stretching the amorphous material.

The vulcanised, or crosslinked, rubber hydrocarbon is hetrogeneous in respect to molecular weight. These crosslinked polymers are regarded as giant three dimensional molecules of indeterminate molecular weight [3]. Such molecules swell in solvents to an extent that depends on the nature of swelling agent and also to the extent of crosslinking.

The more highly crosslinked, the less the swelling in a given solvent. As the number of crosslinks is increased, these polymers, e.g., ebonites containing more than 30% sulfur combined with rubber, show progressively less segmented mobility of the chains between the cross linking points, and consequently lose their long range elasticity and resemble ordinary brittle solids in their elastic behaviour.

Many of the mechanical properties of the highly polymeric materials are molecular weight dependent, although the effect may be overshadowed by other factors such as chain orientation or crystallinity. A polymer of low molecular weight is very weak. As the molecular weight increases the mechanical properties also increase.

2.1 The Origins of Polymer Science

During 1927, Reimer and Tiemaun [4–8] published their work on amino acids and in a short period this opened an entirely new vista for process industries. Polymer technology became a new study and research work in these avenues yielded a wide range of new materials. Research on the chemistry of natural rubber revealed an isoprene link; a monomer of the terpene group very much like the aminoacid links in large molecules of protein. Consequently, polymerisation of isoprene yielded polyisoprene; which was found to have similar properties to natural rubber. This started an avalanche of other polymers using styrene, butadiene, chlorobutadiene, etc. Thus, the beginning of synthetic rubber was announced. The scientific community felt the incongruity of the old term ‘rubber’ and coined a new term to cover the entire range, called ‘elastomers’ which is a contraction of ‘elastic polymers’.

Polymers, which include synthetic materials such as plastics, vinyl, Nylon, polyester, and polytetrafluoroethylene (PTFE) and natural materials such as silk, cotton, starch and cellulose, are used in our lives every day. Since scientists began to control and manipulate polymers in the 19th Century, chemists have created hundreds of durable synthetic polymeric materials from just a few simple building blocks. Experimentation continues today with increasing polymer uses for applications in chemical, instrumentation, mechanical, electrical and electronic industries.

Polymers have been described as giant molecules of a compound of simple small units [9]. The word polymer comes from the Greek words ‘poly’ meaning many and ‘mer’ meaning unit. A monomer is a single unit and a dimer is composed of two. A polymer can have many millions of individual units. These units do not have to be identical. Polymers with two or more different units are called copolymers. The most common forms of copolymers are called ‘random copolymers’ which contain different types of monomers in random order and ‘block copolymers’ which contain stretches of different monomers: for example five A monomers followed by five B monomers. Nylon is a typical copolymer that is composed of two repeating units, a di acid molecule and a diamine molecule. PTFE is a linear polymer formed by the repeating molecular unit CF_2 – a carbon molecule and two fluorine molecules. The special properties of PTFE (widely known by the trademark Teflon) such as its non-adhesive nature and low friction characteristics, make it ideal for non-stick coatings on pots and pans. It is also used to insulate wires, cables and motors.

A polymer characteristic can be influenced by a small number of features. The first is the length of the polymer, which can run from ten units to millions of units. At the molecular levels, the chains of molecules can be branched, unbranched or crosslinked to other strands. They can be aligned or unaligned. They can be flexible or inflexible. Changing any of these characteristics affects the properties of its melting point, flexibility, rigidity and elasticity. Several polymers have been made from surprisingly few simple starting units. The five most common starting molecules are ethylene, methane, propylene, benzene and butylene. All these are obtained form crude oil and natural gas. These molecules are the lightest fractions of crude oil, which is a rich mixture of various hydrocarbons.

2.2 The Polymerisation Process

The most common way of creating polymers is through addition polymerisation - a process which involves three steps, namely polymer initiation, addition and termination.

In initiation, a chemical creates an active free radical. This free radical is quite unstable but very reactive because of unpaired electrons in the molecule. This is a monomer with an unpaired electron. Once this is formed, the addition begins as the free radical reacts with another monomer radical. This reaction results in the formation of another monomer and the chain reaction is started as the addition continues with subsequent monomers. Within a fraction of a second, addition of tens of millions of monomers takes place. Finally, when two of the free radical ends encounter each other and bond together to form a large molecule, the termination occurs as the unpaired electrons are joined.

As discussed, the term elastomer is the modern word to describe a material that exhibits rubbery properties, i.e., which can recover most of its original dimensions after extension or compression. The pioneering work of Staudinger in the 1900s motivated polymer chemists to accept that such rubbery behaviour results from the fact that the material is composed of a tangled mass of long-chain flexible molecules and when such a material is stretched, the individual long-chain molecules are partially uncoiled, but will coil up again when the force is removed because of the kinetic energy of the segments of the polymer chain. The flexibility of such polymer-chain molecules is actually the result of the ability of the atoms comprising the chain to rotate around the simple bonds between them.

The properties of elastomeric materials are greatly influenced by the strong inter-chain, i.e., intermolecular forces which can result in the formation of crystalline domain. Thus the elastomeric properties are those of an amorphous material having weak inter-chain interaction and hence no crystallisation. At the other extreme of polymer properties are fibre-forming polymers, such as Nylon, which when properly oriented lead to the formation of permanent crystalline fibres. In between these two extremes is a whole range of polymers, from purely amorphous elastomers to partially crystalline plastics, such as polyethylene, polypropylene, polycarbonate, etc.

An interesting class of material is comprised of these amorphous elastomers that show the ability to undergo a temporary crystallisation when stretched to a high extension, thus virtually becoming fibres, which then retract to their original dimension when the force is removed. Such crystallising rubbers can demonstrate high tensile strength in the stretched condition, but revert to amorphous state when the force is relaxed because of relatively weak inter-chain or intermolecular forces.

2.3 Developments in Synthetic Rubber

The rapid development of the synthetic rubber industry throughout the war-torn world in the 1950s established the need for some organisation in which the issues of mutual interest could be discussed between the operating synthetic rubber plants in various countries. As a result the International Institute of Synthetic Rubber Producers was constituted, having its main office located in New York, USA.

2.4 Vulcanisation

Charles Goodyear was a key figure in the development of the rubber industry. He found that, by adding certain nonmetals like phosphorous, sulfur and arsenic to the elastomers, they can be hardened and imparted with the property of ‘elasticity’ in a very short timespan [10]. Thomas Hancock of London [10] commercialised this; he called this process ‘vulcanisation’ or ‘curing’ and he also found sulfur to be the best agent for this. Varying the addition of sulfur can control the hardness. Current rubber products have in addition to sulfur, fillers and other agents like accelerators, antioxidants, etc. But for all this, vulcanisation set the trend.

Goodyear discovered vulcanisation whilst he was in prison. In the process of his experiments he guessed that by mixing the raw gum rubber with magnesia and then boiling it in lime he could get rid of the stickiness in rubber. He made some non-sticky samples using this procedure. This was possibly the origin of the use of inorganic accelerators which are now widely used in the manufacture of chemical resistant ebonites as well as soft rubber compounds. He later found that *aqua fortis* (nitric acid) produced a strong curing effect on the rubber since the surface was hardened when the rubber was treated with it. He mistakenly thought that he had discovered the secret of vulcanisation. But he found later that nitric acid destroyed rubber. This may have been the earliest test of chemical resistance of gum rubber; unintentionally conducted by Goodyear with a different purpose.

Though nitric acid was not the cause of vulcanisation it enabled the first steps towards the process of manipulating rubber in this way. Since the nitric acid episode did not solve his problem of rubber stickiness successfully he made further trials and finally discovered true vulcanisation accidentally while boiling gum rubber with sulphur, when a lump of the sulphured gum fell on the stove. It remained for the vulcanisation process to be perfected so that an accurate formula and the exact quantity or degree of heat could be ascertained for manufacturing various kinds of products. This subject later became a focus of Rubber Compounding Technology.

2.5 Range of Rubbers

The outstanding property of rubber in general is resilience, or low modulus of elasticity. The flexibility and physical properties of rubber account for its application in general engineering and automobile industries; whereas its chemical, wear and abrasion resistance as a sacrificial material, plus its insulating properties are utilised in many corrosion and erosion applications in process industries. Rubber lined mild steel, pipes and tankages have been standard materials of construction for hydrochloric acid service for many years.

A general rule is that natural rubbers have better mechanical properties than the synthetic rubbers but the latter have better corrosion resistance. Natural rubbers are superior in certain applications such as with wet chlorine and hydrochloric acid. Natural rubber-based ebonite provides good resistance for such application at higher temperatures up to 90 °C. Corrosion resistance increases with increasing hardness, from a range of 60 on the Shore A scale to 80 on the Shore D scale. Higher proportions of sulfur increase the hardness range in the Shore D scale.

The variety of rubbers available to us to make innumerable types of compounds can be overwhelming. Consider the following list:

- Natural rubber
- Polyisoprene
- Polybutadiene
- Styrene-butadiene
- Butyl rubber
- Ethylene propylene rubber
- Nitrile rubber
- Polychloroprene
- Chlorosulfonated polyethylene
- Silicone rubber
- Polyurethane rubber
- Polysulfides
- Fluro rubbers

To complicate the matter further any one of the above can be blended with another, to produce many new varieties of rubber compounds.

Originally, the rubber industries were supplying many industrial sectors such as fertiliser, caustic soda, paper and pulp, pharmaceuticals, ore and mining. To meet the exacting standards and the technological advances, which were occurring at a furious rate in the process industries, the rubber technologists were required to develop new kinds of elastomers and compound formulating techniques [11] to handle various kinds of corrosive substances. This was supported by a range of research in the field of polymer technology [12-18]. Finally, when the scope for elastomers became infinite, the subject of dealing with elastomers for application in the chemical industry for lining purposes developed into anticorrosive rubber lining technology, a specialised area.

In continuous process industries, where a replacement of equipment cannot be done overnight, sustaining the life of that equipment becomes imperative. For example, a weak solution of sulfuric acid can corrode a two-inch wall of steel in just 8 months. If direct contact of the acid with the metal can be avoided through a protective, acid resistant lining, the life of that equipment can be enormously increased. If we consider the entire spectrum of chemical processing industries, the range of corrosive media handled by these industries is wide. Of course, all the corrosive and abrasive conditions cannot be handled by elastomeric lining alone, but of all the protective linings used, elastomeric lining commands an overwhelming majority.

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3

Rubber Lining for Corrosion Protection in the Chemical Industry

It is a fact of modern society that many ordinary items of everyday use are obtained from complex chemical processes. Life-saving drugs, capsules and tablets, as well as perfumes, are derived from coal. From crude oil and petroleum gases, we obtain fertilisers, plastics, synthetic rubbers, pesticides, detergents, fabrics and coatings and paints. From seawater we can produce vital heavy chemicals including caustic soda, sodium chloride, sodium hydroxide, hydrochloric acid and so on.

During the last few decades, products for road construction have been made in the chemical industry, resulting in heavy demand for raw materials. In turn, this required an increase in transportation of various types of chemicals such as phosphoric acid, hydrochloric acid, sulfuric acid, caustic soda, chlorine gas and other corrosive fumes and gases. The construction of tankers and vessels for transporting these chemicals is a complex job. These cargos of chemicals often pose tremendous challenges and difficulties from a corrosion and safety point of view, as well as the potential atmospheric pollution threat. We have seen many instances of pollution by crude oil leakages from ship tankers into the sea. An incident in 2004 [1], of the bursting of a fibre glass tank holding hydrochloric acid at the Univar's bulk chemical facility near Twinsburg, Ohio, USA, made media headlines in state and federal journals, necessitating President Bush's visit to the site of the bursting of the tanker. Univar is a giant chemical facility operating throughout North America and Canada, transporting bulk corrosive chemicals in tankers for various destinations in the continent.

Many people are unclear about the fact that chemistry has a relevance to everyday life. DuPont's slogan of 'Better things for better living … through chemistry' [2] is relevant in this context. The food we eat is grown with phosphatic, nitrate and urea fertilisers and the food crops are protected with pesticide sprays. The clothes and garments we wear are mostly made of artificial fibres derived from petrochemicals from petroleum gas. Detergents, anti-freeze and synthetic rubbers are all derivatives of petroleum. Many patent medicines are produced from phenol and chlorine [3], a derivative of coal and a by-product of electrolysis of sodium chloride, respectively. Many electronic goods, consumer products, toys, packaging materials, etc, utilise rubbers or plastics. The raw materials for the chemical industry, as with any other raw materials, have to be transported from where they are produced to where they are used.

The main chemicals transported in bulk in tankers are heavy chemicals. These include substances that are produced in large quantities. The most common heavy chemicals are:

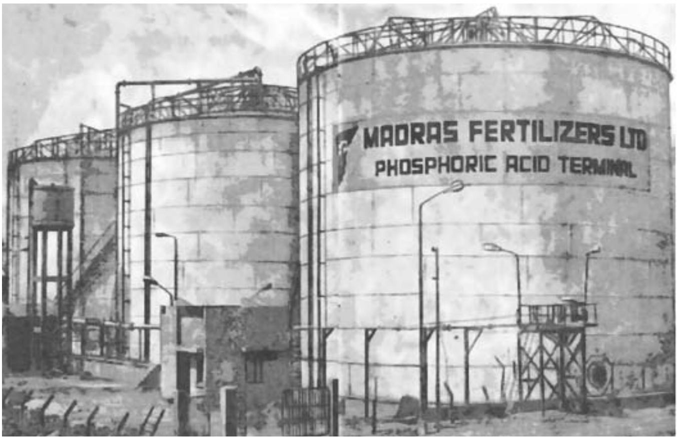
- Sulfuric acid: used in the manufacture of phosphate fertilisers, explosives, removal of oxides from metals in storage batteries and in drying towers in chlor-alkali plants
- Phosphoric acid: used in the manufacture of superphosphates
- Nitric acid: used in explosives, nitrate fertilisers and in electroplating units
- Caustic soda: in liquid and flake forms are used in dye and textile industries
- Other heavy chemicals like hydrochloric acid and chlorine are used in pharmaceutical industries

The potential hazards of these chemicals are enormous and their corrosive effect in the respective industries is phenomenal. The National Association of Corrosion Engineers often gives warning signals [4–6] that billions of dollars are being lost very year through corrosion in such industries, heavily consuming the gross domestic products of many countries; in some cases higher than 4%.

Prevention of this industrial corrosion reduces the monetary loss and damage to the plant and equipment considerably, with a reduction to the pollution threat at a great level. This preventive method through employing anti-corrosive thin coatings and lining reduces loss due to down time of equipment, machineries and transport systems. It is in this capacity that rubber lining occupies a prominent place in helping to reduce industrial loss, due to the corrosive chemicals handled in the plant and transported in tankers from destination to destination, resulting in a huge market potential for the anti-corrosive rubber lining industry.

Rubber lining is one of the best known and proven methods employed to protect chemical process equipment against the corrosive and abrasive attacks of the fluids. One of the most important characteristics of both natural rubber and synthetic rubber is the remarkable resistance to corrosive chemicals, fumes, acids, alkalies and other salt solutions. Without protection, corrosion would be so extensive that most products of modern technology could not exist. The variations and large percentages of corrosive impurities have little influence on the rubber lining up to temperatures as high as 100 °C to 120 °C.

This is the decisive technical difference between rubber lining and stainless steel. Even the deposits of solids or incrustations of a very hard nature, will not have any significant negative impact on the rubber lining. Rubber is the most low cost anti-corrosive lining for most uses as other anti-corrosive materials are either very expensive or cannot be used due to other drawbacks. The issue of service life of rubber lining is of importance. For example, it has been reported that the rubber lining of one phosphoric acid storage tank at the Harbour Terminal belonging to Madras Fertilisers Ltd in India has secured a life of 10 to 15 years with little sign of degradation [7]. From the low degree of degradation, which can be assumed to be negligible, it appears that the lining can give 5 more years of service successfully. Figure 3.1 shows an example of a phosphoric acid storage tank in Chennai, India.



Rubber lining by the Cold Bond System: three of the four phosphoric acid storage tanks, rubber lined for Madras Fertilizers Limited. These three tanks are each 24 metres diameter and 14.4 metres high; perhaps the largest in the world ever to be rubber-lined.

Figure 3.1 Rubber lined phosphoric acid storage tank at Chennai Harbour Terminal, India

The technical advantages of a long-term nature are supplemented by considerable economic advantages. The combination of mild steel and rubber lining as materials of constructions in a chemical industry is much cheaper than stainless steel. An example is given by Heinrichs as [8]:

Construction of tanks in 10 mm thick plates:

- In stainless steel AISI 316, the approximate cost is US$ 900/m^2
- In carbon steel with rubber lining, the approximate cost is US$ 550/m^2
- The difference is US$ 350/m^2, equivalent to 60% in relation to the tank surface. Considering a total surface of 7000 m^2 this translates to a saving of US$ 2.45 million.

The main types of rubber used in the field of anti-corrosion are natural rubber, polyisoprene, polybutadiene, polyurethane, butyl rubber, styrene butadiene, nitrile rubber, ethylene propylene rubber, polychloroprene, silicone rubber, and vinylidene rubber. The wide ranges of available natural and synthetic rubbers offer a versatility of properties to suit almost every corrosive condition encountered in the process industries.

Soft rubber linings are resistant to the diffusion of ionic chemicals through the thickness of the lining. But hard rubber or 'ebonite' linings have strong resistance to diffusion. As diffusion is inversely proportional to the thickness of the lining, the resistance to diffusion can be quadrupled by just doubling the thickness. Raw rubber cannot be used for lining as such; so the final rubber used for lining is prepared by blending many ingredients with the raw rubber such as carbon black, talc, graphite, fillers, etc. To suit individual requirements different formulations are designed and this requires a very high level of skill and knowledge. Moreover, to achieve a good lining, the vessel to be lined should also be free from defects like blowholes, sharp edges, air inclusion and pitting on the surface. Improper lining, either due to defective compounding of rubber or due to the above defects on the vessels, will lead to premature failure of the lining and thus allow corrosion. Table 3.1 gives an idea on the application of rubber linings in the process industries.

Table 3.1 Applications of rubber lining in the process industries

Type of Industry	Equipment	Rubber Used
Caustic soda	Chlorine drying towers	Hypalon
Chlor–alkali	Primary cell trough covers, end boxes	Natural rubber, ebonite, Neoprene
Electroplating	Plating tanks	EPDM, ebonite, butyl rubbers
Fertiliser	Phosphoric acid storage, tanks, fittings	Natural soft rubber, semi-ebonite, Neoprene, butyl rubbers
Halogens	HF absorbers, fluoride dryer, centrifuges	Natural rubber, ebonite, semi-ebonite
Ores and mining	Ball mills, rotary vacuum, filters, digesters.	Natural soft rubber, semi-ebonite, butyl rubber
Organic/aromatic	Distillation/stripping columns, storage tanks	Viton
Pharmaceutical	Crystallisation tanks, centrifuges, digesters	Semi-ebonite and butyl rubber
Pulp and paper	Hypochlorite towers, alkali extraction towers, pipes, fittings	Natural rubber
Thermal plants	Anionic and cationic tanks	Soft natural rubber, Neoprene, ebonite

3.1 Types of Corrosion

Various forms of corrosion in chemical industry have been categorised into eight areas, as discussed below.

3.1.1 Uniform Attack

Uniformity of attack on all the areas exposed to corrosion.

For example, the acid will uniformly corrode a piece of mild steel sheet immersed in dilute sulfuric acid. Corrosion by uniform attack accounts for the greatest loss in practice. The incidence of this kind of corrosion can easily be detected and remedial measures taken.

3.1.2 Galvanic Corrosion

The dry cell battery is a typical example of galvanic corrosion, or two metal corrosion as it is otherwise called. When two dissimilar metals are immersed in a conductive or corrosive medium, there is always the potential for a change in them. Once these metals are connected this difference induces electron flow between them. The less corrosion resistant metal is attacked more than the more resistant metal. This is an electrochemical process. In the case of a dry cell battery, the carbon electrode acts as the cathode (the more resistant materials) and zinc as the corroding anode. The natural phenomenon of corrosion is used in this case for producing electricity.

3.1.3 Crevice Corrosion

Stagnant solution in small holes, gasket faces, lap joints, surface deposits, cervices under bolts and rivet heads are all sources of crevice corrosion. It is also called deposit or gasket corrosion.

3.1.4 Pitting

This form of corrosion results in pits or holes in the metal. Generally a pit has a diameter which is less than the depth. These pits will normally be filled with the corrosion products and will rarely be detected before leaks starts. So pit failure will be sudden and no prevention can be employed as would normally be done in the case of other slow process of perceptible corrosion. The general tendency of pits is to grow in the direction of gravity from the horizontal surfaces downwards. Vertical surfaces show less of this attack.

3.1.5 Intergranular Corrosion

It is generally noted that the grain boundaries are particularly reactive. This is the reason for higher corrosion at grain boundaries, in certain cases, rather than at the grain surfaces.

3.1.6 Selective Leaching

Corrosion sometimes removes one element from a solid solution of alloy and this process is described as selective leaching. This can easily be seen with brass where the surface changes to a copper colour from the original yellow.

3.1.7 Erosion Corrosion

When there is a relative motion between the corroding liquid and the metal or rubber surface the rate of attack of the damage to the surface is increased. The process is called 'sweating off' with the corrosion product thus exposing the base surface again to corrosion. Otherwise the corrosion product (as a newly formed protective layer) would have prevented or slowed down further corrosion, just as in the case of hypochlorous acid solution on natural rubber lining, where the protective corrosion products exhibit very low cohesion and as such prone to be wiped off by the liquid unlike wet chlorine or hydrochloric acid which form a strong layer of corrosion product well adhered to the rubber surface.

3.1.8 Stress Corrosion

When tensile stress is applied in the presence of a corrosive medium the metal cracks and this is called stress corrosion. This does not include cracking owing to hydrogen embrittlement. In the case of stress corrosion, the metal is not affected uniformly and most of the surface is unaffected while fine cracks proceed through it. In stress corrosion, the preferred lining is rubber lining rather than any rigid linings such as fibre reinforced plastics lining, rubber being elastic enough to withstand stress due to thermal expansion of the metals.

The need for protection against corrosion is a prime requirement in the chemical industry. Rubber lining has proven usage in this sector over many decades and has outstanding durability and dependability. A rubber lining, whether soft or hard, is a good selection for corrosion protection in plants in which processing is carried out with acids, alkalies, salt solutions, etc. A wide variety of different plant and equipment including tanks, pressure vessels, vacuum vessels, evaporators, pipes, agitators, stirrers, impellers, runner fans, centrifuges, filter drums and their components, scrubbers, electrolytic mercury cells and electrolyte tanks are effectively protected against corrosion by rubber linings. In chemical plants, the equipment that is protected against corrosion may be made of metal carbon steel, aluminium, stainless steel, concrete or wood.

3.2 The Fertiliser Industry

The growth in world population necessitated the increased use of fertilisers to augment increased supply of food. In the fertiliser industry the manufacturing process involves the use of sulfuric acid, hydrochloric acid and phosphoric acid. The plant, equipment and piping system that come into contact with the acids must be dependably protected against the corrosive attack. Rubber as a construction material is well able to satisfy the variety of requirements on it in this area, which are [9]:

- Resistance to elevated temperatures up to 100 °C and higher
- Resistance to abrasion by particles of solids and slurries and in fumes
- Vacuum-tight bonding of the rubber with the metal
- Surface free of pin-holes
- Chemical resistance

Figure 3.2 illustrates a gypsum agitator in a fertiliser plant being rubber lined.

Figure 3.2 Rubber lining of gypsum agitator for a fertiliser factory

The resistance of certain rubbers to liquid ammonia with a boiling point of – 33 to 35 °C, which is widely used in fertiliser industry are:

- Natural rubber: eminently suitable for cold ammonia gas
- Butyl rubber: resistance is excellent and can be used for liquid ammonia
- Polybutadiene rubber: not applicable
- Neoprene: highly impermeable to ammonia gas rather than nitrogen gas
- Silicone: satisfactory resistance
- Viton: severely attacked by anhydrous ammonia

3.3 Power Plants

Rubber linings have been used for a variety of different applications in power plant for corrosion protection. Special mention can be made of the water treatment plants and scrubbers in desulfurisation of flue gas. For these applications, the rubber lining can be applied in the manufacturer's works or construction site. Rubber linings, especially of butyl or bromobutyl rubbers, have proved themselves eminently in flue gas scrubbers, tanks, pipes and fittings, cyclones and centrifuges. A typical example is the scrubbers in the wet systems where rubber linings have to be applied to thousands of square meters at heights of 70 m and above at times. Even under severe conditions of high temperatures, abrasion by solid particles and permeation by water and gases, the rubber linings have proved to be appropriate materials of construction for protection against corrosion, giving service lives of over 15 years in power plants [10].

3.4 Treatment of Ores

In almost all mining of copper, nickel, iron or gold, acids come into play. The ore must be bleached out of the sludge by treatment with acids. The process takes place in huge tanks up to 30 m in diameter and 5 m in height. The tanks of concrete or steel cannot withstand the aggressive corrosive chemicals employed and the resulting abrasive environment. These tanks must be protected against corrosion and erosion. For decades rubber linings have been successfully used for this purpose.

3.5 The Chlor-Alkali Industry

The chlor-alkali industry has huge requirements for rubber linings based on ebonite, natural soft rubber, Neoprene and chlorosulfonated polyethylene. These are widely used to provide corrosion protection as well as ozone protection, in various equipment such as electrolytic mercury cells, reaction tanks, drying towers, scrubbers, pipes and fittings, etc. The wet chlorine produced as a result of electrolysis of brine solution in the cells is the most corrosive, in addition to the hydrochloric acid which is formed during the process. The corrosion protection is provided by the reaction products of chlorine or hydrochloric acid which form a layer of chlorinated rubber above the base rubber surface. In the case of natural rubber the corrosion protection is given by these reaction products, namely chlorinated rubber or rubber hydrochloride. In the concentrated ozone atmosphere in the cell house, Neoprene linings and components are used. In drying towers where sulphuric acid is handled, chlorosulfonated polyethylene is used.

3.6 Mercury Cells in the Caustic Soda Industry

In order to understand how anti-corrosive rubber linings are used in the caustic soda industry it is useful to have a broad understanding of the design, construction and operation of the process, mainly about the cell house where corrosion is severe. A brief description of design, construction and operation of mercury cells in the caustic soda industry is given next [11].

The production of sodium hydroxide (caustic soda) follows Faraday's law according to which 96500 coulombs (amp.secs) of electric charge entering a cell will produce one gram equivalent of reaction product at each electrode. Because of side reactions that follow, the cells usually require more than this amount of current to produce one gram equivalent of sodium or its corresponding sodium hydroxide, during the electrolysis of sodium chloride. The ratio of the theoretical to the actual current consumed is defined as the current efficiency. In conventional cells the current efficiency is around 95%. The higher the current load (kA) the higher is the output of sodium hydroxide. Figure 3.3 shows an example of a cell house.

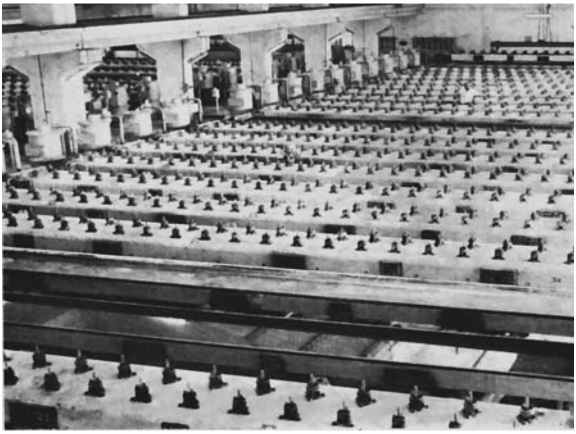


Figure 3.3 Cell house in a caustic soda plant

The mercury cells within the cell house consist of three units:

- Primary cells (known as the electrolyser) where sodium chloride is electrolysed to sodium and chlorine. Sodium combines with mercury to form sodium-mercury amalgam.
- The secondary cells (also called the denuder or decomposer) in which the sodium amalgam supplied by the primary cells reacts with pure water forming caustic soda and hydrogen releasing mercury for recirculation.
- The mercury pump, which takes mercury from the secondary cells and feeds it to the primary cells.

The electrolyser consists of a rectangular trough with a cover on top connected at both ends to the end boxes. The box at the mercury inlet is called the inlet box, and the other is the outlet box. The trough is of mild steel construction with ebonite lined bottom and sides. The covers are of mild steel construction with ebonite lining on the inside surface or only of rubber sheets called flexible cell covers. The covers have holes for fixing anodes.

The anode gaskets and rings are of soft and ebonite rubber, respectively. The inlet box is of rubber lined mild steel construction having a feed brine (sodium chloride) distributor and mercury seal.

The inlet box is constructed so that it distributes the mercury uniformly across the entire width of the cell trough. The anodes are fixed to the cover to hang over the cell bottom. The trough is installed on an inclined frame. The mercury and the feed brine flow from the inlet to the outlet end and the seal arrangement in the outlet box allows only the amalgam to flow out, while the depleted sodium chloride solution (brine) is taken out from the overflow nozzles fixed at the end of the trough.

One of the important constructional features of the outlet box is that its design should be such that the amalgam does not collide with the brine seal plate and thereby the carryover of the brine along with the amalgam to the secondary cell is minimum. Thus the sodium chloride content in the sodium hydroxide liquor is low. Mercury forms a flowing cathode. During the process of electrolysis sodium chloride gets electrolysed to sodium and chlorine ions sodium ions discharging the current at the cathode and amalgamating with the mercury. Chlorine ions discharge at the anode and rise above the brine level in the form of gas, which is taken out from the cell top. The width of the cell trough is generally a maximum of 2.5 meters. Although a short length of the trough is preferred, lengths of 10 to 12 meters are not uncommon.

The secondary cells are of two types; horizontal and vertical. In the secondary cells the amalgam is brought in contact with water, where the sodium electrochemically reacts with the latter to form caustic soda lye and hydrogen gas. The amalgam acts as the anode and graphite as the cathode. The sodium hydroxide lye acts as the electrolyte.

This brief description of the mercury cells in the caustic soda industry reveals how rubber can play a vital role as an anti-corrosive protective material in all the critical equipment and connected piping systems handling acidic and alkaline solutions gases and fumes.

3.6.1 Flexible Cell Covers in the Caustic Soda Industry

As previously highlighted, the cell covers in an electrolytic mercury cell used in the caustic soda industry can be made of mild steel with ebonite lining (called rigid covers) or can be of rubber sheets only (called flexible covers). The flexible rubber cover with holes for holding anodes is a two-layer construction. The bottom layer of 4 mm thickness is a chlorine resistant natural soft rubber of hardness 60 °A and the top layer is a 2 mm thick ozone resistant Neoprene rubber of hardness 60 °A as it is exposed to an ozone concentrated atmosphere in the cell house. The temperature of reaction in the cells is around 80 °C. The cell cover is expected to give a life of about 17 to 24 months to match with that of the anodes. Titanium anodes that may be used in place of the graphite anodes have a longer life and as such the compounds of the flexible cell cover will have to be designed with suitable compounding of both the natural rubber and Neoprene rubber layers with longevity of 24 months to match with the life of titanium anodes. The bottom layer reacts with chlorine producing a protective chlorinated rubber layer thus preventing further attack of chlorine. The top Neoprene layer is ozone resistant.

While compounding both natural rubber and Neoprene rubber the cell house conditions are to be taken into consideration in addition to the mutual compatibility of these two different base rubbers, with regard to their processing characteristics in the calender and curing systems. These compounds are separately calendered and doubled in a doubling devise while warm and then the doubled sheet is wound on drums of about 0.75 m in diameter; then tightly backed by a fine textured cotton duck fabric and cured in the autoclave for about 150 minutes at a temperature of 140 °C. The cured sheets are punched with anode holes. The moulded rubber gaskets and the anode holding rings are fixed with an epoxy-based adhesive.

The proven compounding practice for the natural rubber layer is to load it with 30 phr of graphite, 30 phr of semi-reinforcing carbon black filler and 50 phr of inert filler, china clay. A low sulfur curing system is adopted for heat resistance with a suitable antioxidant to prevent flex-cracking. A typical chlorine resistant soft natural rubber compound formula is given in Table 3.2.

Table 3.2 Typical chlorine resistant soft natural rubber compound

Substance	phr
Smoked sheet RMA1X	100
Zinc oxide	5
Stearic acid	3
Graphite	15
Plumbogine (fine graphite)	15
Fast extrusion furnace (FEF) black	30
Fine China clay	50
Automotive process oil	6
Cyclohexyl benzthiazyl sulfenamide	1.25
Sulfur	1.75
Nonox HFN (blend of arylamine)	1.00

The top Neoprene layer is an ozone resistant layer and at the same time it protects and supports the natural rubber layer beneath it. Therefore it has to be strong. Neoprene is capable of producing high tensile strength in the absence of reinforcing fillers. Many Neoprene (chloroprene) suppliers have reported gum strengths as high as 35 mPa [12–14]. While natural rubber tends to become soft and sticky on oxidation, Neoprene after prolonged periods of exposure tends to increase in modulus, decrease in ultimate elongation and become dry and hard. It is possible to find cracking in Neoprene vulcanisate after prolonged exposure to high concentration of ozone. It has been established that the dynamic properties of Neoprene vulcanisates are affected less than those of natural rubber at temperatures of 80 °C and above. For application in flexible cell cover a 2 phr of phenylbetanaphthylamine accelerator is good enough. Although on heat ageing the Neoprene compounds maintain good breaking strength they are prone to suffer increase in modulus, decrease in extensibility and increase in hardness. However, the tendency of Neoprene compounds to stiffen, lose elongation and finally become brittle at elevated temperatures can be minimised by using high concentrations of zinc oxide, curing to a high state, holding filler loading to a minimum, avoiding volatile softeners and using adequate doses of antioxidants. It was shown by researchers on Neoprene compounding, that non-reinforcing fillers like clay contribute to superior retention of elongation during heat ageing [15].

Ester plasticizers, which are used to produce vulcanisates for low brittle points, are the most deleterious in services involving exposure to ozone. The use of 4 phr of light calcined magnesia and 5 phr of zinc oxide produces a good balance between processing safety and cure rate. It is significant to note that in Neoprene, mineral fillers of the reinforcing types give higher tear strengths than equivalent amounts of carbon blacks. They also give better permanent set. A typical ozone resistant Neoprene compound for cell house application is given in Table 3.3.

Table 3.3 Typical ozone resistant Neoprene compound for cell house application

Substance	Phr
Neoprene WRT	100
Phenylnaphthylamine	2
Light calcined magnesia	4
Semi-reinforcing furnace carbon black	35
China clay	65
Naphthenic process oil (Ealsto 541)	10
Paraffin wax	1
Zinc oxide	5
Tetramethylthiuram disulfide	1
Sulfur	1

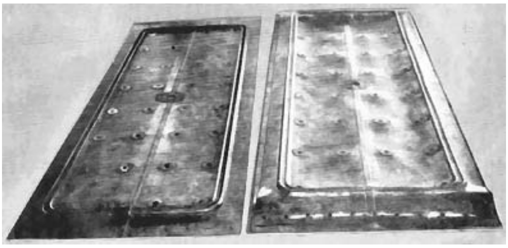


Figure 3.4a Flexible cell covers

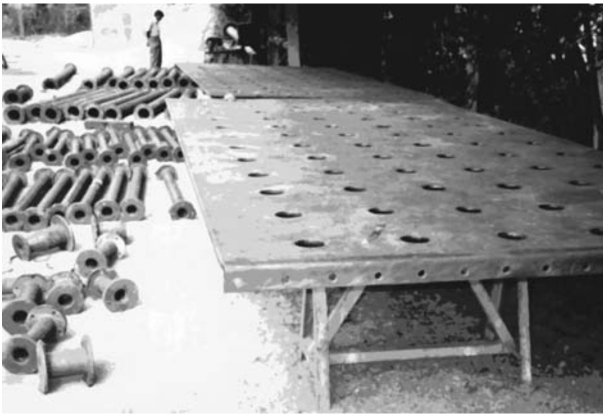


Figure 3.4b Rigid mild steel rubber lined cell cover

3.7 The Steel Industry

Different kinds of rubber linings are used in the pickling tanks, acid regeneration tanks, pipes, fittings, ducts and manhole covers. The electroplating tank lines can have lengths up to 130 m, joined with flanged faces of tanks. Mostly semi-ebonite rubber linings of special composition provide resistance to corrosive pickling acids and salts and electrical resistance. These linings are unaffected by fluctuations in temperature. Ethylene propylene (EPM) rubbers and butyl rubbers are also suitable choices for electroplating service.

3.8 The Transport Industry

For transporting hazardous substances by rail, road or on water, high demands are placed on the safety aspects in transit. For many years, rubber lining has been successfully employed to protect road tankers and ships' cargo tanks. Highly technical compounding has been developed over time to provide corrosion protection against particularly high chemical loadings and against changing loadings (as can frequently occur with transport containers). Figure 3.5 shows a rubber lined road tanker.

Figure 3.5 Foreground: rubber lined pipe fittings

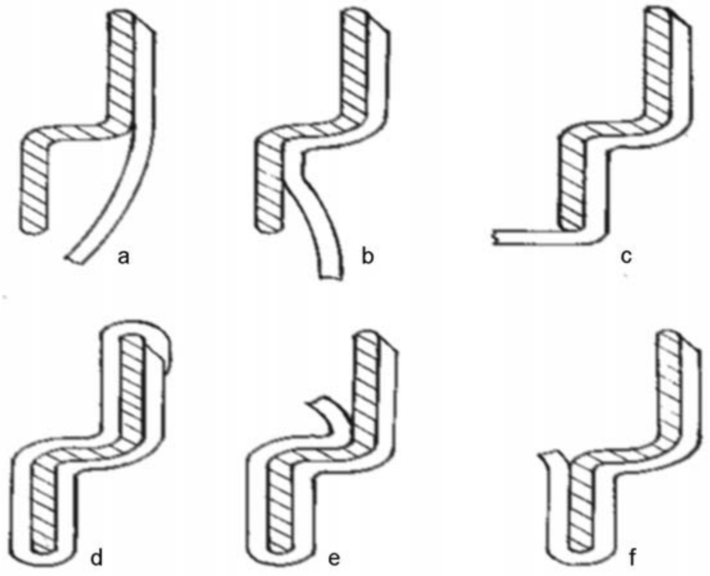


Figure 3.6 Various stages of rubber lining of a baffle plate

The soft rubber linings employed are insensitive to vibration and strong impacts as well as to deformation of the equipment in question. Cracks can occur in hard rubber linings due to heavy loading and knocking but mostly do not occur in soft rubber linings. Natural soft rubber linings can withstand temperatures as low as –40 °C and so can be used in storage tanks operating in low temperature zones during winter. Baffle plates provided inside the tankers prevent fluid knocking and spilling to some extent. A typical rubber lining of all sides of a baffle plate is shown in Figure 3.6.

3.9 The Electroplating Industry

Hard chrome plating is used essentially for wear resistance on moving parts, like piston rings, etc. Bright chrome plating is mainly for aesthetics. For both types of plating, a strong solution of chromic acid is used as the electrolyte. Chromic acid or chromic acid solution is a very strong oxidising agent and one of the most corrosive substances. The corrosive power of chromic acid is 16 times that of dilute hydrochloric acid. It can instantly dissolve metallic iron and convert into magnetic acid. In the electrolytic bath, the maximum operating temperature will be around 100 °C and rubber lining is used extensively.

3.10 The Fluorine Industry

Elemental fluorine is the strongest oxidising agent. It can burn paper without the assistance of oxygen. The halides of fluorine naturally become highly corrosive substances in the manufacture of hydrofluoric acid and metallic fluorides. A range of equipment such as absorbers, centrifuges, drum filters, neutralisers is lined with rubber. Moreover the pumps used for recirculation in the absorbers are lined with Hypalon rubber linings.

3.11 The Explosives Industry

Nitrate-based explosive industries use nitric acid as a very strong oxidising agent. Storage of this acid is a constant problem and a choice of material for nitric acid service is very difficult. Titanium – a costly metal – exhibits outstanding resistance to nitric acid in all concentrations and temperatures above the atmospheric boiling point. Titanium exhibits excellent resistance to fuming nitric acids. Amongst rubbers butyl and EPM rubbers exhibit much better resistance to nitric acid at around 50% concentration at ambient temperatures for short durations.

3.12 The Pulp and Paper Industries

These industries use chlorine and hyposolutions for bleaching purposes and hence ebonite and chlorine resistant soft natural rubber are used as anti-corrosive linings.

3.13 The Ore and Mining Industries

Amongst all processing industries, only in these industries is the emphasis on wear resistance rather than corrosion. In mining industries, the process focuses more on material handling rather than any physical or chemical conversions taking place during the refining operations. For example in the excavation process of iron ore, conventional conveyer systems through to sophisticated fluidised systems are used [16, 17].

Cost and safety of these processes are the governing factors. In a fluidised system, the particles are transported as slurry using screw pumps, through large pipes. These pipes and connected fitting are subjected to constant wear by the slurry which contains hard mineral. Sometimes, depending on the accessibility of the mineral source, elaborate piping system will be laid. As a high output industry any disruption in the work will result in heavy budgetary deficiency. Anti-abrasive rubber lining greatly enhances the life of equipment and reduces the maintenance cost. The scope for anti-abrasive rubber lining is tremendous and the demand is ever increasing in these industries.

Different rubber compounds are used in the manufacture of floatation cell rubber components for various corrosion and abrasion duty conditions. Floatation as applied to mineral processing is a process of concentration of finely divided ores in which the valuable and worthless minerals are completely separated from each other. Concentration takes place from the adhesion of some types of solids to air bubbles and wetting of the other types of solids by water. The solids adhering to air bubbles float on the surface of the pulp because of decreased effective density caused by such adhesion whereas those solids which are wetted by water in the pulp, remain in the pulp. This method is probably the most widely used separation technique in the processing of ores. It is very extensively used in the copper, zinc, nickel, cobalt and molybdenum sections of the mineral treatment industry and is used to a lesser extent in gold and iron production. The various rubber compounds used in the lining of flotation cells and in the manufacture of their components for corrosive and abrasive duties are:

- Natural rubber: 55 ± 5 on the Shore A scale
- Neoprene: 50 ± 5 on the Shore A scale
- Hypalon: 60 ± 5 on the Shore A scale
- Nitrile: 60 ± 5 on the Shore A scale

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4

Choice of Rubber Compounds for the Ore and Mining Industries

Rubber has been used by the mining industry, both in the form of cured rubber and in its uncured state, for bonding and vulcanising to metal surfaces of tanks and vessels for over half a century. It has been used to protect such items of the plant and equipment from the deleterious effects of abrasive wear, caused by elements such as coal dust, ore particles in slurry and solid form and dusty fumes.

Despite the introduction of synthetic elastomers, ceramics and other abrasion resisting metals such as manganese, natural rubber holds a dominant position in this field of application and is the primary choice for abrasion resistance. Synthetic rubbers (particularly styrene-butadiene rubber which is dominant in the tyre industry sector) are used in dry abrasion application such as general purpose abrasion resistant sheets and conveyor belt covers, since the rubber can be reinforced with fine particles of carbon blacks to achieve dry abrasion resistance close to that of natural rubber. It should be noted that styrene-butadiene rubber is inferior to natural rubber in cutting and chipping resistance.

The mechanics of abrasive wear are complex and this has been the subject of considerable research in recent years [1]. However, no usable formula appears to have been derived which will accurately forecast the wear behaviour of any abrasive resisting rubber in practice. The main reasons for this are considered to be the sporadic velocity, flow, changing density and consistencies, as well as the heterogeneous nature of the ore particles, slurries, vapours and fumes prevalent in the mining industry. Rubber has to resist the above idiosyncrasies of the medium. As such a constant wear pattern could not be predicted for any type of rubber though one type of rubber can be approximately and relatively better than another. At times design changes in the plant are required to alter sporadic velocity due to gravity flow and inconsistent densities of the ore particles and slurries.

Wear can be described as an undesirable deformation of the surface of an object, moving or fixed part of the equipment by way of removal of small particles due to mechanical action such as abrasion, impact, friction, etc. In addition to the mechanical reasons, deformation could arise due to chemical action such as in the case of impellers in the fertiliser industries which are exposed to the reacting phosphoric acid fumes containing dust particles of phosphates.

In the process of wear of a material of construction, four elements are involved:

- The parent material subjected to wear
- The part next to the worn part, i.e., the contact material or media
- The environmental conditions which prevail partially or completely between the parent material and the contact material such as temperature, mechanical forces such as friction, impact, etc
- Load and motion of the contact media or the parent material

The measure of wear depends on the state of the medium as solid, liquid, slurry, dust, fumes or gases; the type of motion and its velocity; and the load.

For example, dry sliding motion, lubricated sliding, sliding on irregular surfaces of different geometrical forms, sliding in the granulated material, and heavy loads acting continuously, intermittently or sporadically produce different types and measure of wear.

4.1 Conveyor Systems

The main transportation of material in the mining industries is by means of a conveyor and piping system [2]. In the case of the conveyor system, the part that is most abused is the belting and this accounts for a sizable percentage of the cost of the equipment. The function of the belt is to carry the normal quantity, and at times the overburden of the ore, and to transport it to the dumping yard or consuming units separately. The life of the belting depends upon the nature of the ore material conveyed, its abrasiveness, hardness, size and shape, the impact at the loading point and the flow velocity.

Generally a belt consists of a carcass made of rubberised fabric, steel cord and the rubber top. The carcass is the tension member. This is covered on the top, the edges and the bottom with different qualities of rubber compounds to protect the tension member from damage and the rubber acts as a binder in addition to its primary function of protecting the belt against the wear.

The cover rubber of belting is the most abused and wearing component. The wear of the cover rubber is the main deciding factor on the life of the belting. Often in the mining industry, reconditioning of the beltings is adopted for economic reasons. The cost of reconditioning is approximately 30% of that of new belts. The life of the reconditioned belt is around 60–70% of the life of the new belts. The Neyveli Lignite Corporation in India established the first and the biggest belt reconditioning plant in South East Asia [3].

A comparative statement showing the quality of the reconditioned belt compared with the new belt is given in the Table 4.1. An independent authority conducted this test for NLC (Neyveli Lignite Corporation) in West Germany [3].

Table 4.1 Properties of new and reconditioned belts

No	Description of the test		Unit	NLC Reconditioned Belt*	New Belt	
			Top cover	Bottom cover	Top cover	Bottom cover
1.	Strength	MPa	27.9	27.1	27.6	27.1
2.	Elongation	%	500	520	510	510
3.	Hardness	Shore A	63	63	64	65
4.	Tear resistance	N/mm	18	19	15	18
5.	Abrasion	Loss mm^3	133	135	130	142
6.	Specific Gravity	–	1.10	1.10	1.11	1.11

*Reconditioned after 10,000 hours of working

Source: Seminar on 'Wear in mineral handling and processing – problems and solutions' New Delhi, India, 1979 by NPC and IIME.

Similarities can be seen in the physical properties of the rubber compounds used in the reconditioned belt when compared with the new belt. It can be inferred that residual life of around 60–70% of the carcass is protected by reconditioning of the top and bottom layers.

While rubber shows excellent wear properties in the friction induced abrasion range of 0–5 ° impact angle, in the 5 – 50 ° impact range it tends to be mechanically damaged by impact. So the angle of incidence of the medium has a significant influence on the wear resistance. Special ribbed surfaces of the rubber improve the wear resistance in such cases, see Figure 4.1.

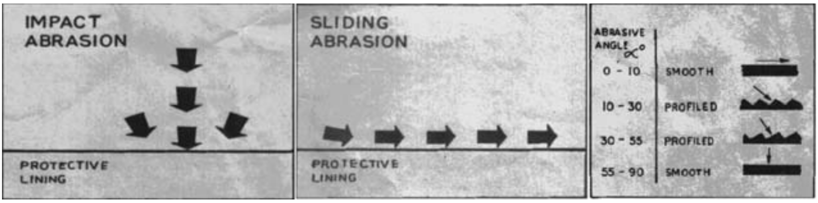

Figure 4.1 Impact abrasion, sliding abrasion and abrasive angle. Reproduced with permission from Trelleborg AB, Sweden

Natural rubbers, such as pure gum with a durometer hardness of 40 on the Shore A scale, display surprising long life in sliding abrasion. Such linings are used in sand and slurry handling pumps and pipings where particles are in fine size and no grit is present.

Where resistance to chipping and tearing is required, pure rubber must be compounded with carbon black to give it a tough composition and hardness of 60–65 on the Shore A scale. Such linings are used in chutes, hoppers, bunkers, dampers, etc.

4.2 Slurry Transportation

Soft rubber linings have been finding wider use in the coal and iron ore slurry transportation piping systems, where the particle size does not exceed 3 mm. Sharp particles in longer sizes can cause extensive gouging. A properly compounded and applied rubber lining can outlast metal at a rate of 10 to 1 in many cases.

A typical recipe for iron ore slurry in water at an ambient temperature in the concentrated plant of an iron ore mine is given below:

- –325 mesh: 64%
- +325 mesh: 19.1%
- +200 mesh: 12.2%
- +150 mesh: 4.3%
- Solid density: 2.95
- Specific gravity of the slurry: 1.36
- Velocity of pumping: 4.4 m/s
- Flow rate: 37,585 litres/minute

Since the flow causes sliding abrasion at a low angle of incidence in the piping, the rubber which can be suggested for this application is a low durometer hardness (40 on the Shore A scale) natural rubber. For lower flow rates at ranges of 1,200 litres per minute up to 4,000 litres per minute, a hard rubber or a semi-ebonite rubber can be used since the abrasive wear of the finely meshed particles will be negligible.

In coal slurry transportation pipelines, severe abrasion and corrosive wear occur due to abrasiveness of ash, magnetite and the oxidising effect of sulfur. For medium pressures, rubber hosepipes with or without steel reinforcement have been used.

The method for solids transported in slurry form is called hydraulic transportation. Today there are long distance rubber lined pipelines carrying a variety of minerals such as coal, limestone, rock phosphate, copper concentrate, nickel refinery tailings, iron ore concentrates and tailings in various parts of the world. The most important slurry pipelines in operation around the world are given in Table 4.2.

Table 4.2 Long distance commercial slurry pipeline systems in operation or under installation in various parts of the world

System	Length (km)	Diameter of pipe (mm)	Capacity (million metric tons/year)	Year of operation
Coal				
Ohio-USA	174	273	1.2	1957
Black Mesa-USA	440	457	4.4	1970
ETSI-USA	1673	965	22.7	1983
Alton-USA (Two pipelines)	295	559	9.6	1985
	112	323	2.4	1983
Iron concentrate				
Savage River, Tasmania	86	244	2.25	1967
Waipipi, New Zealand	8	219	1.0	1971
Pena Colorado, Mexico	48	219	1.6	1974
Siera Grande, Argentina	32	219	2.0	1978
Las Turchas, Mexico	26	273	1.5	1976
Samarco, Brazil	397	508/457	12.0	1977
Chogin, N. Korea	61	n/a	4.1	n/a
Kudremukh, India	66	457/406	7.5	1980
Copper concentrate				
Bougainville, Papua, New Guinea	27	168	0.9	1972
Irian, Jaya, Indoneisa	111	114	0.3	1972
Pinto Valley-USA	18	89	0.4	1974
KBI-Turkey	61	143	1.0	n/a
Limestone				
Trinidad	10	219	0.5	1959
Rugby-England	92	273	1.5	1964
Calaveras-USA	27	194	1.4	1971
Columbia	27	194	0.4	1944
Phosphate				
Valep-Brazil	113	244	1.8	1978
Nickel refinery Tailings				
Western Mining Australia	6	114	0.1	1970
Gilsonite				
American Gilsonite-USA	116	168	0.4	1957

Source: Report on 'Hydraulic transportation of mineral ores' by IIT, New Delhi.

The primary reason for the acceptance of long distance slurry transportation as a reliable mode is its attractive economics [4, 5]. The pipeline system widens the economic reach of the mineral deposits. Rubber lining of the pipes for slurry transportation has a longer life and generally lower cost. Rubber lined parts or piping are suitable for small sized particles. Larger particles tend to cut into hard rubber particularly if they have sharp edges leading to uneven wear. Rubber lining is not confined to natural gum rubber alone, although this is the most common constituent. Natural rubber is safe for temperatures up to 70 °C, while synthetics are available for duty conditions up to 95 °C.

A wide variety of minerals and fluids are handled in the mining industries; encompassing a range of temperatures, acids, and so on. Equipment, which is exposed to these corrosive and abrasive environments, is prone to dreadful wear. If failure of service lives of equipment due to this is to be avoided, this equipment must be protected with rubber lining. Many years of experience has proved that rubber lining is the answer for applications where high resistance to abrasion is required. Rubbers are light, flexible and being resilient they have the effect of reducing vibration due to the load, while the minerals and ores are being conveyed.

4.3 The Future of Hydraulic Transportation of Solids

Materials that are currently being transported over long distances by pipelines include coal, iron ore, limestone and copper concentrates. For hydraulic transportation over long distances to be economic, it is necessary that solids are reduced to an optimum size. To keep solids in suspension, a certain minimum velocity must be maintained. This velocity increases with the size of the particle. The increased velocity has a bearing on the wear life of the rubber lining. Wear in a slurry pipe line system increases with the cube of the velocity as well as increasing directly with the particle size.

To transport 25 million tons of coal per year, only one meter diameter pipe is required. All the disadvantages of rail transportation are overcome including noise, dust, spillage and obstruction during traffic. Under favourable installation conditions, hydraulic transportation cost can be 50–60% less than the cost of rail transport. Slurry proportions for efficient transportation through rubber lined pipes are usually around 50% solids by weight.

Operating pressures in long distance slurry pipe lines are in the 7,000 to 1,000 kPa range. Pumping stations are spaced at intervals of 50 to 80 km. The fine size of solids used for long distance transportation causes low wear rates and pipe line lives of 15 to 50 years may be possible. Another important area for rubber to prevail in the mining industry is the rubber pump liners that are made of either Neoprene, natural rubber, butyl or Hypalon rubbers. Global requirement, according to an Australian liner manufacturer Warmer Pumps, is huge for submerged vertical pumps. These pump liners of smaller sizes are manufactured by moulding technology. Huge pumps liners are being made in the USA by hand forming techniques.

Whereas slurry refers to a relatively thin or watery, dilute suspension, another term ‘sludge’ denotes mud, heavy phase, concentrated suspension or a high viscous fluid. Both words imply the existence of a substance which can be made to flow through a piping system, but which is not like a simple homogenous fluid such as water.

The transportation of sludges and slurries in pipelines is advantageous, but poses more problems arising from high viscosity, nonhomogenity of the fluid system and the tendency of suspended materials to segregate and settle. The tendency to settle varies with the particular flow condition. Particle density, shape and size as well as size distribution, concentration and composition influence the settling characteristics.

A particle tends to settle because of its own weight, i.e., downward gravity force. It can be easily seen that as the velocity of flow is increased, the slurry flow becomes turbulent and tends to maintain the particles in suspension as well as transport them in the main direction of flow. The degree of turbulence may vary from one location to another in the flow system and the settling can occur preferentially in certain places where the turbulence is absent or the flow rate is low. Since slurry is not usually in a homogenous phase, there prevails the problem of determining the effective physical properties such as density and viscosity. Since the flow behaviour of the slurry varies from location to location, the rubber lining composition and application technique have to be designed to take these aspects into consideration. For example, in a slurry flow system in an ore concentrator plant where the flow is turbulent, sporadic and gravitational, the rubber lined pipe nozzles, reducers and bends in the piping system sustain most of the damage. In such cases, the piping layout itself is to be preferentially modified.

4.4 Abrasion Resistance

Abrasion resistance is a composite property that a number of other basic properties contribute to in varying degrees depending on the nature of service. Because of the elasticity of rubbers, some sharp projections do not pierce the rubber as they rebound on impact from a soft rubber. However, hard rubbers are prone to cracking and chipping. The abrasion resistance of both natural and synthetic rubbers can be varied by adopting different concentrations of reinforcing fillers while compounding rubber. At optimum concentration of reinforcing fillers, like carbon black or silica, the abrasion resistance of both natural and synthetic rubbers reaches a maximum. At higher proportions of fillers, rubber becomes excessively stiffer and less resilient. The factors of compounding, choice of fillers and other ingredients limit abrasion resistance of rubbers used as lining for handling minerals and slurries.

A few case histories of the use of rubber lining in anti-abrasive applications are given below.

4.4.1 Feed Launders for Hindustan Dorr-Oliver Ltd

Iron ore with a solid content of 25–30% in water is being handled in these feed launders. A feed launder is a mild steel, rubber lined chute through which ore slurry is conveyed to a concentrator tank. The velocity of the slurry is 0.66 m/s. As a result, 6 mm thick soft natural rubber compound of hardness 40 on the Shore A scale is well suited for this application.

4.4.2 Acid Handling Bins for Ceylon Mineral Sands Corporation, Sri Lanka

The materials handled in the bins are 20% solid by weight and have a flow of 2.9 tons of water per hour and 178 litres/minute of pulp. The size of the material is 100 to over 325 BS specification mesh. Maximum acid concentration is 20% hydrochloric acid. The temperature in the system is 60 °C. A 6 mm thick natural rubber lining of shore hardness 50 on the Shore A scale is used to protect the equipment against the abrasive environment as well as the corrosion effects of hydrochloric acid.

4.4.3 Regrinding Ball Mill in the Copper Project at Khetri in Rajasthan, India

For wet grinding copper ore in the ball mills, at ambient temperature, a 6 mm thick natural rubber compound of 45–50 on the Shore A scale is used successfully as an abrasion resistant layer.

4.4.4 Pipes, Launders and Chutes in an Iron Ore Mining Project

This relates to a project in Karnataka, India installed by the Canadian company, Metchem. Pipes of different diameters, 25 mm up to 450 mm, with a length running over a total of 12 kilometres, in lengths of 1 m to 6 m, launders and chutes are protected with abrasion resistant soft natural rubber lining of hardness 40 on the Shore A scale, with a thickness varying from 6–10 mm, using a chemical adhesive bonding system. This served well for over ten years. The rubber lined pipes used couplings made by Victaulic with grooves fixed with natural rubber sealing rings for joining since the pipes were flangeless. The pipes were transporting iron ore slurries of specific gravity 1.02 to 2.3 with a slurry velocity of 6 m/s to the pelletising plant.

4.4.5 Rotary Vacuum Drum Filters

This relates to drum filters, designed by Eimco, in the USA. These filters are used in illmenite beneficiation and titanium dioxide plants. The filters, including parts like agitators and troughs are lined with a semi-hard flexible ebonite of natural rubber to protect the equipment against the abrasive action of the ore and solid particles in the slurries.

4.5 Spherical Digesters in a Chlor-alkali Plant

Illmeniting sand with steam and hydrochloric acid is handled in the spherical digesters. The temperature in the digesting process is ambient to more than 130 °C. Therefore, brick lining is applied on a butyl rubber lining of 5 mm thick with hardness of 55 on the Shore A scale. The rubber serves as a cushioning medium beneath the brick lining, as well as resisting the temperature at the brick rubber interface of about 100 °C. See Figure 4.2 of rubber lined digesters in the ore industry.

Figure 4.2 Rubber lined spherical digesters in an ore industry

The anti-abrasive or anti-corrosive rubber linings are applied to the metal surface by adopting different kinds of bonding systems such as ebonite bonding, chemical adhesive bonding or self-vulcanising cement bonding.

In the ebonite bonding procedure an ebonite layer is used as a bonding ply between the soft rubber and the metal. Usually this ebonite layer is designed to be flexible to absorb any shock transmitted from the soft rubber layer above. This is achievable by a low sulfur addition to the compound around 15/20 parts by weight of rubber. The vulcanisation procedure adopted is either autoclave curing or open steam curing.In the chemical adhesive bonding, proprietary adhesives based on polyisocyanates are used for bonding the soft rubber to the metal, instead of the ebonite layer.

In the self-vulcanising cement bonding method, precured soft rubber sheet is bonded to the metal by a cement which cures at ambient temperature thereby effecting the required bond strength between the soft rubber and the metal. This technique is known as the cold bonding technique.

In all of the above cases, the metal surface is to be sandblasted to provide a whitish rough finish which will ensure good anchoring of the adhesive between the metal and the rubber.

There is yet another type of lining called the Triflex lining. Triflex is a three ply, soft-hard-soft natural rubber construction. The soft rubber is compounded for maximum rubber to metal adhesion. The middle hard rubber layer, a flexible ebonite composition, serves to provide diffusion resistance. The outer layer (exposed to the fluid media) resists abrasion, ozone and weather. Soft rubber has the advantage of being flexible and cannot be cracked except on ageing. But it has the tendency to permit diffusion of fluids, especially at higher temperatures, resulting in loss of adhesion from metal, often with formation of liquid filled blisters. Hard rubber has better chemical and diffusion resistance than soft rubber, but it has the disadvantage of being brittle and is subject to cracking not only from flexing or physical damage, but also from severe thermal changes. Triflex can be considered a laminated construction of hard rubber sandwiched between two plies of soft rubber. This forms a cushion for the hard rubber and since it is a three layer construction the composition or thickness of any given layer can be changed or modified to suit a particular requirement.

Although Triflex is a three-layer construction, it becomes a completely homogenous membrane upon vulcanisation. The compounding technique adopted for each layer is a tricky job and calls for considerable knowledge and expertise in compounding technology, especially in the choice of base rubber, filler loading and curing systems of the different layers which are made into one single membrane upon curing.

4.6 Dry Abrasive Conditions

In dry abrasive situations, such as conveying of ore aggregates and gravels, a harder rubber (60 Shore A) is a very cost effective lining. Blends of natural rubber with synthetic rubber are used to enhance cutting and gouging resistance in heavy thicknesses. While these rubber sheets are in competition with special steels with manganese, the latter have no energy absorbing or sound deadening properties as rubber does. For heavy impact wear, the sheet thickness may be 15 mm to 25 mm or more. Such heavy liners are often made as custom liners. Since the predominant wear mechanisms in dry abrasion resistance are cutting, chipping, and fatigue wear which are related to rebound resilience, the curing system, the choice of rubber and reinforcing fillers used is very critical. While autoclave curing or hot water curing of heavy linings up to a thickness of 25 mm or more is achievable, chemical curing of thickness more than 6 mm is not advisable as the penetration of chemical curative and the curing system is not designed for maximum fatigue life.

The quality of rubber sheets varies widely within the supply industry and factors in addition to hardness and price per kilogram should be considered by the mining engineer in the choice of the most suitable rubber for the application. Rubber compounds which are suitable for dry abrasive applications are not suitable for wet abrasive applications and this should be the primary step in the choice of rubber compounds. It is important to judge rubbers for both wet and dry applications by at least the parameters of hardness, specific gravity, polymer type and polymer content in the compound. To choose or assess the rubber compound for wet abrasion resistance without considering the first four parameters is dangerous. Other factors such as cutting and chipping resistance are more important in dry abrasive application. It is important in both the applications that the rubber thickness should be adequate to prevent the abrading particles penetrating to the vessel surface as otherwise all advantages of rubber lining is lost.

4.7 Wet Abrasive Conditions

In the South African mining industry most processes for recovering precious metals, coal, minerals and diamonds are wet methods, involving the suspension of solids in water [1]. In the control of such wet abrasive conditions in the pumping of fine particles size slurries, particle size separation in cyclones and in floatation cells, the choice of soft natural rubber lining is the most cost effective.

Maximum resistance to wear is obtained by using Linatex (Rima Tip Top, Canada and Linatex Sdn, Bhd, Malaysia) which is manufactured by the latex process, a process similar to the manufacture of surgical articles such as rubber gloves and condoms. Linatex, a high rubber content product, is the only commercial product available of this sort worldwide. However, there has been progress recently that has resulted in conventionally manufactured rubber sheeting almost matching the wet abrasion resistance of Linatex at considerably lower cost since the latex processed Linatex is expensive. It is more economical to use a thicker lining of a technologically compounded rubber in the conventional manufacturing system to achieve the same wear life than the nominal thickness of 6 mm in the latex processed Linatex. Increase in thickness of lining in a pipe design will restrict flow, which in turn increase pumping pressure and velocity. This will increase wear rate. As such the option of higher thickness of lining is to be discussed with the mining and chemical engineers before decisions are finalised in equipment such as sump, tanks and launders, and pipes.

Soft natural rubber sheets, in cured or in uncured form, from any manufacturers of abrasion resistant rubber lining generally has a specific gravity close to 1.00 g/cm^3, i.e., in the range of 0.98 to 1.02 and with the natural rubber content of a maximum of 90%. For wear resistance only minor cost savings are possible on specific gravity alone as the cost of the lining is always calculated on the surface area of the tank. At a specified thickness the price per square meter of the sheeting, and not per kilogram, is of paramount importance. Such sheeting obviously has a hardness of 35–40 on the Shore A scale.

Currently, the rubber industry and the user industry as a whole tend to specify rubber compounds by hardness alone. Specifications for anti-abrasive rubber linings are quite common with as little information as '40 Shore A, 6 mm or 5 mm thickness'. Hardness alone is no measure of rubber performance. Mining engineers should be aware that hardness is not a reliable guide for suitability of sheets for slurry abrasion resistance, since it is easy to achieve the same hardness by loading the compound with large quantities of cheap fillers and oils and achieve a lower cost per kilogram. Such compounds will have higher specific gravity and may in fact be more expensive as the cost per square meter area will be higher and abrasion resistance poorer. In addition, the mining engineers are exposed to the dangers of getting attracted by the measure of the quality of sheets by appearance, whereas, in fact, rubbers containing large quantities of cheap fillers and oils calender more easily and have better surface appearance than sheets of higher rubber content. This should not be confused with the rubber compounds containing special fillers and additives, which are added to improve resistance to mine acids.

In fact, both natural and synthetic rubbers are most suitable for protecting chemical processing plants and equipment against wear and abrasion caused by the minerals handled. Liners for slurry pumps and casings and impellers conveying dusty acidic fumes use rubber linings, which withstand the abrasion due to high tip velocities in the impellers. The successful development, manufacture and application of these abrasion resistant rubber linings require a combination of many skills. The development and formulation of a suitable anti-abrasive rubber lining for critical applications calls for an extensive knowledge of raw materials, their specification and compounding techniques, and the duty conditions.

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5

Raw Materials for Rubber Lining

A wide variety of materials are required for the manufacture of rubber lining. A basic necessity is to identify and decide on the correct choice of materials to suit individual requirements of the compound for each type of application.

The raw materials for manufacturing rubber lining compounds are grouped as:

- Rubber (natural or synthetic)
- Process oils
- Activators
- Plasticisers
- Curing agents
- Accelerators
- Antioxidants
- Fillers
- Solvents
- Adhesives and bonding agents

Their respective properties are discussed next.

5.1 Natural Rubber

While at room temperature natural rubber, having considerable strength and appreciable elasticity, is liable to oxidise to a sticky product. This high molecular weight polymer has a lower temperature limit to its rubbery state. At the glass transition temperature (T_g) there is fairly abrupt change to a glassy state. At temperatures more than T_g, it becomes rubbery. Various grades of natural rubber are available on the international market as smoked sheet and crepe form. The emphasis in grades is a visual grading by appearance, rather than technical properties. The current process involves size reduction of the source material, drying of the particles produced in deep bed or apron dryers, and within a few hours to packing in pressed bales normally weighing 33 kg, which are wrapped in polyethylene sheet.

The Standard Malaysian Rubber Scheme gives important parameters like dirt level and plasticity retention index (PRI). PRI is the percentage retention of rapid plasticity after ageing for 30 minutes at 140 °C. It is a measure of oxidisability. All but the poorest quality grades of natural rubber contain 90% of *cis*-1,4-polyisoprene hydrocarbon in a mixture with naturally occurring proteins, resins, sugars, etc. The composition of the non-rubber depends on the coagulation procedure used and varies somewhat between clones, some high yielding types tending to reveal acetone extracts of 2.5–4.5%, nitrogen content of 0.3–0.5% and ash content of 0.2–0.6%.

5.2 Synthetic Rubbers

In addition to natural rubber, synthetic rubbers can be utilised in many forms.

5.2.1 Polyisoprene Rubber

Two types of synthetic polyisoprenes are commercially available; 96.98% *cis* isoprene rubber (IR) produced using titanium-based ziegler catalyst and 92% IR using an alkyl-lithium initiator. Tables 5.1 and 5.2 give analytical data of the two types of polyisoprene rubbers as compared to natural rubber, and the strength properties of vulcanisates of IR, natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR). The most important factor in IR is the stereo regularity of the polymer chain. The second key property is low hysteresis, giving low heat build up during flexing. The linear structure of 92% IR causes the cold flow retention to be generally low. The high-branched structure in 96% IR prevents cold flow and 92% *cis* IR shows false Mooney values above molecular weights of 500,000.

Table 5.1 Polyisoprene *versus* natural rubber – analytical data

	Type of polymer		
Property	**Ziegler IR**	**Lithium IR**	**NR**
Cis content (%wt.)	96	82	98-100
Limiting viscosity no.	2.5-4.5	8-11	6-7
Gel content %wt	10-20	0	High level, depending on age
Macro structure	Branched	Linear	Branched
Ash content %wt.	0.15-0.3	0.05	Approx. 0.5
Total metal content	400-3000	70	Approx. 1000 ppm
Mooney viscosity	60-90	-	Approx. 120
Colour	White	White	Dark Brown

5.2.2 Polybutadiene Rubber

Three types of BR are manufactured commercially. The high *cis* (97%) 1,4-polybutadiene is polymerised by a Zeigler-Natta type catalyst system, consisting of either a cobalt or nickel salt or organic compounds of these metals with an alkyl aluminium halide. The medium high *cis* (92%) 1,4-polybutadiene is also polymerised by a Ziegler-Natta type catalyst system, the transition metal being titanium. The low *cis* (40%) 1,4-polybutadiene, polymerised in the presence of alkyl lithium initiator has the lowest T_g and therefore the highest resilience of all known rubbers. But its green strength is low owing to its elastic recovery in the unvulcanised state.

5.2.3 Butyl Rubber

The monomers are polymerised in solvents such as methyl chloride, using Friedel-Craft catalysts such as aluminium chloride. The butyl elastomers are self-reinforcing, with a high pure gum tensile strength of 25 MPa. The abundance of methyl side groups in the polymer chains brings about a considerable steric hindrance to elastic movements. Although T_g values of around –65 °C have been measured, the resilience of vulcanisates at ambient temperatures is very low. On the other hand, the densely packed structure permits low gas permeability. Mainly as a result of rather rigid, highly saturated chains, the polymer excels in ozone, chemical and abrasion resistance.

5.2.4 Ethylene Propylene Rubber

These polyolefin rubbers are produced in two main types: the saturated co-polymers, ethylene propylene rubber (EPM), and the unsaturated ethylene-propylene diene terpolymer (EPDM). The monomers are co-polymerised in ziegler natta type catalysts. The EPDM types are capable of sulfur vulcanisation as they contain, in addition to olefins, a non coagulated diene as the third monomer.

For polymers with high ethylene content, under optimum cure time, tensile strength varies from 20 MPa to 125 MPa. Values for compression set can be as low as 1%. The most striking feature of both EPM and EPDM vulcanisates is their excellent resistance to oxygen and ozone, with the latter being slightly less resistant.

5.2.5 Chloroprene Rubber

This was the first commercial synthetic rubber, which became available to the rubber industries in 1935 [1, 2]. It is manufactured by polymerising 2-chloro-1,3 butadiene in the presence of a catalyst, emulsifying agents, modifiers and protective agents.

Pure gum vulcanisates of chloroprene rubber (CR), like those from NR, show high levels of tensile strength. They have tensile strength within the range 7–17 MPa, elongation at break in the range 200–600% and hardness in the degree of 40–95 international rubber hardness. The resilience is lower than that of NR but CR is highly resistant to oxidising agents. Vulcanised CR shows a high level of resistance to flex cracking. For acute service conditions, compounding with the available protective agents may enhance this. Because of the chlorine in the molecule, CR has inherent flame resistance and products made from it are normally self-extinguishing.

5.2.6 Chlorosulfonated Polyethylene Rubbers

These are amorphous, vulcanisable elastic polymers usually marketed under the name Hypalon, a registered tradename of DuPont. They are prepared by heating polyethylene in carbon tetrachloride solution with sulfur dioxide and chlorine, yielding polymers containing 29–43% chlorine and 1–1.5% sulfur.

Tensile strengths of chlorosulfonated polyethylene rubber (CSM) vulcanisates are around 3.5 MPa, depending upon formulation. In resilience, the elastomer compares favourably with other synthetic elastomers, though generally its resilience is lower than NR vulcanisates. Flex and abrasion resistance are very good and CSM will not support combustion.

5.2.7 Acrylonitrile Butadiene Rubbers

Amongst all the synthetic elastomers (except Thiokol which has many limitations), acrylonitrile butadiene rubber is the most solvent resistant. It is a copolymer of butadiene and acrylonitrile, and is also known as nitrile rubber. Molecular weights are in the same range as SBR (100,000). Mooney viscosity range is 20–90. Vulcanistion is carried out with sulfur. It is the acrylonitrile group, namely cellulose nitrate, that confers oil resistance to this polymer and the nitrile content can vary from 10–40%, leading to increasing solvent resistance.

Carbon black reinforcement is necessary for nitrile rubber as its gum strength is low. It exhibits excellent resistance to hydrocarbon solvents but less to polar solvents like phenol, ketones, and strong acids. Because of its T_g of –20 °C to –40 °C, it has poor low temperature properties; therefore, the desirability of a high nitrile content for resistance to solvents such as gasoline has to be balanced against low temperature stiffening. Nitrile rubber can form ebonites that have superior resistance to heat ageing and outstanding resistance to swelling by many organic solvents.

These are generally manufactured by the emulsion copolymerisation process. The commercially available nitrile rubbers differ from one another in three aspects: acrylonitrile content, polymerisation temperature and mooney viscosity. The content of acrylonitrile has a profound effect on the properties of vulcanised nitrile rubber, influencing its resistance to oils and fuels.

Nitrile rubbers give compounds with inherently poor tack and the addition of coumarone or phenolic resins helps overcome this deficiency. Phenolic resins may also be used to reinforce nitrile rubbers and to produce easily processible compounds that can be vulcanised to a high hardness.

5.2.8 Styrene-Butadiene Rubbers

This is the most important general purpose of synthetic rubber and represents more than half of all synthetic rubber production. It is a copolymer of 1,3-butadiene and styrene, and is a descendent of the original Bunas first produced in Germany during the 1930s [2].

SBR is an amorphous elastomer, with irregular chains. It does not exhibit crystallisation either on stretching or cooling and therefore exhibits negligible gum strength, unless it is reinforced with a fine particle size carbon black. It is compounded much like natural rubber.

It is not as tacky as natural rubber and shows a lower green strength in uncured stock. However it shows higher abrasion resistance than natural rubber. Since the T_g of SBR is lower than natural rubber, SBR shows poor low temperature properties. This rubber is not generally a preferred rubber for chemical resistance applications though its hard rubber compounds (ebonite) can be used to make extruded profiles and moulded components for lining accessories such as division strips, end rings, chlorine-handling internal pipe distance pieces, etc. See Figure 4.1 for an example of pipe internals assembled (tubular liquid distribution distance pieces) made from SBR ebonite for a caustic soda factory.

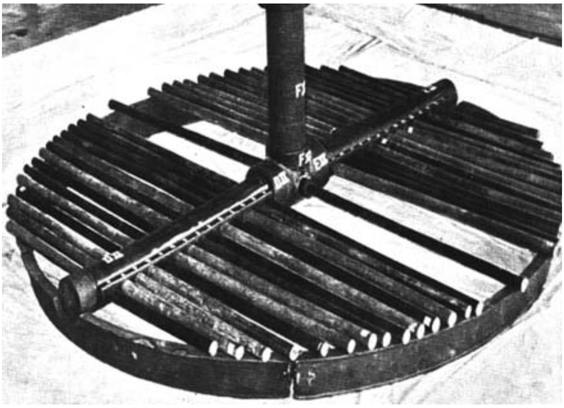

Figure 5.1 Ebonite internals for brine filter in the chlor-alkali industry: assembled view

For reference, ASTM Elastomer (Rubber) Designations for various synthetic rubbers are given in Table 5.2.

Table 5.2 Designations of various synthetic rubbers

Abbreviation	Elastomer
ABR	Acrylate butadiene rubber
BR	Butadiene rubber
CR	Chloroprene rubber
EPM	Ethylene-propylene rubber
EPDM	Ethylene propylenediene rubber
IR	Isoprene rubber
IIR	Isobutylene, isoprene or butyl rubber
SBR	Styrene-butadiene rubber
SIR	Styrene-isoprene rubber
NBR	Acrylonitrile-butadiene rubber
NCR	Acrylonitrile-chloroprene rubber
PBR	Vinyl pyridine-butadiene rubber
PSBR	Vinyl pyridine styrene-butadiene rubber
XNBR	Carboxylic- acrylonitrile-butadiene rubber
CIIR	Chloroisobutylene-isoprene or chlorobutyl rubber
BIIR	Bromoisobutylene-isoprene or bromobutyl rubber
MQ	Dialkyl siloxane rubber
CSM	Chlorosulfonated polyethylene rubber

5.3 Vulcanising and Curing Agents

The various curing agents used for manufacturing rubber lining compounds are sulfur, organic peroxides, accelerators with available sulfur and metallic oxides.

Sulfur is available in finely powdered form packed in polyethylene bags. It vastly improves the properties of raw rubber; by processing it with sulfur it can be converted into nontacky, tough elastic materials.

Organic peroxides, like benzoyl peroxide, 2-4, dichlorobenzoyl peroxide, tertiary butyl-perbenzoate are used for natural and synthetic rubbers.

Accelerators used include hexamine, diphenyl guanidine, ethylidene aniline, mercaptobenzothiazole, dibenzothiazole disulfide, *N*-Cyclohexyl benzothiazole sulfenamide, sodium diethyl dithiocarbamate, tetramethylthiuram disulfide, tetraethyl thiuram disulfide, dipentamethylene thiuram tetrasulfide, sodium isopropyl xanthate, zinc butyl, xanthate and so on.

These accelerators form the entire range from moderate to ultra accelerators depending upon the sulfur addition and the nature of polymer used. Magnesia, zinc oxide, calcium oxide (known as burnt lime) and litharge are the metallic oxides primarily used as curing agents in rubber lining compounds. During compounding and sheeting, the rubber compound is continually subjected to heat. This is particularly evident in mixing and so usually accelerators are used towards the end of the mixing cycle. Retardants are added to prevent premature vulcanisation.

Table 5.3 Strength properties of vulcanisates of IR, NR, SBR and BR

	Type of polymer				
Property	**Ziegler IR**	**Lithium IR**	**NR**	**SBR**	**BR**
Tensile strength (MPa)	30	25	31	25	17
Tensile strength (N/mm)	70	60	110	45	35

5.4 Materials for Reinforcement

5.4.1 Carbon Blacks

The five most important properties of carbon blacks are:

- Particle size/surface area
- Structure
- Physical nature of the surface
- Chemical nature of the surface
- Particle porosity

Carbon black is the most important and powerful filler for rubbers. Each of the above characteristics of the carbon black has its effect on the properties of rubber in which carbon black is incorporated and careful selection of grade is necessary to ensure a correct balance of processing and vulcanising properties. The furnace black type, which has fine particle size, is used in lining, where high strength and resistance to abrasion are required.

Graphite is a mineral filler, used as an inert filler in general compounding, but is of great importance in rubber lining compounds as it imparts good chemical resistance. It is a regularly used filler for achieving compounds for chlorine and acid resistance. Low ash graphite is better suited for chemical resistance.

Nonblack fillers are used where colour or other properties are important. Some of the options are discussed next.

5.4.2 China Clay

This is essentially hydrated aluminium silicates derived from natural deposits. There are soft clays, hard clays, calcined clays and treated clays. This is a common filler in the manufacture of acid resistant ebonites, natural soft rubbers and in Neoprene compounding for phosphoric acid duties.

5.4.3 Talc

These are finely ground natural minerals consisting mainly of silicates of magnesium and aluminium, used as inert fillers in heat resisting compounds. They also help to reduce permeability of rubbers to gases. Talc is also widely used as a lubricant to prevent uncured stock sticking to itself and other surfaces, especially in the pipe lining operations. These are regularly used in the manufacture of adhesive solutions in the rubber lining industry.

5.4.4 Titanium Dioxide

This is a white pigment used as a reinforcing filler (which is comparable in volume with zinc oxide) and it is also an excellent heat-resisting filler for silicone rubbers. The rutile form gives a rather creamier, more reflectant colour, which is more stable at high temperatures. They are widely used fillers in the manufacture of white or light colour chemical resistance compounds for the pigmentation industry.

5.4.5 Zinc Oxide

This is an accelerator activator and reinforcing filler that gives compounds high tensile strength and resilience, but only moderate hardness. It is used at high loadings to produce plastic and easily mouldable compounds that, however, tend to stick to mills and calenders at high processing temperatures. In ebonite-based adhesive bonding solutions and white compounds, zinc oxide is used dominantly in the lining industry. For hot water curable compounds, this is an essential ingredient.

5.4.6 Lithopone

Lithopone is a mixture of 30% zinc sulfide and 70% barium sulfate, precipitated simultaneously. It is used mainly in cheaper white or coloured compounds as a whitening agent [3].

5.4.7 Litharge

This is red lead monoxide, used as in inorganic accelerator for the curing of soft natural rubber lining in an autoclave. High temperature curing leads to blooming of lead film, which is the chemical resistance layer, but impairs bonding with metal.

5.4.8 Antimony Trioxide

This white semireinforcing filler is used in flame resistant compounds and sometimes as a colouring agent.

5.4.9 Zinc Stearate

Zinc stearate is a source of soluble zinc for accelerator activation for translucent compounds or in cases where maximum activity with minimum quantity is desired. It is used as a lubricant for uncured stock, having the advantage over talc of dissolving in the rubber during the curing.

5.5 Plasticisers, Softeners and Extenders

These materials are added to rubber primarily to aid the processing operations such as mixing, calendering and extruding. They are also used along with fillers to reduce compound cost. In addition, the green strength and shrinkage level are maintained at optimum usage convenience while applying the rubber sheets during the lining operation.

5.5.1 Peptisers

These are used to increase mastication efficiency by increasing the rate of molecular breakdown, particularly in natural rubber. Normally less than 0.5 phr are used, but higher dosages are required for synthetic rubber. As sulfur inhibits their action, these are normally added before mastication. Zinc salt of pentachlorothiophenol and di-*o*-benzamidophenyl disulfide are commonly used as peptisers in lining compounds.

5.5.2 Process Oils

These oils function in a physical rather than in a chemical manner. Their effect is independent of temperature of mixing to aid processing, reduce viscosity and ease filler incorporation. Petroleum oils are used as extenders to reduce the cost of compound. The types of oils used as processing aids and extenders are broadly classified under the heading paraffinic, naphthenic and aromatic according to the value of viscosity gravity constant. Dosage level is controlled to prevent blooming at the metal-rubber interface during curing.

5.5.3 Paraffin Wax

Paraffin waxes, of melting point approximately 55 °C, are used as processing aids. They bloom to the surface and protect ozone sensitive elastomers against cracking under static stress.

5.5.4 Resins

Various kinds like coumarone resins, petroleum resins, high styrene resins and phenolic resins are used to give excellent flow characteristics during moulding, calendering and extruding.

5.6 Antioxidants and Antiozonants

Double bonds, although vital for sulfur vulcanisation of rubbers, provide the weak link as far as the degradation by oxygen or ozone is concerned. Rubbers containing high amounts of unsaturation such as NR, SBR and BR are more prone to oxidative degradation or attack by ozone than elastomers containing low amounts of unsaturation such as butyl rubber and EPDM. The majority of commercially available antidegradants fall into two main classes:

- Products derived from amines, mostly aniline or diphenylamine, are usually called staining antidegradants as they tend to discolour nonblack vulcanisates on exposure to light.
- Products derived from phenol are often referred to as nonstaining antidegradants.

5.7 Adhesives and Bonding Agents

Proprietary bonding agents are used almost exclusively in modern manufacturing processes for metal-rubber bonded products. Isocyanates were proved to be of value in the immediate postwar period, but their moisture sensitivity and tendency to be wiped off the metal during processing have proved as disadvantages. The majority of commercially available adhesives in use today are a complex mixture of undisclosed composition, and in many instances are specifically used for particular rubbers and substrates.

Bonding agents are applied as one or two coat systems. The primer coating is formulated to have good adhesion to metal and consists of polar materials dissolved in suitable solvents. The cover coat may consist of a mixture of several polymers, usually of intermediate polarity and rubber like, rather than resinous in nature. The formulation involves considerable knowledge and is very complex in nature.

5.8 Solvents

These are used for preparing adhesives and for metal cleaning by removing grease, oils, dirt, etc. Trichloroethylene, toluene, xylene, ethyl acetate, methyl ethyl ketone and hexane are the most commonly used solvents in rubber lining manufacture and application. Sometimes a mixture of one or two of the above solvents is used for evaporation make up of the adhesive solutions. For closed tank linings trichloroethylene is the preferred solvents from the safety point of view.

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6 Elastomers Used in the Rubber Lining Industry

In Chapter 5, a general outline of base rubbers was given. In this chapter, more details about the rubbers most frequently used in the lining industry are given.

6.1 Neoprene Rubber

Commercial types of Neoprene rubber undergo changes on storage. From a practical stand point these changes result in a reduction of processibility, an increase in rate of cure, a reduction in processing safety and changes in plasticity. The effects vary considerably from one Neoprene type to another and among the general purpose types, Neoprene W has by far the least tendency to change on storage. The changes are the result of chemical reactions, and therefore are influenced markedly by the temperature of storage, elevated temperatures accelerating the phenomenon and reduced temperatures retarding them. Oxidation plays a major role in the changes that are observed to accompany the extended ageing of raw uncompounded Neoprene. Two types of oxidation occur; chain scission and creation of additional centres of reactivity. Chain scission reduces the average polymer chain length and results in a softer polymer, having a low potentiality for the development of tensile strength. In the raw polymer, the creation of additional centres of reactivity induces the formation of additional crosslinks with a consequent increase in nerve and toughness. In compounded stock, such increased number of reactive centres due to oxidation, accelerates curing at both processing and curing temperatures.

During processing for increasing the molecular break down of Neoprene, peptisers are used. The most effective peptisers are guanidines such as di-*o*-tolyl guanidines and dithiocarbomates such as piperidinium pentamethylene dithiocarbamate [1]. Aromatic mercaptans which are widely used in peptising natural rubber (NR) will also peptise Neoprene rubber but exert a strong retarding action on the rate of cure. Neoprene type W having greater stability resists both mechanical break down and chemical peptisation. Murray and Thompson [2] have made an extensive study of processing problems with Neoprene. They recognise that Neoprene is capable of existing in three distinct phases which depend on the temperature.

Below 71 °C it exists in what is called the elastic phase. In this phase Neoprene coheres tightly so that strong running bands are obtainable on a mixing mill.

Between approximately 71 °C to 93 °C it exists in a ‘granular phase’. In this condition Neoprene loses cohesion to it but tends to stick tightly to the mill rolls.

Above 93 °C the Neoprene enters a plastic phase in which it is very soft and has only weak cohesion to itself, showing very little tendency to stick to the mill rolls and has almost no nerve.

A clear apprehension of this three phase cycle in Neoprene gives a good clue to proper processing of all types of Neoprene stocks, while warming in the mill and sheeting in either the mill or the calender. Some small scale manufacturers are skilled to produce fine sheeting from the mixing mill alternatively from a calendering machine. See Figure 6.1 for an example of sheeting from a mixing mill of size 41 cm x 107 cm.

Figure 6.1 Sheeting from a rubber mixing mill

Processing in a range from 71 °C to 93 °C, where Neoprene exists in the granular phase should be avoided as far as possible. Best dispersions are obtained when fillers are incorporated when the elastic phase is below 71 °C. Fine calendering of high quality stocks having minimum calender shrinkage and carefully controlled thickness of 1 mm which is to be doubled up to the required thickness say of 3 mm, 4 mm, 5 mm or 6 mm in a special device is required for lining application. This is carried out in the plastic phase above 93 °C. However most sheetings where careful control of thickness is not required, is best carried out at temperatures where elastic phase prevails. Crystallisation that takes place in Neoprene at a temperature considerably higher than in natural rubber sometimes influences the processing of Neoprene stocks. This phenomenon may result in a marked stiffening and loss of tack in an uncured compound as a consequence of exposure at room temperature for several days. This effect, which is readily reversible with heat, is off set in order to enable lining applications where thickness building and laminating are involved.

The unique character of Neoprene vulcanisation is that rubber accelerators as a class are not effective. As a matter of fact several have measurable retarding effects and it has to be understood that mercaptobenzothiazole is an extremely potent retarder in Neoprene vulcanisation. Salicylic acid is a fast accelerator leading many a times to scorching or premature vulcanisation at higher dose levels [3].

Sodium acetate is an efficient retarder for Neoprene compounds. It is selectively preferred for mercaptobenzothiazole or benzothiazyl disulfide since its retarding effect does not persist at normal curing temperatures.

Neoprene is resistant to non oxidising mineral acids at elevated temperatures, to concentrated sodium hydroxide and to animal and vegetable oils. It is weather resistant and ozone resistant. The ozone resistance of Neoprene is well deployed in lining of equipment in the cell houses in caustic soda industry where ozone environment prevails. Its good elongation at low operational temperatures, at -46 °C and its excellent abrasion and tear resistance make it an ideal candidate for tanks lining in chemical industry. Special compounding makes Neoprene more resistant to water and a variety of aqueous solutions. Properly compounded it is self-extinguishing when exposed to flame.

6.1.1 Compounding Neoprene for tank lining application

Lining with Neoprene sheets requires excellent building tack. G type Neoprenes are quite tacky, with red lead (lead tetroxide – Pb_3O_4) curing system insuring a good resistance to water. At times blends of G and W types of Neoprene are used to balance the level of building tack and to eliminate possible handling and processing problems. The G types differ from W types in that the former are interpolymerised with sulfhur and contain a thiuram disulfhide stabiliser. The two classes are distinguished easily by their colour – the G types are amber while W types are either creamy white or silver grey. A typical blend can be 80 parts of G type and 20 parts of W type Neoprene. The selection of fillers to control tack is important because some compounding ingredients such as clay tend to produce a dry stock. Silica fillers help to retain good tack in Neoprene. Tackifiers such as coumarone-indene resins are used in compounding Neoprene for increased tack. Oils and waxes which bloom out during vulcanisation and even during storage of unvulcanised stock should be avoided. Swabbing the dry Neoprene sheet surface with toluene provides instant tack for application.

Red lead is an ingredient generally used in all Neoprene compounds for tank linings for good water and chemical resistance. But it should not be used in compounds of Neoprene designed for contact with food or potable water. Tubes or pipes for conveying potable water are made of ethylene-propylene diene terpolymer (EPDM) rubbers.

While calendering the Neoprene stock it must be prewarmed uniformly before being fed into the calender rolls. Stock temperature will change as the quantity of the stock at the nip varies. This causes fluctuation in viscosity of the stock and in roll pressure leading to rough sheet with differing thickness. Roll temperature in calendering must be accurately controlled. The processing behaviour of Neoprene at the calender or mill is temperature sensitive and varies from one compound to the other. Generally the temperature differentials of the calender rolls for Neoprene calendering are:

Top roll -	90 °C
Middle roll -	85 °C
Bottom roll -	35 °C/40 °C

Air blisters can be avoided easily in thinner sheets that can be plied up to the required thickness, rather than one step calendering of a thicker sheet that induce formation of air blisters during calendering.

Shrinkage can cause premature failure of the lining. The place to minimise shrinkage is at the calender or at the warming/sheeting mill. High temperature processing reduces shrinkage.

In addition to proper compounding of the elastomeric lining it is important that the tank is designed and fabricated so that the lining can be applied without formation of air pockets between the lining and the metal surface. Air pockets promote permeation of the liquids media leading to damage of the metal surface at the place and resulting in total lining failure.

The metal surface of the tank/vessel to be lined with Neoprene should be either sand or shot blasted and cleaned with a solvent to make the surface free from any grease or oil. One coat of Neoprene based primer is applied over which one coat of isocynate bonding agent is applied and allowed to dry. A top coat of Neoprene based tie-cement is then applied and the lining with Neoprene sheet is done. The tie-coat will have a solid content of about 25%. The drying time for the prime coat can be four hours and for the other coats the drying time can be one hour between coats [4]. The drying time given here is only indicative as it depends on the type of solvent or the mixture of solvents. Normally longer drying time is given for the prime coat as the prime coat film thickness is more than that of the subsequent coats. In essence the coatings should be thoroughly dried before the lining sheet is applied to avoid blister formation during vulcanisation caused by rapid evaporation of residual solvent in the coating. The lining is applied very carefully without stretching of the sheet. All the air must be rolled out from beneath the lining with a knurled roller. In other words, the metal surface of the tank must be free of any pits and rough welds. Welded corners should be radiused and should not be square.

The lined tanks are cured *in situ* to achieve good adhesion with metal. Neoprene linings can be cured with air, steam or hot water. Many curing cycles for Neoprene are adopted depending upon the compound type, size and shape of the equipment.

Typical curing cycles for Neoprene linings are given in Table 6.1.

Table 6.1 Typical curing cycles for Neoprene linings

Curing medium	Temperature	Time of cure (h)
Air	70 °C	96
Air	100 °C	24
Air	121 °C	8
Air	141 °C	4
Open stream in autoclave	120 °C at 2 kg/cm^2 pressure	6
Hot water	98 °C	48

In autoclave curing best results can be obtained with high pressure and curing temperatures, i.e., at 3 to 4 kg/cm^2 pressure and 134 °C to 144 °C temperature. The usual procedure followed is to subject the rubber lined vessel to air pressure of about 2 kg/cm^2 at the beginning of the cure cycle which ensures good contact between metal and rubber and then introduce steam and raise pressure and temperature to complete the cure. Typical cure cycles for ebonite and soft rubber are represented in the curves as shown in Figures 6.2a and 6.2b.

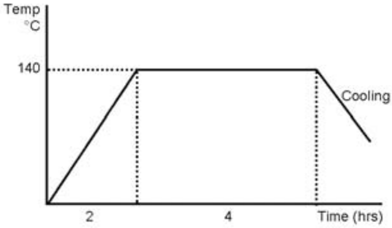

Figure 6.2a Autoclave curing cycle for soft rubber lining

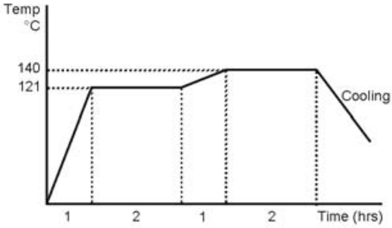

Figure 6.2b Autoclave curing cycle for ebonite lining

At the completion of the cure cycle, and during the cooling process, air is again applied so that the pressure on the lining is maintained to prevent distortion or shrinkage. Fast cooling will create stresses on the adhesive bond, leading to failure due to debonding.

6.2 Hypalon Rubbers

This elastomer is manufactured by DuPont de Nemours and Co. Inc., Wilmington, DE, USA. This has outstanding resistance to ozone and generally is more resistant to acids than Neoprenes. It is attacked by esters and ketones. It is applied in tanks which handle corrosive sodium hypochlorite and in drying towers in caustic soda plants, where sulfuric acid is handled and in electroplating service, where chromic acid is used. The temperature range where this rubber can be used is –5 °C to 125 °C. While compounding Hypalon rubber, the fillers largely used are clay and barytes rather than any reinforcing fillers like carbon blacks. The non black fillers do not leach out and discolour the acid medium as the black fillers do. Furthermore, vulcanisates which contain barytes tend to exhibit a somewhat better resistance to volume swell than do compounds containing carbon black. Whiting cannot be used in Hypalon lining for acid service.

The chemical name for Hypalon is chlorosulfonated polyethylene and it has excellent resistance to heat, ozone and oxidising chemicals and has good abrasion resistance. It can be compounded for outstanding resistance to oxidising chemicals, such as sodium hypochlorite solutions in sulfuric acid saturated with chlorine and concentrated phosphoric acid. It is one of the few synthetic rubbers that can be mixed in any colour without loss in mechanical properties.

The uncured Hypalon compound behaves much like a thermoplastic resin. It is tough and nervy at room temperature, but its viscosity is reduced rapidly as it is warmed by working on a two roll mill. By contrast Neoprene is not as tough as Hypalon at lower temperatures.

6.2.1 Compounding Hypalon for tank lining

Hypalon does not break down during mastication in the sense that natural rubber and Neoprene do. These rubbers undergo an irreversible chemical change (i.e., a reduction in molecular weight) when they are worked in the mixing mill.

The reduction of toughness that occurs as Hypalon is milled is strictly temperature sensitive and is temporary and reversible. Compounds of Hypalon can be reworked in the calender or mill without significant change in processing behaviour as long as a scorch free accelerating system is used. The processing operation with any one production stock is consistent from batch to batch if the best temperatures in rolls are determined and maintained. The thermoplasticity of raw or compounded Hypalon disappears with vulcanisation and hence does not reappear in the cured finished sheets. Because of thermo plasticity and lack of breakdown, Hypalon compounds tend to be dry and non tacky at room temperatures, but prewarmed stock gives good flow, knitting and ply adhesion during the lining operations.

The selection of plasticisers for use in a Hypalon compound as in any other compounds depends upon such factors as compatibility, processing requirements, cost and the ease of application of lining and curing. Petroleum oils are used because of low cost. Paraffinic waxes are effective but they must be used sparingly; if used in excess, they bloom to the surface making application impossible. Solvents like trichloroethylene, xylene or toluene will have to be used on the surface to freshen the same. Polyethylene glycol is very effective at low processing temperatures. Aromatic oils are compatible with Hypalon, improving tack of the calendered sheets during application of the lining. Even though resin and tackifiers can be used in Hypalon compounds, still noticeable increase in tackiness will not occur when the stock is cold. Generally it can be observed in Hypalon stock that chemical resistance is decreased when the level of resins and plasticisers is increased.

Processing aids are used in Hypalon compounds to minimise sticking to calender rolls. Microcrystalline waxes are effective release agents and are widely used because of their good solubility. A polyethylene glycol such as Carbowax 4000 is useful at temperatures below 77 °C. Low molecular weight polyethylene such as a C_6 polyethylene are effective at temperatures above 77 °C, but when added on a cold mill it can actually aggravate sticking. It is good to use small amounts of several process aids to help release over a range of temperatures without exceeding the compatibility of any individual processing aid. In compounds containing litharge, stearic acid and stearates should be avoided because they may tend to promote scorch. Blends of naphthenic and aromatic plasticisers give easier processing compounds than aromatic oils alone. Large amounts of aromatic oils tend to make the Hypalon compound sticky. Naphthenic oils are compatible in amounts up to 15 to 20 phr. Reinforcing fillers such as silica and fast extrusion furnace (FEF) carbon blacks are used to increase the green strength of highly plasticised compounds. Such stocks are some times soft and become tender when hot, though they may not be sticky. Three to five parts of *cis*-4-polybutadiene or EPDM rubber may be added to such stocks resulting in more body and improved release. It is not necessary to add a cure pack for these polymers as they are in small quantities. When used in such small levels they do not seriously affect cure rate or vulcanisate properties. Polybutadiene will give some reduction in scorch time.

The Mooney viscosity and the cure rate of Hypalon compounds do not change appreciably under typical storage conditions. Temperature is a factor as mentioned earlier because of thermoplasticity. Because of longer heat exposure mill mixed compounds are likely to be scorchier than those mixed in internal mixers. A typical mixing time for a normal batch is approximately 25 minutes depending upon the types and amounts of fillers and plasticisers. Fillers should be added as soon as smooth blend is formed. Since Hypalon does not break down, no time should be spent working the polymer alone. After mixing, the stock should be cooled as quickly as possible.

Mixed stocks should not be stored in conditions of high humidity. Because moisture absorbed by Hypalon compounds under high humid condition acts as an accelerator causing an increase in mooney viscosity and subsequent scorching. Mixed compounds of Hypalon should be used as quickly as possible. Unaccelerated stock can be stored for a comfortable period in accordance with production schedule and when final calendering is scheduled the accelerators can be added. The calendering temperatures can be between 60 °C to 93 °C. Uneven roll speeds are preferred and the top roll is usually hotter than the middle roll. Cool calendering obviously helps to eliminate trapped air. Higher temperature produce smooth surfaces with the upper temperature limits dictated by the tendency of the hot sheet to sag and distort, as it leaves from the bottom roll of the calender. Stock fed to the calender should have almost the temperature of middle roll. Temperature variation in feed stock causes uneven gage and a rough surface.

Division strips, caulking strips and end rings used for fixing filter grids on the Hypalon lined filter drums for sulfamic acid slurries are extruded from Hypalon compounds. The extrusion temperature condition are maintained as follows:

Screw	Cool (atmospheric temperature)
Feed area	50 °C
Barrel	60 °C
Head and die	93 °C – 107 °C

Extrusion of Hypalon tends to be soft when hot. The die correction for the profiles for accommodating shrinkage and swelling of the stock should be done based on a few trials. As soon as the correct profile comes out of the die, it should be thoroughly cooled in a cooling tank with soapy water.

Hypalon lined tanks are used for best possible resistance to oxidising acids. The litharge curing systems can be used for black or non black compounds. However, for minimising the absorption of hydrochloric acid, a low level, i.e., less than 10 phr of litharge should be used. For minimum absorption of water, the optimum amount is 20 phr. An epoxy curing system is best suited for wet chlorine environment for the tank lining. This gives good building tack also. However, it becomes weaker than litharge in taking up the hydrochloric acid, generated during cure. This limits the over all uses of the epoxy cure. However the epoxy cure has to be considered when conditions warrant its use. A level of 15 phr of epoxy resin is good enough to replace of 25 phr of litharge.

The curing system based on magnesia would be used to provide resistance against concentrated sulfuric acid and other drying agents. If there is a possibility where the lining is exposed to 30% hydrochloric acid, magnesia should not be used.

The litharge cures are safe and provide scorch free cures. Therefore they are generally preferred in designing compounds for lining. The dosage of dipentamethyline thiuram hexasulfide (Dupont’s Tetrone A-DPTH) in a litharge cured stocks can be varied from 1.5 to 2 phr and 0.5 phr of benzothiozyl disulfide can be added for additional safety. Carbon blacks are added for aiding calendering. But when the sheets are cool, they become tough. Medium thermal carbon blacks with some clay will alleviate this problem. Epoxy resin cured stock gives handling advantages over litharge cured stocks. It is safer from the point of view of shelf life, pliability, tack and gives better cured adhesion with the metal surface. It is slower curing than litharge and so preferred for thicker lining.

During processing of Hypalon compounds for tank lining application it should be kept in mind that the total heat cycle (the heat history of the stock) must be kept to a minimum. It is to say that at the optimum or more practical temperatures of the exposure time of the stock should be minimum at each stage of processing starting from mixing. In the mixing operation, more than in any other operation, the heat exposure or heat life of the stock is more. The following mixing tips can be helpful:

- Use a short mixing cycle as far as possible
- Do not prolong the time after mixing litharge and acceleration
- Cool the mixed stock as quickly as possible.

Mill mixing should be completed in 30 minutes. Properly compounded stock may have a Mooney viscosity of about 30 to 35 (MS 1 + 4 at 121 °C; MS: Mooney viscosity with a small rotor).

Mixing mill temperature can be 85 °C to 90 °C. In Banbury mixing the cycle will be 5 minutes. Dumping should be done before the temperature goes up to 110 °C, especially if a litharge cure is used. From a scorch safety point of view, masterbatches of litharge can be used, such as 10% EPDM with 90% litharge.

Calendering of Hypalon stock is a tricky job. The shelf life for the mixed stock before calendering preferably should be kept to a maximum of 24 hours and a minimum of 12 hours. Such resting period for the compounded stock leads to successful calendering resulting in smoother sheets. The good finish of the calendered Hypalon sheets depends upon the total loading in it and the calendering temperatures. In general a 30% volume loading will result in smooth calendering and the sheet is released smoothly from the rolls.

The suggested temperatures of the calender rolls are:

Top roll	60 °C
Middle roll	55 °C
Bottom roll	Room temperature

Low molecular weight polyethylene such as a CPE6 is often used at 3 to 5 phr levels to provide safer stocks and to prevent sticking on roll surface when roll temperatures are at times increased slightly to get smoother and tacky sheets enabling plying up to the required lining thickness. Hot calendering also reduces cured shrinkage. Hypalon is less tacky than Neoprene and so it is advisable when plying up the sheets to augment tack by using temperature that can be tolerated and yet avoiding sticking to the rolls. It should be noted however that uncured Hypalon sheets soften considerably during cure at high temperatures causing plies to knit better and form a satisfactory cured lining.

For adhering the Hypalon sheet to the metal surface, invariably a tie-gum or tie-solution in toluene can be used over the isocynate coat (i.e., Chemlok 205) for better integrated bond with the metal. The technique of application of Hypalon lining is almost same as that of Neoprene. The curing in autoclave, in open steam or hot water is also similar to that of Neoprene.

6.3 Butyl rubber

Butyl rubber was developed by the research department of Standard Oil Company [4], New Jersey in the 1930s which later became a constituent of the Exxon Corporation.

Butyl rubbers are copolymers of isobutylene and isoprene. Like natural rubber, butyl rubber too does not break down on mastication or during the normal mixing process. The compound viscosity is controlled by selection of raw polymer grade, carbon black type and loading and oil type and loading. Relatively high loadings of paraffinic or naphthenic oils are employed for typical butyl applications such as tubes, etc., but such heavy loadings are not advisable in lining compounds.

Butyl rubber like Hypalon, Neoprene or nitrile rubber is a speciality polymer which can be compounded for a soft, deformable elastic vulcanisate similar to the other elastomers, but having certain distinctive characteristics, like low permeability to all gases and resistance to ageing and ozone cracking. Butyl has poor oil resistance and medium low temperature flexibility.

Halogenated butyl rubbers called halobutyls such as chlorobutyl rubber (CIIR) and bromobutyl rubbers are later developments. Zinc oxide is a vulcanising agent with low levels of sulfur for halobutyls and stearic acid. Sulfenamides accelerate vulcanistion of halobutyls. Bromobutyl shows higher cure reactivity than CIIR. Both bromobutyl (BIIR) and CIIR will cure with zinc oxide, but only BIIR will cure with sulfur alone, no zinc oxide or accelerator being necessary. BIIR can be cured with 0.5 phr of sulfur, 1.3 phr of dibenzothiazyl disulfide and 1 phr of stearic acid. Sulfur levels as low as 0.5 phr will give a rapid cure.

Zinc dithiocarbamate can be used in small quantities (0.25–0.75 phr) with zinc oxide cures used in heat resistant and improve compression set.

The tensile strength of pure gum butyl compound is the highest. As the filler loading increases, the tensile strength falls. In practical formulations 50 to100 phr of general purpose furnace black or fast extrusion furnace black (FEF) is added and 100–150 phr of mineral fillers such as hard clay, talc or silicas are added. Higher levels of carbon blacks make the lining sheets unsuitable at times for spark testing at higher voltage, as at this voltage the rubber is burnt due to excessive carbon. If high loadings of carbon blacks are unavoidable, the spark testing voltage has to be reduced. The recommended plasticisers are highly saturated hydrocarbon oils and waxes. The maximum level of ozone resistance is achieved when low unsaturated grades of butyl are vulcanised to the highest state of cure. In general plasticisers reduce ozone resistance.

Butyl vulcanisates are not serviceable in continuous contacts with hydrocarbon oils and solvents as swelling is more. Butyl is resistant to vegetable and animal oils. Strong acids and bases do not attack butyl neither do strong oxidising agents or reducing solutions. Concentrated nitric acid or sulfuric acid however, cause degradation to a level less than natural or Neoprene rubbers. In compounding for minimum swell, the factors of highest importance are high filler loadings high reinforcement and maximum state of cure. If butyl sheets are compounded for resistance to mineral acids, chemically sensitive fillers like calcium carbonate should be avoided. To protect the non black butyl compounds from sunlight, it is necessary to use adequate loadings of high opacity pigments such as titanium dioxide.

For zinc oxide at, for example, levels of 15 to 45 phr, good filler dispersion is essential for better dimensional stability in calendered sheets. Butyl sheets are used in storage tanks, digesters and other large equipment handling phosphoric acid, hydrochloric acid and sulfuric acid very effectively in fertiliser and chlor-alkali plants. When high temperatures are encountered, carbon bricks or acid resistant bricks are lined over the rubber lining.

Butyl rubber is used in specialty application such as reservoir or canal linings, tank linings, pharmaceuticals and sealing caulks. The low unsaturation and low permeability of the rubber molecule contribute to the chemical inertness of the butyl rubber.

In Europe exhaust gas from chimneys in power plants was desulfurised in scrubbers and other equipment using butyl rubber lining for more than 25 years [5]. Service lives of butyl rubber lining of more than 15 years have been reported. Many countries like USA, Japan, Austria, Netherlands, Denmark, Finland and England followed the procedure of applying butyls or halobutyl in the flue gas desulfurisation plants. Using the wet scrubbing process for separation of phases in lime stone or calcium hydroxide suspension more than 150 plants of this kind have been rubber lined with butyl and were in operation throughout Europe.

In many cases of scrubber lining *in situ* self-curing butyl rubber linings are used which is curable in 15 to 20 days time at atmospheric temperature. In some other cases pre-vulcanised butyl or bromobutyl rubber sheets are applied using contact adhesives based on isocynates. The tie coat between the bonding adhesive and the lining is made from CIIR that has good compatibility with the lining and the bonding agent and good adhesion strength. Butyls or halobutyls meet the following rubber lining functions in scrubbers such as:

- Low diffusion and permeation
- Resistance to acids and salts
- High abrasion resistance
- Thermal resistance at a maximum temperatures of 90 °C
- Oxidation resistance
- Low ageing
- Ease of application

Coal fired power plants have soft butyl linings in their plants and equipment which give a service life of about 15 to 20 years. In this case either pre-vulcanised or self-curing butyl lining of 4 mm thickness with a durometer hardness of 55 A has been used. In lignite based power stations, bromobutyl gives a life of 10 years. Operating times in many plants are increased, leading to changes in the condition of the linings. Rubber lining swells, become embrittle, develop cracks and increases the layer thickness. If embrittlement predominates, in other words deterioration of the mechanical properties like elongation and tensile strength occurs, the rubber lining is not able to cope up with the mechanical stress caused by suspension or sludges as the case may be. When such situations are noticed, relining is to be done after removing the old lining.

In vulcanising butyl rubbers, sulfur vulcanisation is generally used with higher accelerator levels as in the case of EPDM. Unlike EPDM, this elastomer has sufficient chain regularity to permit crystallisation on stretching so it can exhibit high gum strength. Butyl rubber has a T_g of –72 °C. It shows a low resilience at room temperature with a high hystersis loss. It is therefore a useful damping rubber. Butyl rubber cannot be blended with high unsaturation rubbers in sulfur vulcanisation.

6.4 EPDM Rubber

EPDM rubbers are amorphous polymers. Like any other non crystallising polymeric materials, the mechanical properties of the unfilled EPDM rubbers are very poor and as a result, addition of reinforcing fillers becomes important for giving strength to this rubber. In general special physical properties of high values are not required in the case of EPDM rubber compounds since their application areas are critical chemical and acid environments and water and gas systems. Usually easy processing, semi reinforcing carbon blacks are used in EPDM compounds. Its low density enables use of high loadings of extender oils and inert and semi reinforcing fillers from the point of view of economic consideration. EPDM rubbers have high esteem in process industries handling nitric acid and chromic acid corrosive environment in small concentration at around 5% in application such as electroplating industry. Another variety of oil extended EPDM is available in the market.

These may be used for low hardness compounds in areas where impact abrasion is predominant. EPDM is at times referred as ‘crackless rubber’ since it has high tear resistance. For producing high hardness compounds blends with natural rubber, styrene-butadiene rubber (SBR) and high styrene resins are recommended.

General curing system for EPDM rubbers will be a thiazole (mercaptobenzothiazole or dibenzothiazole disulfide) accelerator with a thiuram and/or a dithiocarbamate. For high heat exposure condition in a process industry, sulfur donor types like tetra methyl thiuram disulfide may replace a larger part or all of the sulfur.

The main chains of the EPDM molecule have no double bonds and thus EPDM does not deteriorate due to molecular scission even after prolonged exposure to sunlight and high ozone concentration. Commercial grades of EPDM rubbers contain a maximum of 15 double bonds per 1000 carbon atoms in contrast to butyl rubbers, or styrene butadiene copolymers with 150–200 double bonds per 1000 carbon atoms in the main chain. Thus ozone, resistance to heat and other atmospheric exposure hazards such as UV radiation and humidity are excellent. Because of its molecular structure and if suitably compounded, EPDM compounds are resistant to weathering of all kinds.

Although EPDM do not possess the excellent low air permeability of butyl rubbers they have good low temperature properties, ageing and better processibility. The many commercial grades available are differing in polymerisation processes such as solution or emulsion polymerisation, Mooney viscosity, molecular weight distribution and the ratio of ethylene and propylene. Because of the absence of double bonds in the main molecules, peroxide cures are used for curing and the cured products excel in heat resistance. Peroxides cures can be adopted if the application requires resistance to temperature of 150–175 °C and a very low compression set in tank flanges. Because of their excellent electrical insulation properties and high dielectric strength, EPDM is the preferred rubber lining compound in electroplating tanks in steel industry. It is flexible above –50 °C. EPDM is resistant to polar solvents such as alcohol, glycol, ketone and phosphate ester, acids, alkalies, salts and fats.

However EPDM does not possess resistance to hydrocarbon oils and solvents. EPDM grades are suitable for use in pipe system in drinking water application. The combined effects of heat resistance and low compression set increase the service life of EPDM compounds. Most EPDM grades conform to several international approvals and regulations for use in drinking water application, such as the Water Regulation Advisory Scheme of the UK (WRAS; *www.wras.co.uk*), The German Technical and Scientific Association on Gas and Water (DVGW; *www.dvgw.de*) and the Food and Drug Administration of USA (FDA; *www.fda.gov* and *www.epa.gov*).

EPDM's specific gravity is the lowest of all synthetic elastomers enabling it to admix with large quantity of inert fillers. Copolymer of ethylene and propylene monomers (EPM)/ethylene propylene terpolymer (EPT) rubber belongs to this category and stands for ethylene propylene terpolymer. EPDM has the skeleton structure of a methylene linkage. Various commercial grades of the rubbers are available based on processibility and curing characteristics. EPDM rolls are used in printing industry since they are highly resistant to ester plasticisers. In general, the mixing behaviour of EPDM rubber or EPM/EPT rubbers is excellent and very much comparable when compared with butyl or Neoprene or Hypalon rubbers. The aim of mastication is to reduce the Mooney viscosity of the rubber to aid further processing. Since most grades of EPDM rubbers are set at low Mooney levels, additional reduction of viscosity may not be needed and further reduction due to mechanical breakdown is also not very marked. EPDM has the advantage of minimum fluctuation in the viscosity of the compound enabling it to be easier for pre warming operation prior to sheeting. The low Mooney viscosity enables saving of energy in internal mixers.

Addition of 2 to 5 phr of alkyl-phenol resins improve tackiness of EPDM stocks. In blends with other synthetic rubbers such as SBR, the co-curability is an important factor while designing the overall curing system while compounding. The important factors to be considered here is to synchronise the curing speed between two polymers, using studies in oscillating disk rheometer charts. However, blends with styrene-butadiene rubber do not have as much acid resistance as 100% EPDM.

EPDM has a very low unsaturation which is sufficient enough for sulfur vulcanisation and low enough to reduce oxidative degradation. Because of its irregular chain structure, EPDM is amorphous and shows no crystallisation, unlike natural, Neoprene or butyl rubbers, on stretching. Hence, it exhibits poor strength and requires carbon black reinforcement. At higher ethylene contents say at > 60% the elastomer is semi crystalline and exhibits controllable green strength and crystallisation on stretching. A higher proportion of accelerator is to be used because of low unsaturation. It has good low temperature behaviour the glass transition temperature (T_g) being –60 °C and good resilience.

6.5 Silicone Rubbers

These rubbers are based on atoms of silicon chains rather than carbon atoms. Their unique structure is responsible for their extreme temperature properties. The most common types of silicone rubbers are specfically polysilaxanes. The Si-O-Si bonds can rotate much more freely than the C-C bond or the C-O bond. So the silicone chain is much more flexible and less affected by temperature. Silicone rubber is vulcanised by the action of peroxides which crosslink the chains by abstracting hydrogen atoms from the methyl side groups, allowing the resulting free radicals to couple into a crosslink. Some varieties of polysiloxanes contain some vinyl methyl siloxane units, which permit sulfur vulcanisation at the double bonds.

Siloxanes are soft and weak rubbers even with fillers like silica. Carbon black fillers do not work well. Silica fillers give a tensile strength of about 5–8 MPa. However the fillers offer excellent resistance to stiffening at very low temperatures, as well as softening at elevated temperatures thus retaining their properties, because of the great flexibility of the polymer chain. However, these silicone rubbers cannot be stable at 250 °C for longer time more than three months as they tend to degrade. For chemical plant lining applications silicone rubber is not suitable.

The main chemical routes for vulcanisation of silicone elastomers are 1) Elevated temperatures cures and 2) Room temperature vulcanisation mechanisms. Organic peroxide cures are used in elevated temperature cures. Since the organic peroxides are inhibited by most carbon blacks, non black reinforcing fillers such as precipitated silicas, titanium dioxide and zinc oxide are used. Room temperature vulcanisation is normally used with low consistency silicone elastomers.

The uses of silicone elastomers are varied. Many grades are available for specific uses like for high tensile strength, toughness and low compression set properties. Silicone rubber is the chosen rubber for high temperature applications in the engineering industry. It has excellent weather and thermal stability, ozone and oxidation resistance and extreme low temperature flexibility. It is more permeable to gases than natural rubber. Silicone rubber retains its rubber like properties and dielectric (preventing flow of elasticity) characteristics over extreme temperatures. It is extremely inert. It remains relatively unaffected by long exposure to water, ozone and ultraviolet light. Silicone rubber has high thermal conductivity and 1 – 1.5 times more than that of resinous or organic rubber. This property is important in application where heat dissipation is required. The silicone rubbers are capable of working through and after fire. The total decomposition of the polymer leaves a brittle silica ash an excellent dielectric on its own. Conventional organic rubbers decompose to form conductive carbon deposits with no insulation properties. Manufactured from quartz and oil, silicone rubbers are unique among elastomeric materials due to the properties inherent in their chemical structure.

6.6 Fluorocarbon Elastomers

These were developed by DuPont and 3M companies in USA during the 1950s. They are the most resistant elastomers to heat, chemicals and many solvents. But they are expensive elastomers. The most common types are copolymers of vinylidene fluoride and hexa fluoropropene. The fluorine atoms give chemical inertness and hydrogen atoms in the methyl group give rubbery properties. Vulcanisation of fluorocarbon elastomers are effected by diamines which cause crosslinks by reacting with the fluorine atoms. These elastomers are generally designed for high temperature use with mechanical properties as secondary considerations. Tensile strengths of 12–15 MPa are generally achievable at ambient temperatures, and they change very little after exposure to high temperatures. Thus these elastomers have an indefinite life at 200 °C and can be heated to 315 °C up to 48 hours. They have poor low temperature properties, reaching a brittle point at –30 °C when compared to nitrile rubber at –40 °C.

Fluorocarbon elastomers are non crystalline polymers exhibiting rubbery properties only when crosslinked. DuPont developed additional types of these elastomers for improved low temperature and chemical resistance properties. Fluorocarbon elastomer compounds show excellent resistance to automotive fuels and oils hydrocarbon solvents, aircraft fuels and oils, hydraulic fluids and chlorinated solvents of certain types. They show excellent resistance to highly aromatic solvents, polar solvents, water and salt solutions, dilute acids, dilute alkaline solutions oxidative environments, amines and methyl alcohol. Hexafluropropylene containing polymers are not recommended for use in contact with ammonia, strong caustic lye (50%) above 70 °C, and polar solvents like methyl ethyl ketone and low molecular weight esters. Propylene containing fluorocarbon polymers can tolerate strong caustic lye. The thermal degradation temperature of fluorocarbon rubbers is 500 °C.

Gum viscosity of fluorocarbon elastomers is of primary importance in the determination of processibility, as this factor affects vulcanisate properties especially com pression set. Gums are available with Mooney viscosity (ML 1+10 at 121 °C; ML: Mooney viscosity with a large rotor) values of 5–160. A Mooney viscosity range of 20–60 is preferred for the optimum combination of flow and physical properties. Higher viscosit ies can cause excessive heat built up during the mixing operation without a compensatory gain in physical strength and compound viscosity. As in other elastomers it depends on gum viscosity and on filler selection. A preferred range of gum viscosity is MS at 120 °C is 25 – 60.

Fluorocarbon elastomer can be mixed in any conventional mixing equipment and with standard mixing technique. Normally post curing is done at elevated temperatures as it develops maximum physical properties and imparts cure homogenity. The general post curing system is 24 hours at 200 °C to 250 °C. Most applications of fluorocarbon elastomers are in the transportation areas. Aerospace industry account for a negligible percentage of consumption whereas more than 50% is in the transportation sectors. Segments like petrochemical, industrial pollution control and pneumatic applications are demanding more and more fluorocarbon elastomers.

6.7 Natural Rubber

Natural rubber is essentially polyisoprene $(C_5H_8)_n$. Every fourth bond in the chain is unsaturated and every fourth carbon atom carries a methyl group. It is to the presence of the unsaturated bonds in the chain that natural rubber owes much of its versatility. On stretching, natural rubber displays long range elasticity provided the extension is not too great or the duration of the same is not too long. However, at elongations greater than 200 to 300%, the x-ray diffraction picture of the structured rubber develops the pattern characteristic of an oriented crystalline polymer. If, however, the rubber is stretched very slowly to smaller extension or at high temperatures viscous flow occurs.

The very high extensibility and tensile strength of natural rubber are therefore not entirely due to entanglements of randomly coiled polyisoprene molecules, but also to the formation of crystallites under stress. It is of interest to note that those synthetic rubbers which do not crystalise on stretching have uniformly low tensile strength. The following table gives the stretching crystalisation of elastomers (Table 6.2).

Table 6.2 The Stretching Crystallisation of Elastomers

Name	Chemical Name	Vulcanising Agent	Stretching Crystallisation	Gum Tensile Strength
Natural Rubber	*Cis*-1,4-polyisoprene (>99%)	Sulfur	Good	Good
Styrene-butadiene rubber	Polybutadiene-*co*-styrene	Sulfur	Poor	Poor
Butadiene rubber	Polybutadine *cis*-1, 4 (>97%)	Sulfur	Fair	Fair
Isoprene rubber	*Cis*-1,4 Polyisoprene (>97%)	Sulfur	Good	Good
EPDM	Polyethylene-*co*-propylene-*co*-diene	Sulfur	Poor	Poor
Butyl rubber	Polyisobutylene-*co*-isoprene	Sulfur	Good	Good
Nitrile rubber	Polybutadiene-*co*-acrylonitrile	Sulfur	Poor	Poor
Chloroprene rubber	Polyacroprene (mainly *trans* form)	MgO or ZnO	Good	Good
Silicones	Polyalkylsiloxane (mainly polydimethyl-siloxane)	Peroxides	Poor	Poor
Fluorocarbon elastomers	Polyvinyledene fluoride-*co*-hexa fluoropropene	Diamines	Poor	Poor
Polysulfide rubber	Polyalkylene sulfide	Metal oxides	Fair	Poor
Polyurethanes	Polyurethanes	Di-isocynate	Fair	Good
Hypalon	Chlorosulfonated polyethylene	Sulfur	Varies with proportions of chlorine and sulfonyl groups	Varies with proportions of chlorine and sulfonyl groups

Source: M. Morton in *Kirk-Othmer's Encyclopedia of Chemical Technology*, *Fourth Edition*, Volume 8, Eds., J.I. Kroschwitz and M. Howe-Grant, Wiley-Interscience, New York, NY, USA, p.906 and 907.

For the most effective development of rubber-like elasticity, permanent interlocking of the chain molecules at a few points along their length to form a loose three dimensional network is desirable. The crosslinks should be sufficient in number to ensure a prominence of structure, in other words, a suppression of viscous flow and yet not so numerous as to seriously restrict the internal segment mobility of the polymer chain. A very convenient way of effecting this crosslinking is to react the natural rubber with sulfur. Sulfur linkages are formed between the chain with strengths comparable to those linking the carbon atoms of the polyisoprene chains in the starting material. This process is known as vulcanisation and occurs as a consequence of the presence of highly reactive double bonds in the polyisoprene chains. The effect of vulcanisation is to raise the T_g of the amorphous polymer and to lower the melting point of the crystallites formed on stretching the amorphous material. Table 6.3 shows how the T_g for natural rubber increases with increasing extent of vulcanisation as effected by increased dosage of sulfur.

Table 6.3 Effect of Vulcanisation on T_g with increased proportion of sulfur

Percentage of sulfur	T_g (°C)
0	-65
0.25	-64
10.0	-40
20.0	-24

Crosslinked polymers are to be regarded as giant three dimensional molecules of indeterminable molecular weight, i.e., varying molecular weight that can be described as molecular weight distribution. Such molecules swell in solvents to an extent that depends on the nature of the swelling solvent and also on the extent of crosslinking. The more crosslinked the molecule is, the less the swelling in a given liquid media. As the number of crosslinks is increased, these polymers, as they are often called hard rubbers or ebonites containing more than 30% sulfur combined with the natural rubber molecules, show progressively less segmented motion of the chains between the crosslinking points. Consequently, they lose their long range of elasticity and resemble ordinary brittle solids in their elastic behaviour. Many of the mechanical products of a high polymer are molecular weight dependent, although the effect may be sidelined by other factors such as chain orientation and crystallinity. In the case of chemical resistance as judged by the swelling of the polymer in a liquid media over a period of time, the high crosslinking density plays a vital role in providing increased chemical resistance. Natural rubber ebonites exhibit very good protection against acid attack because of their highly crosslinked molecular structure.

The corrosion of metals by non oxidising acids occurs when the metal is able to displace hydrogen ions from the solution. The corrosion effects that arise in the petroleum refining industry are connected with the presence of corrosive sulfur compounds formed by thermal decomposition of sulfur particularly hydrogen sulfide, or of hydrochloric acid produced by the hydrolysis of magnesium and calcium chloride present in the subsurface water. The sulfur compounds are particularly corrosive in petroleum refining at temperature above 260 °C. Chemical corrosion involves so many factors that each case should be considered as a separate problem requiring special treatment. Selection of materials of construction as protective lining on the metal surface should be based on accumulated experience on general principles and on the result of tests designed to simulate the process conditions in the actual plant.

Under these aggressive corroding environments, rubbers play an important role to protect the plant and equipment, facilitating high temperature operations, higher reaction velocities and maintaining equilibrium in a chemical process. Natural rubber as a protective medium is much used in the form of either soft vulcanised rubber, ebonite or semi ebonite which has the disadvantage of higher sulfur content leading to blooming at the surface but with a great advantage for bonding with metal. It is reliable up to about 80 °C to 100 °C. Soft rubber containing less sulfur is often used at temperatures up to about 70 °C. Neoprene has the advantage of being inert to oils and greases when compared with natural rubber. Butyl is used extensively having the great advantage over natural rubber as it will resist oxidising acids, e.g., 5% to 10% nitric acid up to 50 °C. Thiokol (polysulfide rubber) when compared with natural rubber is not highly resistant to chemicals but its resistance to solvents is outstanding.

After the discovery of vulcanisation by Charles Goodyear, it was Nelson Goodyear who patented a process for making ebonite under US Patent 8075 in 1851 [6] by heating the rubber with large proportions of sulfur. The commercial manufacture of hard rubber products started a few years later and thereafter ebonite became an important branch of the rubber industry. Though during the subsequent years, and until today, newer types of hard plastics came into existence to replace hard rubber. The hard rubber industry continued to stay in its position of importance by virtue of its unique characteristics main one being its chemical resistance. The chemical inertness, high strength and good appearance of hard rubber have led to many applications with it. Hard rubber, like soft rubber, is compounded with many ingredients other than sulfur. It may contain varying proportions of fillers incorporated for the purpose of obtaining desirable characteristics. Large proportions of ebonite dust, known as polyisoprenesulfide is manufactured from waste and used as a filler in ebonite compounding. Fully cured ebonite products are not capable of bringing in vulcanisation reaction when mixed with raw rubber. This is indicative of the strong bond which exists between the sulfur atom and the rubber molecule. The study of rubber hydrocarbon's reaction with sulfur shows that some substitution of sulfur is also taking place in addition to addition reaction. The chemical analysis of fully vulcanised ebonite shows a combined sulfur content of more than 32%. Sulfur obviously reacts with rubber very slowly at room temperature. Vulcanisation of hard rubber is carried out usually at temperature between 130 °C and 160 °C. The commercial period of vulcanisation of hard rubber generally ranges from about 15 minutes to 20 hours or even longer, depending on the composition and dimensions of the product, type of curing process and on the temperature used. The hot water curing process, which is adopted at client's site takes as high as 48 hours of curing period. Thick sheets of ebonite require relatively long periods at low temperatures. Heavily loaded and highly accelerated compounds can be cured for a short period at 150 °C to 160 °C.

The hard rubber reaction liberates considerable heat during the curing process. This heat liberated suddenly at an early stage of vulcanisation reaction is accompanied by a vigorous evolution of hydrogen sulfide gas indicating that substitution or decomposition is taking place. At higher temperatures of vulcanisation sulfur combines chemically with rubber at a rapidly increasing rate. If vulcanisation is carried out at 120 °C to 130 °C, the rate of reaction and consequent heat evolution is kept down. This, in conjunction with longer time available for heat flow from the centre of the mass of the compound results in only a moderate internal temperature rise compared with the result of vulcanising at higher temperatures.

In vulcanising thick articles of ebonite such as pipe internals whose wall thicknesses are 2.5 cm to 5 cm, low temperatures and long periods of vulcanisation must be used. Otherwise the material becomes a porous and brittle mass as a result of excessive internal temperature. The general practice in the manufacture of thick articles is to use compounds containing high percentages of hard rubber dust, mineral fillers and reclaimed rubber that reduce the heat evolution during vulcanisation. The use of accelerators should be done with caution in hard rubber vulcanisation especially of thick articles. Their use is, at times, attended with difficulties such as scorching, porous surface, discolouration and brittleness in the final product. Further the slow accelerators for soft natural rubbers will accelereate the hard rubber vulcanisation. An example of this is diphenyl guanidine. Lime and magnesia are frequently used in small percentages to accelerate the vulcanisation of hard rubber. Light calcined magnesia is most commonly used.

Hard rubber dust is used as a common filler in ebonite compounding. It facilitates mixing and reduces excessive shrinkage in the sheetings from the mill or calender. With the use of hard rubber dust, the possibility of blowing or bursting during vulcanisation is greatly reduced. In anticorrosion compounding formulation fillers, such as barytes, whiting and clay, are widely used for greater hardness and toughness and heat resistance as well as for economy.

It may not be possible to form a detailed picture of the molecular structure of ebonite. Combined sulfur is present partly as crosslinks between neighbouring rubber chains (intermolecular sulfur) and partly as sulfur atoms linked to two carbon atoms in the same chain forming a carbon sulfur ring structure (intra-molecular sulfur). The elastic modulus of ebonite is high, i.e., at high temperature is about 10 times that of a pure gum vulcanisate while its swelling in active swelling liquids is only about one-eighth. The dependece of modulus and swelling on degree of crosslinking would therefore indicate that ebonite is much more densely crosslinked than a soft vulcanisate. The swelling action of a liquid on ebonite is not similar to its swelling action on a soft vulcanised rubber. Although with increasing sulfur content over the range from soft to hard vulcanisates swelling almost decreases the extent of the decrease depending on the nature of the liquid, being greatest with aliphatic hydrocarbon, slightly less with aromatic hydrocarbons, significantly less with halogen and sulfur compounds and least with polar liquids, such as hydrogen chloride H^+CL^-. Consequently the relative swelling capacities of two liquids may be reversed on passing from soft rubber to ebonite. Thus petroleum usually swells soft rubber more than nitrobenzene, but with ebonite, the later provides the greatest swelling.

The swelling time of ebonite is usually greater than (10–15 times) that for soft rubber in the same liquid. Carbon disulfide is an exception since it swells ebonite almost as quickly as soft rubber. Moreover with ebonite there are greater differences between the swelling times of different liquids than with soft rubber.

With soft rubber the swelling time is generally shorter, the less viscous the liquid, but this relationship does not apply to ebonite through which the least viscous liquids like acetone ethyl acetate and petroleum ether, diffuse slowly.

Therefore, although the viscosity of a liquid does influence its rate of penetration into ebonite, the permeability of the ebonite is so greatly increased by absorption of the liquid that its swelling capacity has much more influence on this rate rather than the viscosity itself. It may be useful to understand at this juncture what permeability of a rubber or ebonite is to gases or liquids.

Permeability is a process in which liquid or gas molecules dissolve in the elastomer, on one side of the membrane and diffuse through the other side and there escape out. The solubility of a gas or liquid in a given elastomer is closely related to its tendency to condense and is also related to the interaction between the gas/liquids molecules and the elastomer molecules.

The rate of diffusion in a given elastomer is found to be related chiefly to the size of the liquid/gases molecule. It is observed that the presence of polar group or methyl group in the polymer molecules reduces the permeability to a given liquid/gas. Therefore butyl, Neoprene and nitrile, along with ebonite, have a low value of permeability when compared with natural soft rubber vulcanisates.

Long swelling time and low swelling maximum mean better resistance to the swelling action of the liquid. In general ebonite of a given vulcanisation coefficient resists swelling better if produced by a long cure on a low sulfur package. This procedure also results in a higher elastic modulus (Young's modulus) at room temperature and in higher yield temperature, in other words, greater resistance to high temperature deformation. The effects on all these properties – modulus, yield temperature, and swelling – imply that the lower temperature and long cured low sulfur ebonite has a more closely knit molecular structure.

Swelling is strongly dependent on the chemical nature of the vulcanised elastomer and the high proportion of combined sulfur in ebonite gives it a much reduced affinity to aliphatic hydrocarbon acids and water.

6.8 Synthetic Ebonites

Some details of synthetic hard rubber (ebonites) are given next.

Fully cured SBR ebonites are brittle on bending through a sharp angle and will fracture more easily than natural hard rubber. Electrical properties of nitrile hard rubbers are inferior to those of SBR and NR hard rubbers. The softening point of nitrile hard rubber is slightly higher and its resistance to petroleum solvents and hydrocarbons is excellent. Polybutadiene hard rubbers have identical properties similar to those of SBR and NR hard rubbers. Chlorobutadiene hard rubbers could not be made and information on ebonites of this rubber is not available. Polysulfide rubbers when compounded with high percentages of sulfur do not yield vulcanisates comparable to hard rubbers.

Isobutylene-isoprene rubbers, the copolymers containing 98% isobutylene and 2% isoprene cannot be made into hard rubbers because of the lack of adequate unsaturation. However a very hard butyl rubber vulcanisate can be obtained by admixture with SBR and high levels of sulfur. The water absorption of NR ebonite is 0.45% to 0.5% at a relative humidity of 97.2%.

The high water absorption values of nitrile ebonite (about 3.3% to 4.5%) could not be anticipated. just because a soft vulcanisate made from similar copolymer absorbs less water than a NR vulcanisate.

Nitrile hard rubbers surpasses all of the other synthetic ebonites in resisting the swelling action of solvents like benzene, gasoline, carbon disulfide, nitrobenzene, petroleum, ether, transformer oils, hydraulic fluid, and so on (Table 6.4).

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Table 6.4 Effect of Acids on Hard Rubbers

Acid	Satisfactory effect	Unsatisfactory effect
Hydrochloric acid (12 weeks at 20 °C)	Natural rubbers Buna 85 Buna S Buna SS	Perbunan Perbunan extra
Sulfuric acid dilute (12 weeks at 20 °C)	Natural rubber Buna 85 Buna S	Perbunan Perbunan extra
Hydrofluoric acid (2 weeks at 20 °C)	Heavily loaded blends of natural rubber with Buna 85/Buna SS	Perbunan Perbunan extra
Nitric acid (8 weeks in 32% at 20 °C)	Neoprene rubber Buna SS	Perbunan Perbunan extra
Chlorine gas (4 weeks at 70 °C	Natural rubber Buna 85	Perbunan Perbunan extra

Buna 85 is polybutadiene (the number represents Mooney viscosity), molecular weight -80,000. Hard rubber has high softening point and excellent chemical resistance. The coefficient of vulcanisation to the ebonite stage is 39.3. The coefficient of vulcanisation is the number of unit weight of sulfur combined with 100 units by weight of unsaturated hydrocarbons. Buna S is a butadiene styrene copolymer with 70/30 to 68/32 ratio. Buna SS contains a high proportion of styrene. Perbunan are nitrile rubbers

7

Compounding Elastomers for Rubber Lining

Neither the natural rubber obtained from plantation nor the synthetic rubbers from the manufacturers can be used for rubber linings immediately. They must be compounded with other chemicals and agents to obtain a balance of properties to suit the end use. Working temperature, oxidation during ageing, exposure to corrosive environments and other detrimental influences such as mechanical abuse, abrasion, flexing, etc, need to be fully studied before compounding. The interconnected operations are mastication, mixing, shaping in extruder or moulding press or calender, handling of sheets for lining and application with hand tools and finally the vulcanisation or the curing process. Vulcanisation involves crosslinking of the polymer chains at intervals through sulfur atoms. Depending on the proportion of sulfur used, vulcanised rubbers can be made ranging from soft and elastic to hard and rigid types [1].

The chemistry and compounding and vulcanisation of all types of rubbers used for rubber lining applications are quite complex and information on these are not readily available to chemical engineers. The best practice is to discuss the chemical process with the rubber lining manufacturers and to obtain proper rubber selection for a given condition and the type of vulcanisation, whether in an autoclave or by pre-cured method or by open steam curing, or by hot water curing or by a self-curing methods. For immersion testing or for testing the bond strength of the lining, counter samples are to be lined as representative samples and cured along with the rubber lined vessel.

Although the inherent chemical resistance of the rubber chosen is quite suitable for the given duty conditions, many a times the bond or adhesion failure is the cause of lining failure. Therefore much care is taken while applying the lining especially at joints, seam, corners and flanges.

For correct rubber compounding of lining compounds a thorough knowledge and understanding of the following points are vital:

1) The type of rubber basically suited for the service conditions required.

2) The process by which the product will be manufactured, i.e., by extrusion, moulding, calendering, hand laying and forming.

3) The complete physical and chemical properties of the compounding ingredients and their reactions with acids and oxidising agents.

4) Processing methods and pressure and temperatures in the case of moulding, calendering, extrusion, and so on.

5) Comparative study and evaluation of gum and mixed vulcanisates of various types of rubbers.

6) An intimate knowledge of the end use and its application.

7) Design of rubber products where their mechanical and chemical aspects are involved.

8) The various duty conditions prevailing in chemical process industries.

9) The differences in the usage of rubber compounds for various applications. For example, compounds used for anticorrosive tank linings are quite different from compounds tailored for other dynamic working conditions and mechanical applications [1].

Even in the case of compounds for tank lining there are variations in compound formulation depending on the type of vulcanisation to be adopted for the same duty conditions, namely equipment which either can or cannot be vulcanised in autoclave. Equipment which cannot be vulcanised in autoclave would require one of the following methods to be used:

- Open steam curing
- Hot water curing
- Self-vulcanising
- Cold bond lining
- Curing by using the vessel itself as an autoclave

In the case of open steam curing and hot water curing, the vessel is to be insulated outside to provide heat retention at the adhesive layer so that proper bonding of the rubber to metal is ensured. In the case of curing by using the vessel itself as an autoclave, the same is to be designed to withstand the temperature and pressure conditions of the curing process as well. This is to be ensured by the vessel/tank fabricator. It is a good practice to insulate the outside of the vessel while the lining is cured with steam. The pressure in this case is 0.1 MPa. Self-vulcanising linings are not very popular except in case of non critical equipment. The cold bonding method involves the use of precured rubber and room temperature curable bonding adhesive. This method is mostly followed for large sized tanks.

During lining, the humidity in the atmosphere should not be high. The preferred humidity is 65%. (The term humidity is usually taken to mean relative humidity. Relative humidity is defined as the amount of water vapour in a sample of air, compared to the maximum amount of water vapour the air can hold at any specific temperature. It is expressed as a percentage.) While lining large tanks it happens that during daytime, sunlight heats up some portion of the tank. Hence in these portions the adhesive may get cured faster, resulting in poor bonding. Proper sunlight protection for such tanks have to be ensured and compounding formulation technique have to take this aspect into consideration.

The working conditions to which the lining will be exposed is an important factor. For instance, the presence of abrasives in the working medium produce constant bombardment of the abrasive particles on the rubber, thereby imparting kinetic energy to the rubber which manifests as heat. Unless there is sufficient cross sectional material of rubber, this heat generation on rubber will raise the temperature deteriorating the rubber. This can be counteracted by providing a sufficiently thick stock of the rubber sheet.

7.1 Design of compound formulations

The design consideration of compound formulations for rubber lining is dealt with in the following sections.

7.1.1 Choice of Ingredients

It should be recognised that appreciable shifts in properties are sometimes made possible by special compounding variations. For instance, the heat resistance of natural rubber vulcanisates may be improved considerably by variation of the vulcanising recipe. The normal sulfur vulcanisation system is capable of many variants which will govern the chemical nature of sulfur crosslinks, i.e., whether it is essentially a mono, di or polysulfide linkage. The nature of sulfur crosslinks can have considerable influence on the heat and chemical resistance of vulcanisates.

For a particular application, the base rubber or when desirable and possible a blend of different rubbers has to be chosen according to the broad spectrum of final properties required. This must then be combined with an appropriate vulcanising system, and the reinforcement if any and colour whether black or non black additives. Sufficient processing aids are then included to ensure proper mixing and processing. It should be remembered that reinforcing fillers of finer particle size are as a rule, progressively more difficult to incorporate during mixing yielding stiffer stocks and are also generally more expensive. Excessive reinforcement should therefore be avoided when not critical. Any permissible diluents or special additives for specific effects are then added to the formulation list.

Protective anti degradants are chosen according to the severity and the type of service and to their relative effectiveness and compatibility to the base polymer. The steps in which the ingredients are mixed must also be borne in mind and the appropriate ingredients grouped accordingly. For example antioxidants are commonly added early in the mixing cycle and the crosslinking agents last [2–5].

7.1.2 Viscosity Control

For the rubber in raw state, the choice of correct viscosity level is important to ensure easy mixing and further processing. Most types of synthetic rubbers are available at various viscosity levels, a nominal Mooney viscosity (ML 1 + 4 at 100 °C; ML: Mooney viscosity with a large rotor) of 50 being common. For easy mixing and processing with high filler loading a Mooney viscosity of the order of 30 is necessary, but on the other hand, a viscosity level of 50 or more should be selected when mixing with oil diluents for economical compounding or when the process demands certain level of strength (green strength) in the unvulcanised stock. Quite a good number of low molecular weight synthetic rubbers are available which are in liquid form. These can be added to solid rubbers as general process aids for softness. Especially for lining applications the Mooney viscosity of unvulcanised sheet rubber should preferably be in the range of 40 to 45. It will be difficult to apply the rubber sheets in bends and corners in tanks and in areas to be fully lined such as baffle plates and perforated plates with stiff sheets of high Mooney viscosity. See Figure 7.1 of a rubber lined perforated plate fitted in a tank.

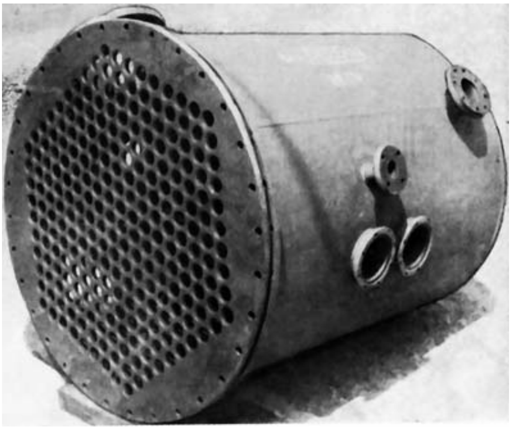

Figure 7.1 Rubber lined perforated plate fitted in a tank

7.1.3 Nerve Control

Most rubbers exhibit a degree of elastic recovery on deformation in the raw state even before vulcanisation, say, like natural and Neoprene rubbers. This 'nerve' as it is called is excessive and it must be reduced during the mixing process to a controlled level so that processing will be reproducible and the calender sheet stocks will exhibit dimensional stability, an essential factor in rubber lining application. Depending on the type of rubber, the elastic recovery can be reduced by a suitable degree of mastication as measured by Mooney viscosity values or plasticity retention index, by increasing filler levels, by choice of filler type or by addition of factice or extenders. However usage of factices and extenders should be kept to a minimum level for compounds for acid resistance. Similarly use of reclaim rubber should be avoided in corrosion resistance rubber lining compound as they impart inferior chemical properties.

7.1.4 Sticking to mill rollers

During mill mixing or sheeting operation, sticking to the roll surface can sometimes be a problem and additives to aid release are necessary. Certain soft tacky stocks or those containing intermediate loading of mineral fillers are most likely to present this problem. Fatty acids or their derivatives or microcrystalline waxes are useful additives to control this. But care must be taken with regard to their compatibility with the base rubber to avoid blooming and to ensure stock coalescence.

7.1.5 Sheeting

While sheeting in a calender, the stock must be soft so that they penetrate the interstices of the layers easily, and tacky so that ready adhesion between plies is ensured. Inevitably, such stocks can give rise to handling problems and call for ‘compromise compounding’. Natural rubber and Neoprene rubbers compounded with resins such as coumarone indene or petroleum resin produce good sheeting stocks.

To obtain good calendering characteristics, compounding requirements are similar to those described to reduce elastic recovery. These minimise undue swell or shaping and contribute to shape retention. until this is made permanent by crosslinking. Internal lubricants assist in reducing drag promoting a smooth surface. Waxes, fatty acids and their derivatives are useful additives.

7.1.6 Tack

Forming operations which involve building layers of stock together require the compound to have tack, the property of autohesion or adhering rapidly and strongly to itself when surfaces are brought into contact. This surface condition is required to last for a considerable period of time. Excessive filler loadings are best avoided since they may have a drying effect on the stock surface. NR and chloroprene rubber (CR) can be compounded readily to give good tack levels. Other general purpose rubbers require suitable resins [6]. EPDM and butyl rubbers are difficult to tackify. But excessive use of solvents to give tackiness is undesirable, since if traces remain trapped, vapour blows or porosity may result during vulcanisation.

7.1.7 Scorching

Vulcanisation systems are normally designed to be as fast as practicable, subject to certain limitations. Scorching is vulcanisation at an undesirable state in processing and storing of stock. The heat unavoidably generated during mixing and processing causes prevulcanisation. Delayed action vulcanisation systems are necessary to minimise prevulcanisation. For sulfur cured stocks sulfenamide acceleration is widely used augumented by additives such as cyclohexylthiophthalimide or certain sulfenamide derivatives. Table 7.1 shows the parameters used in rheometer/Mooney viscometer studies.

Table 7.1 Parameters used in rheometer studies

1. Initial viscosity (L_o)	Effect of mastication time and procedure of milling. Effect of peptisers
2. Minimum viscosity (L_i)	Joint effect of accelerators and processing characteristics and flow properties in moulding, sheeting and extruding
3. Thermoplasticity T_p (L_o-L_i)	Plastic effect before chemical reaction starts.
4. Induction time (t_1) i.e., time for one unit rise above L_i (minutes)	Time when chemical reaction starts.
5. Scorch time (t_2) time for two units rise above L_i (minutes)	Characterises processing safety
6. Maximum cure (L_f)	Highest crosslinking reached
7. Optimum cure time (t_{90}) (minutes)	Time to reach optimum cure level
8. Cure rate $100/t_{90}-t_2$ (minutes)	Comparative value of cure activity

7.1.8 Hardness and Modulus

Hardness and modulus of a vulcanisate are commonly increased by the use of particulate fillers, the greatest effect being obtained by the reinforcing types or by the use of crosslinked resin systems. These may be phenolic types or monomers capable of being grafted *in situ*. Carbon blacks of fine particle size exert relatively more effect and that the quantity required varies from one rubber to another, being least for CR and the most for SBR. For a given non black filler type decreasing particle size gives a progressively increased hardness. Changes in accelerator system produce relatively small differences in hardness and modulus. Sulfenamides tend to produce slightly harder vulcanisates than thiazoles. Boosted accelerator systems, give small hardness increases over those produced by straight systems. Softeners and plasticisers reduce hardness and at normal levels plasticisers reduce hardness, acceptable processing requires additional fillers or reinforcing agents to counteract the effect.

7.1.9 Elasticity

Vulcanised rubbers show viscoelasticity and the departure from perfect elasticity are evaluated by measurement of resilience, creep and stress relaxation. Compounding which contributes to a more tightly knit crosslinking system occupying the maximum possible volume proportion of the vulcanisate will enhance the elastic properties as displayed by resilience. Appropriate antioxidant protection of the polymer will give further improvement. At normal levels of addition softeners and plasticisers have little effect [7].

7.1.10 Strength

At relatively low hardness levels, say a Shore A of 50, the highest tensile strength levels are most easily obtained using high gum strength polymers, which crystallise on stretching, as in the case of NR, IR and CR. Low gum strength rubbers require low particle size reinforcing fillers to develop maximum strength and the reinforcement is accompanied by increased extension modulus and hardness. When compounding for high temperature service, the rapid fall in tensile strength values of many high strength vulcanisates at elevated temperatures has to be borne in mind, and if need be ‘compromise compounding’ has to be resorted to. ‘Compromise compounding’ is compounding done to reach optimum levels of properties for end use with limited sacrifice of essential properties to give maximum ageing and service requirements.

7.1.11 Resistance to Tear

Reinforcement with carbon blacks of decreasing particle size does not always produce a noticeable effect on tear resistance. Aluminium silicate vastly improves tear resistance in CR compounds. Tear resistance falls appreciably with rise in temperature.

7.1.12 Resistance to Flex-cracking and Fatigue

When rubbers are subjected to cyclic stresses in service through either repeated or intermittent flexing or compression, the initiation and development of crack is a frequent cause of failure. At high rates of flexing heat-build up increases and compound formulation should allow for this. The nature and stability of the crosslinking system, the choice of protective agents, the degree of dispersion of curatives and fillers and localised strain can all influence performance on flexing. If compounding is done to reduce resilience, additional heat will be generated by flexing and if severe cracking will result. For exacting service, the precise operating conditions must therefore be considered before choosing the base rubber.

When anticipated, flexing is of constant amplitude, extension modulus should be kept as low as possible in products like flexible cell covers and hoses in caustic soda industries. Another important factor is the degree of cure. Prolonged vulcanisation cycles will degrade thermally susceptible rubbers.

7.1.13 Resistance to Heat

Proper selection of crosslinking system, for example a low sulfur and thiuram accelerated formulation and choice of mineral fillers like clay, activated calcium carbonates, etc., can increase appreciably the maximum service temperature of the rubber. Combination with good heat resistant antioxidant system is capable of increasing the typical service temperature of natural rubber from around 70 °C to 100 °C and sometimes above this for intermittent exposure.

7.1.14 Resistance to Flame

By using halogen containing rubbers such as CR, it is possible to produce vulcanisates which are self extinguishing when an applied flame is removed. In such cases tricrysylphosphate and liquid chlorinated paraffin wax should be used as processing aids in place of hydrocarbon oils and waxes. In case of fillers, carbon black should be kept at minimum levels. Reinforcing mineral fillers along with antimony trioxide and zinc borate assists in forming a hard surface crust on exposure to flame.

7.1.15 Resistance to Gas Permeation

For a particular rubber, the gas solubility increases as the molecular weight of gas increases and is also greater for gases of increased polarity. Solubility is also influenced by temperature and rubber type. The solubility of a given group of gases follows a similar pattern but tends to decrease as the solubility parameter of the rubber increases.

By reducing the relative volume content of rubber in the vulcanisate increase in filler content reduces permeation. Fillers having lamellar particles such as talc, mica or graphite, produce a proportionally greater reduction in permeability than equivalent volume of other regular fillers. But the mechanical and strength properties are affected; especially tear resistance. It is important to ensure that all particulate fillers are well dispersed and free from agglomerates and gritty impurities, otherwise mechanical imperfection and pin holes in sheeting can seriously impair gas retention properties and lead to leakage of the acids.

7.1.16 Bonding

For successful rubber to metal bonding, it is found that highly polar rubbers such as CR or NBR may be bonded more readily than NR and SBR having lower polarity. In compounding rubber stock to be applied to a cement film, carbon black loading is normally preferred for high bond strengths and the use of ingredients capable of blooming to the surface of the unvulcanised rubber stock should be avoided. A delayed action acceleration system is preferred to ensure that optimum contact between stock and cement surface has been achieved before the onset of crosslinking.

When bonding compounded rubber to fabric, for the manufacture of fabric reinforced expansion joints in the chemical plant piping systems, mechanical anchoring between cotton/Nylon/fibre and compounded rubber should be sufficient to ensure good adhesion. Synthetic fibres require treatment with chemical coatings to secure maximum adhesion and bond [8, 9].

7.2 Processing Characteristics

The primary step in the processing of rubber is mixing the ingredients into it. Before mixing, the raw rubber is to be masticated to a plastic state, followed by further processing in extruder, in calendering machine and prevulcanised sheet winding machine, application of lining on to the tanks, vessels, etc., and finally curing in the autoclave or any other curing systems mentioned earlier.

Each of the operations are discussed step-by-step next.

7.2.1 Mastication

Natural or synthetic rubber is very tough and nervy in raw stage. To make them suitable for the subsequent processing, they are made plastic by the process of mastication. The mastication is done in a two roller rubber mixing mill, having two horizontally placed chilled cast iron rolls driven by a motor of suitable horse power depending on the production capacity. Suitable heating and cooling arrangements are provided by steam and water lines in the hollow rolls. These two rolls are revolving towards each other with a differential speed, the friction ratio being normally 1:1.2. Due to the friction between the gap of the rolls (the nip), the tough raw rubber is sheared off, its molecular weight reduced and it becomes plastic by this mechanical process of mastication. Mastication can be accelerated by the addition of certain chemicals called ‘peptising agents’. The time for molecular breakdown of raw rubber is shortened by agents called also as peptisers. The degree of free flowing condition or plasticity resulting due to mastication or peptisation is called the Mooney viscosity. This is an important process parameter and each batch of raw rubber should confirm to the desired value of Mooney viscosity, before it is released for further processing. The Mooney viscosity is measured in a Mooney viscometer or a ‘rheometer’. When the raw rubber is masticated to the desired level of plasticity or viscosity, it is passed for mixing with other chemicals. Quite often, the raw rubber is premasticated and kept in storage for further processing.

7.2.2 Mixing

The mixing of the masticated rubber with the chemicals is done in the same two-roller mixing mill. The following things should be considered in the mixing process: sequence of addition of chemicals, the nip adjustment between the rolls, the differential temperature of the rolls, the mixing cycle time, and the technique of cutting, cross folding, blending and homogenising the stock in the mill.

The mixed stock of rubber is called the compound or the compounded stock. The normal sequence of addition is as follows:

- Rubber and peptiser
- Antioxidants and accelerators
- Activator
- Plasticiser
- Fillers
- Process oils
- Vulcanising agent

This order of addition can be changed depending upon the type of rubber, curing characteristics, storage system, and so on. Quite often masterbatches of peptising agents and vulcanising agents with rubber are made and added instead of straight addition of these agents, to ensure good dispersion.

The nip distance during mastication and initial addition of chemicals should be at a minimum and then increased slowly during addition of fillers and finally during cross folding, blending and homogenising, it is again reduced. The nip distance can be varied from 1 mm and 5 mm.

The temperature of the two rolls can usually be 55 °C to 70 °C and the mixing cycle time ranges between 45 minutes to 90 minutes for various types of compounds. Certain compounds of Hypalon and butyl rubber may need a longer mixing time.

The cutting and blending techniques depend on the skill of the individual operators. After mixing the compound, it is stored for at least 24 hours at 20–22 °C before taking up for further processing.

7.2.3 Calendering

The compound produced in the mixing mills is processed through a calendering machine for taking out sheets for lining or for making other products. The calender machine virtually consists of three or four rolls, the configuration of the rolls can be anywhere from vertical to a Z shape, the central roll being driven by the main drive and the top and bottom rolls by friction gears.

The calendering operation consists of processing the warmed stocks of compounded rubber in the top nip of the calender and allowing it to pass through the bottom nip (see Figure 7.2) and then drawing it towards the doubling device fixed in the conveyor system in front of the calendering machine. The two nips are suitably adjusted as well as the temperature differentials of the rolls to obtain a smooth and shining rubber sheet. The sheet thickness that can be obtained in the calender is from a minimum of 1 mm to 5 mm. However, in practice, the thickness of the sheet over 2 mm is achieved in the doubling device by plying 1 mm calendered sheet one over the other until the maximum thickness of about 5 mm or 6 mm is achieved.

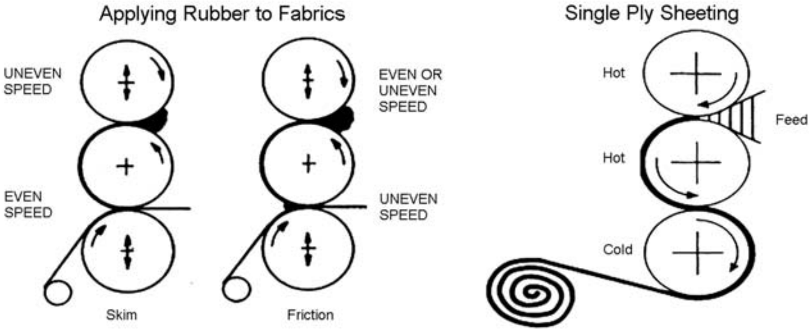

Figure 7.2 Calendering of rubber sheet

This practice of building higher thickness by plying up layers of 1 mm sheet is followed to produce sheets which are 100% free of pin holes which are detrimental to the lining application. The operating temperatures during calendering are normally as follows for most rubbers:

Top roll	60 °C
Middle roll	65–70 °C
Bottom roll	50–60 °C

For Hypalon and butyl rubbers higher temperatures may be required [10–11]. The calendering temperatures given are only indicative. The processing temperatures of mixing, extruding or calendering and plying up, are mainly based on the type of compounds, the base polymer and the experience of the rubber technologists with the particular type of the equipment. The process parameters are often given by the suppliers of rubbers in their technical literature which are very useful to the rubber compounder. Readers are recommended to refer to the suppliers of technical literatures for more information [10, 11].

Suitable provision for heating and cooling by means of steam and cold water lines are provided in the calendering machine.

The calendered sheets after doubling to the desired thickness are wound on metallic spools in the winding device at the end of the conveyor system backed by a cloth liner support and they are stored for at least 24 hours in an air-conditioned room at a temperature of 20–22 °C. Afterwards they are issued for lining, and for prevulcanised (PV) sheet manufacture in the custom-built PV plant.

7.2.4 Prevulcanised Sheet Winding (PV Plant)

In this plant, the calendered sheets are wound on rubber lined steel drums of approximately 700 mm diameter and 1.5 meter face length with cloth liner supports. The cloth liner should be wet with cold water, and also sprinkled with water during winding. In a single drum at least 2 to 3 sheets of about 10 to 12 metres long can be wound up. The winding is done with a mild pressure given by the tensioning device attached in the PV sheet winding plant. The sheets which are tightly wound on the drums are then ready for vulcanising in the autoclave. For lining work done *in situ* the rubber sheets are vulcanised after winding on drum as described previously in the PV sheet plant at the factory. These sheets are then transported to the site where the cold bond lining is carried out in chemical tanks. This PV plant is a custom built one and designed to suit individual needs of production capacity. Idler rollers, kept at constant distance in the plant, keep the sheet from getting wrinkled, as the sheet is passing through them with tension.

7.2.5 Extrusion

In some equipment, such as filter drums, extruded profiles such as division strips are affixed on to the lined sheet rubber and then cured. These profiles can be strips of different cross sections for enabling other components to be fixed in the rubber lined equipment such as drum filters (see Figure 7.3).

Figure 7.3 Rubber lined filter drum fixed with division strips

Warmed rubber stock is fed into the hopper of the extruder fitted with a required die of the profile in the die head. The cross-sectional diameter of the profile will have to be less than the screw diameter in the extruder. For extrusion of larger diameter profiles, the head needs to be designed accordingly. Making and filing of the die for profiles is the most difficult process. The die design is generally manipulated by hand. One has to take into account the die-swell and elastic recovery of the stock during die-making and extrusion of the profile. Compound design and die design go hand in hand and several trials are made to arrive at the exact profile in the extruder.

7.2.6 Moulding

Many moulded components are affixed on the rubber-lined surface such as anode sleeves in mercury cells used in caustic soda industry. These moulded components are either made from natural soft or ebonite rubbers or Neoprene rubber compounds. While moulding, the flow characteristics of the rubber compound and shrinkage need to be taken into consideration. Some aspects of mould designs are described next.

Mould material – Most moulds for rubber moulding are made of steel. The metal should be close grained and of uniform and fault free texture. A carbon content of 0.25% to 0.45% is preferable. Moulds are sometimes made of aluminium alloys or manganese bronze with a high silicon content. Moulds difficult to machine by conventional methods can be made using these alloys.

Mould dimension – The size of the mould is limited by the size of the moulding press. The mould size limits the number of cavities that can be cut in it. Plate thickness should never be less than 9.5 mm at the thinnest point. The closing plate should be 18 mm thick so that dowel pins and locating pins remain firm.

Rind cavities – In compression moulding, the rubber stock is extruded and cut into blanks having greater volume than that of the finished product. During the moulding process the excess in volume has to go somewhere outside the main cavity. Rind cavities are provided as a shallow grove around the main cavity separated by flash ridge. Resistance of the excess compound as it flows past this ridge creates a sealing pressure that forces the rubber stock into all areas of the cavity and prevents further flow of excessive rubber thereby ensuring the consolidation and homogenisation of the moulded product.

7.3 Proportion

The proportion of ingredients mixed with rubber for various applications differs vastly. Rubber compounding is a vast field of technology to reckon with. The general quantity range in a typical compound formulation for various ingredients is given in Table 7.2 taking the base rubber as 100 parts as a guidance for rubber compounding.

Table 7.2 Basic Compound Formulation

Ingredients	phr
Base polymer or blend of polymer	100
Crosslinking agent (sulfur)	0.5 to 35
Accelerator	0.5 to 5
Activators	1.0 to 5
Antioxidants	0.5 to 2
Reinforcing fillers (carbon black and minerals)	25.0 to 200
Processing aids (peptisers, softening agents tactifiers, etc.)	0.0 to 25
Inert diluents (mineral fillers and extending oils)	25.0 to 100
Colouring additives	25.0 to 100

7.4 Silica and Carbon Filled Butyl Rubber Vulcanisates

In 30% nitric acid, silica fillers impair the resistance of vulcanisates while all types of carbon black improved it. The silica filled compounds failed completely in one to five days at 20 °C whereas the unfilled vulcanisates retained 70% of their initial strength after 25 days immersion. The carbon black loaded compounds are unchanged after this treatment. At higher temperature (up to 70 °C) channel blacks gave the best resistance. The failure of the silica filled vulcanisates is due to the formation of holes and pits on the surface. For carbon blacks a protective layer is formed on the surface due to nitration of the polymer and the enhanced intermolecular attraction of the NO_2 groups. In any case rapid failure occurs at temperatures of 90 °C to 100 °C.

In 50% sulfuric acid at 90 °C butyl rubber shows the best resistance with carbon black loading particularly with channel and lamp blocks. Silica filled compounds lose up to one-third of the strength of the rubber with considerable swelling at 70% concentration of sulfuric acid.

Vulcanisates filled with a silica filler are particularly resistant against 20% hydrochloric acid at 70 °C failing gradually if the temperature is raised to 90 °C.

Channel black filled vulcanisates resist 75% phosphoric acid at 125–135 °C even after 25 days of immersion.

Butyl vulcanisates swell considerably in oleic acid and lose their physical properties. Silica fillers however give better resistance in 20% formic acid.

In oxalic acid a slight swelling (5%) occurs for butyl vulcanisates and as such physical properties are not very much affected. Acetic acid on the other hand attacks the black loaded rubbers more than light coloured rubbers. The best resistance is possible with a combination of silica and titanium dioxide fillers.

Although swelling of all butyl vulcanisates in ethyl alcohol and isobutyl alcohol at 70 °C is low, white pigment loaded butyl compounds lose up to 45% of their initial strength. In contrast, the black loaded butyl lose about 10 to 20%. The resistance in 40–50% solution of sodium hydroxide and potassium hydroxide at 100 °C is good, the degree of swelling not exceeding 1%.

7.5 Compounding Elastomers of Low Cure Functionality

Cured properties of elastomers with a very low number of cure functional sites such as butyl and EPDM rubbers are independent of curative (accelerators) levels used. However, varying the levels of unsaturation during polymerisation can alter cured physical properties often without processing difficulties. For butyl and EPDM rubbers only a small fraction of the monomer units in a chain take part in the crosslinking reactions. For example, if an average chain contains 10,000 monomer units only about 50–250 would normally be involved in the crosslinking.

Elastomers can be classified depending on how the crosslinking reactions are accomplished as follows:

Class A

Most or all of the monomer units in the chains are capable of participating in the crosslinking (vulcanisation or curing) reaction. This class includes natural rubber, butadine rubbers, SBR and nitrile rubbers. The crosslink density in this class is controlled by the amount of curing agents in the compound.

Class B

Most of the monomer units in the chain cannot react with the curing agents. The ability to form networks depends on the incorporation of a minor fraction of the monomer units which can react.

The best known examples of these rubbers with limited cure functionality are EPDM and butyl rubbers where a small amount of a diene is copolymerised with the main monomers. Polychloroprene also behaves as a member of this class, when cured with diamines and thioureas. In this case the cure functional group occurs as a result of a small fraction of 1–2 polymerised units among the predominant 1–4 polymerised chloroprene.

For rubbers in class B, changing the level of accelerators should have little effect on the basic properties. Selection of isoprene level in the butyl rubber may in some cases be an alternative to more conventional compounding techniques. Similar principles should apply to polychloroprene and EPDM which also contain small number of cure active sites.

The response of butyl rubber vulcanisate properties to changes in accelerator levels is expected to depend on the relative levels of isoprene units in the rubber and accelerators, as explained next [12–16].

When the accelerators are present in amounts in excess of the isoprene units, vulcanisate properties should be insensitive to the accelerator level.When the accelerator level is less than equivalent to the isoprene level, changes in the accelerator level may be reflected by changes in the crosslink density as shown by changes in physical properties like hardness, modulus, tensile strength, elongation and resistance to chemicals.

While compounding butyl rubbers, the relationship between the level of accelerators and the levels of unsaturated sites in the rubber molecules should be taken into consideration.

When the level of accelerators is less than roughly equivalent to the level of unsaturation, it is possible to exert some control over the degree of crosslinking by varying the accelerator quantity.

When using a particular grade of butyl rubber, it is usually necessary to control the vulcanisate properties by variations in filler and plasticisers since accelerators levels have little effect.

The unsaturation level of rubbers has a major effect on vulcanisate properties, physical, chemical and resistance to chemicals.

7.6 Chemical Reaction of Polymers

It is quite useful to have some basic understanding of the chemical reactions of polymers with acids and other corrosive chemicals while designing a lining compound. An exhaustive study although inevitable in the context of rubber lining can only be made as a separate topic which is not within the scope of this book. However some typical reactions of polymers with some important chemicals are described next.

The reactivity of the functional group is said to be independent of the molecular weights of the polymer. Polymers undergo chemical reactions as simple compounds which can generally be called low-molecular weight compounds except that in the former the reactants can be delivered to the sites of reactions. The main chemical reactions that rubbers undergo are nitration, sulfonation, oxidation, reduction and vulcanisation.

Unsaturated polymers undergo reactions such as isomerisation, cyclisation, addition, epoxidation and hydrogenation. Saturated polymeric hydrocarbons undergo substitution on the main chain or the side chain. Loaded butyl vulcanisates were shown to be less resistant than pure gum butyl to sulfuric acid according to work done by Baldwin and Schatz [17]. This is attributed to the absorbing effects of fillers. It was noted further by Baldwin that resistance to sulfuric acid was much better at a concentration level of 85% sulfuric acid by weight. Channel blacks being strongly absorptive bring about rapid deterioration.

7.6.1 Resistance to Halogens

In the presence of light, halogens attack both vulcanised and unvulcanised butyl rubber. Whether vulcanised or unvulcanised the effect of the reaction is to produce rapid deterioration in molecular weight. A strip of butyl vulcanisate suspended in bromine gas degrades rapidly. In a few minutes the specimen becomes fluid enough to drip to the bottom of the vessel. Chlorosulfonated polyethylene is resistant to ozone being better than Neoprene and butyl rubber compounds [18].

7.6.2 Resistance to Hydrogen Sulfide

Among the numerous gases, hydrogen sulfide is of appreciable importance in its chemical effect on butyl. Baldwin points out that hydrogen sulfide may destroy either sulfide or disulfide crosslinks which form during vulcanisation. But with crude rubber of butyl the reagents have no effect. Zinc oxide reduces this tendency by reacting with hydrogen sulfide thereby decreasing the effective concentration of hydrogen sulfide.

7.6.3 Epoxidation by Hypochlorous acid

Olefins may be converted to chlorohydrin by treatment with hypochlorous acid. The chlorohydrin if treated with sodium hydroxide, hydrogen and chlorine are stripped off. This process is dehydrochlorination, since hydrogen and chlorine are stripped off when reacted with sodium hydroxide. This reaction of rubber (an olefin) with hypochlorous acid is significant, since the dehydrochlorination prevents the formation of a protective layer of chlorinated rubber or hydrochloride.

7.6.4 Hydrochlorination of Rubbers

Synthetic polyisoprene rubbers were found by Harries during 1910 [19], to be successfully hydrochlorinated. These synthetic polyisoprenes resemble natural rubber, which is also a polymer of isoprene which occurs naturally and therefore hydrogen chloride is rapidly added when the rubber is exposed to it thus forming a protective film of chlorinated rubber or hydrogen chloride. Polybutadiene, and butadiene acrylonitrile rubbers do not add hydrogen chloride from hydrochloric acid.

7.6.5 Heat evolution during vulcanisation of ebonites

Hard rubber or ebonite whether from natural rubber or from synthetic rubber, can be defined as highly vulcanised rubber, containing a large proportion of combined sulfur. Hard rubbers made from natural rubber have vulcanisation coefficients between 25 and 47. The theoretical vulcanisation coefficient value for natural rubber is 47 and for synthetic rubbers it is in the range of 35 to 47. The coefficient of vulcanisation is usually defined as the number of units by weight of sulfur combined with 100 units by weight of unsaturated hydrocarbon. The theoretical coefficients are corrected for impurities/non rubber constituents in the raw rubber.

The vulcanisation reaction involved in the formation of ebonite is strongly exothermic. The overall heat produced in forming a 68:32 natural rubber-sulfur ebonite is about 300 cal/g, since the specific heat of the compound is 0.33, this heat would be theoretically sufficient to raise the temperature above 1000 °C. Clearly, therefore, unless the greater part of this heat is dissipated during the cure session, overheating will occur sometimes leading to explosion which can cause damage to equipment. The main factors, therefore, which influence the temperature rise at the centre of sheet are curing temperature, reactivity of the compound and the thickness of the lined sheet being cured. Heat generation is more in a reactive compound (accelerated compound) and the system is thermally unstable resulting in overheating. If the reactivity and heat generation are reduced by a diluent filler, the temperature rise will be reduced. Changing the composition of the compound also can alter its thermal conductivity, reduced conductivity retarding heat loss making the system unstable leading to overheating.

If the sheet is made thicker, the central reactive layer is thicker and hence more heat is generated and heat loss is retarded. If the generation of heat exceeds loss the system becomes unstable. If the sheet is made thinner, the increased loss quickly overtakes the less heat generation and the temperature rise is small. Therefore, the curing temperatures of ebonite are very important. A reduction from 130 °C to 120 °C moves the heat loss upwards and the heat generation downwards thus reducing temperature rise.

From the previous observations it can be seen that the margin between instability and the temperature rise of only a few degrees is small, especially for changes in the thickness of the sheets, because the reaction is based on two basic factors namely the amount of heat generated and the rate of heat loss. The choice of curing temperature is very critical since a difference of 10 °C can determine whether the internal temperature rise is negligible or dangerously high in ebonite curing. Strongly exothermic reaction does not start at the beginning of the cure. As such a stepped up cure cycle for ebonite is adopted (Figure 6.1 gives values for the cure cycle for Neoprene which are similar to those for ebonite). Thick walled tubes and internals of ebonite are either cured in hot water at low temperature or cured in autoclave in steps to avoid explosive reactions. Furthermore, since the heat evolved in ebonite curing is 300 cal/g, the total weight of lined rubber loaded inside the autoclave plays a vital role. The lower the weight the fewer the number of calories of heat are generated, i.e., the higher the weight, the more heat is produced.

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8

Manufacturing and Application Procedures

To process rubber compounds, for lining applications, as stated earlier, it is necessary to convert the elastic, tough and nervy state of the raw rubber into a complete plastic state. This conversion process called mastication, is achieved by mechanical means or by chemical means by the use of certain chemical ingredients called peptisers. Mastication is the first operation in the processing of solid rubbers to manufacture a product.

The molecular weight of rubber is around 300,000–500,000. After mastication, it is reduced and for a reduction in molecular weight of about 150,000, the required concentration of oxygen is about 0.02% [1]. Oxygen stabilises the broken ends of the rubber molecules during mastication by acting as a radical acceptor. Other than the atmospheric oxygen, a peptising agent like pentachlorothiophenol (Renacit VII, Bayer Germany) acts as a radical acceptor. Thus, peptisers accelerate the mastication process.

Mooney viscosity is used to measure the extent of mastication. Mooney viscosity is the torque required to rotate the disk in the shearing disk viscometer. When the disk or rotor as it is called, is rotating without any load, the Mooney viscosity reading is ‘zero’. When a torque of 100 Nm is applied on the rotor the viscosity scale is read as 100. This is the scale in the Mooney viscometer (ASTM D1646 [2]).

The Mooney viscosity as a measure of the extent of mastication is determined using a shearing disk viscometer. The viscosity of the unmasticated natural rubber ranges between 75–90 Mooney units (ML 1+4 at 100 °C). ML denotes large rotor, 1 + 4 signifies initial preheating time of 1 minute and the testing period of 4 minutes. After mastication the viscosity of the rubber is reduced to about 55/60 Mooney units from over 80 units. Addition of peptising agents will accelerate this process and further reduce this value.

Usually in the manufacture of rubber compounds for tank linings, the Mooney viscosity of the masticated rubber is maintained at 30–35 units, which is achievable, either by premastication or by the use of peptisers. The premastication normally takes about 30–40 minutes at 70 °C in the mixing mill. With the addition of peptisers this time can be reduced to 15–20 minutes.

The main purpose of mastication for producing lining compounds in addition to homogenious dispersion of ingredients, is to avoid undesirable shrinkage during calendering, storing, lining and curing operations. The optimum mastication level required for mixing any other compounds for moulding or extrusion requirements for mechanical products, can be 50 to 55 Mooney units. Lower Mooney levels in these cases will lead to excessive mould flow causing air blisters in moulded products, whereas for lining applications low Mooney compounds are preferred.

Thus, the Mooney units measure the extent of mastication or the plastic flow of rubber to enable better dispersion and mixing of ingredients and curatives. In addition to this, the Mooney units can give an indication of the curing nature of compounded uncured rubbers.

Mooney viscosity is an important process parameter and each batch of raw polymer should conform to the requisite value of Mooney viscosity, before it is released for further processing.

8.1 Rubber Lining

This is essentially a manual job. The lining is done on chemical process equipment using green rubber as well as prevulcanised rubber. A vessel lined with green rubber is vulcanised in an autoclave using steam at atmospheric pressure or using hot water in the vessel itself. A vessel lined with prevulcanised rubber is cured at ambient temperature. The lining sequence starts from the choice of compounds, equipment surface preparation, coating of adhesives and thereafter actual lining of the rubber sheets on to the walls of the vessels. The different stages of lining are described next.

The choice of compound depends on the nature of the media to be stored in the tanks/vessels to be lined. As an example, for all tanks in a phosphate-based fertiliser plant, the lining can be natural, Neoprene or a butyl rubber based one [3]. These tanks sometimes handle phosphoric acids containing defoaming agents. When in the defoaming agent, oxo-alcohols are present, a butyl lining can be used but if oleic acid is present, a Neoprene lining is suitable. When the defoaming agents are minimal and the temperature is ambient and the tanks are used only as a storage vessel, natural rubber is used as a lining. Similarly for lining of equipment which will handle different types of corrosive chemicals, which might include small quantities of other chemicals, careful consideration of the media and usage conditions needs to be done before selecting a suitable lining compound. Rubber lining of vacuum vessels is another critical task. Equipment, such as vacuum evaporators, and vacuum dechlorinators used in chloralkali plants, operate under high vacuum conditions. Rubber lining of such vessels calls for a high quality of material and workmanship. It is preferable that such vessels are vulcanised in an autoclave, wherever the size of the vessels suits the size of the autoclave. If the vessels cannot be accommodated in the autoclave because of size limitations, the lining is pressure cured using live steam (steam which does not condense whilst in use), using the vessel itself as an autoclave with proper insulation outside. In such cases, the vessel should be properly designed to withstand the working pressure with a maximum factor of safety. This is very important because if the vessel could not withstand the working pressure it might yield at the welded joints leading to deformation of the vessel, which may lead to accidents. If the vessel is to withstand a working pressure of say x kg/cm^2 a factor of safety of 1.5 times the working pressure should be allowed for in designing the vessel. The working pressure normally adopted in such cases is 2 kg/cm^2.

8.2 Role of Impurities

The presence of defoaming agents in phosphoric acid storage tanks would have to be known in advance by the rubber lining firm to enable them to take this into account while compounding, as otherwise the rubber lining could fail due to a selection of the base rubber without consideration of the deforming agent. Depending on the type of rock phosphate, the addition of defoaming agents also varies. In many countries, oleic acid is extensively used as a defoaming agent. Table 8.1 gives the proportion of the oleic acid used in different types of rocks.

Table 8.1 Proportion of oleic acid used in different types of rocks

Source of rock phosphate	Kilograms of rock phosphate per ton of rock	Kilograms of oleic acid per ton of P_2O_5
Low grade Jordan	3.5	10.2
High grade Jordan	1.0	2.7
Moroccan	1.4–1.8	4.5
UAR	4.5–5.4	18.1
Tunistan	5.4–6.4	18.1

Source: *Plastics and Elastomers as Construction Materials in the Chemical and Fertiliser Industry*, unpublished report by MIL Industries Ltd., Chennai, India and Societe Chemie de Gerland France.

It can be seen that while operating the plant from different sources of rock supplied, the amount of oleic acid added will vary widely and unless proper choice of the rubber compound is made, taking into account both the type and quantity of the defoaming agent present, damage to the rubber lining could occur. Even though the original amount of oleic acid added to the phosphoric acid in the storage tank may get progressively reduced, during draining the acid for downstream processing, it is possible that there will be an accumulation of the oleic acid around any sharp corners present. For example in connecting bend pipes it is possible that there is an accumulation in higher percentages of up to 3% to 4% which can cause damage to rubber lining. In anticipation of such an eventuality, it is preferable to line such equipment with Neoprene rubber based compound that is resistant to oleic acid. Similarly in the case of handling and transporting hydrochloric acid, it is necessary to know the source of production of the hydrochloric acid, i.e., whether it is made by direct synthesis or obtained as a by-product from other organic industries. For hydrochloric acid made by synthesis there is no impurity that will affect the lining. In the manufacture of organic chlorinated products, the hydrochloric acid obtained as a by-product contains a certain percentage of derivatives, which also attack the rubber lining. If the contamination is within the limit of solubility in hydrochloric acid, the rubber lining may not get appreciably damaged. But if they go beyond the limit of solubility, the damage and swelling on the lining is very rapid. Generally these chlorinated derivatives are heavier than hydrochloric acid and they get collected at the lower portions of the rubber lined tanks and the lining gets damaged at these portions. Thus, it is necessary that while specifying the medium handled, not only the main constituent is mentioned but also each impurity present is to be specified to enable the rubber technologist to choose a suitable lining compound.

8.3 Working temperature

The working temperature of the rubber lined vessels influences not only the proper choice of polymer, but also the type of adhesive used for bonding. For a temperature higher than the range of 70 °C to 125 °C, usually a brick lining over a rubber lining is provided to protect the rubber lining thereby increasing the life of rubber lining. Table 8.2 shows the effect of the temperature on interface of brick to rubber and rubber to metal with different thickness of brick layers.

Besides the working temperature, it is also necessary to consider the mechanical shocks to which the equipment is subjected.

8.4 Lining Thickness

The thickness of the lining depends on the severity of corrosion or erosion. The diffusion of liquids is inversely proportional to the square of the thickness of the lining at a given temperature. That is to say, a 6 mm thickness is four times more resistant than a lining of 3 mm thickness. The speed of diffusion in the temperature range 30–80 °C is proportional to the temperature increase.

Table 8.2 Temperatures on interface of brick to rubber and rubber to metal with different thickness of brick layers

Liquid temperature (°C)	Room temperature (°C)	Brick lining thickness (mm)	Interface Temperature (°C)	
			Brick/RL	RL/Steel
33.9	26.7	102	17.5	10
	32.2	–	18.3	12.2
	37.8	–	20	14
43.3	26.7	102	22.2	14
		204	15	8
	32.2	102	24	15.6
		204	17	10.6
	37.8	102	25.6	18
		204	18.4	13
49.4	26.7	102	25.6	15.7
		204	17.3	9
		306	13	6.7
	32.2	102	27.2	17.8
		204	19	12.6
		306	14	8.5
	37.8	102	28.3	20
		204	20.6	14
		306	16.1	12
65	26.7	204	23.5	14
		306	16.1	9.5
	32.2	204	25.5	17
		306	18	12
	37.8	204	27.2	19
		306	21.1	14
80	32.2	306	80	66.7
	37.8	306	84	70.6
111.1	32.2	306	98.9	80
	37.8	306	102.2	85.6
126.6	32.2	306	107.8	86.7
	37.8	306	111.7	91

Values are based on ceramic bricks.

RL: Rubber lining thickness: 6 mm.

Metal thickness: 10 mm.

Note: Temperature measurements at rubber/steel and brick/rubber lining interfaces were not very accurate because of experimental difficulties encountered while the concern was to protect the rubber against mechanical damage. However, the readings give indications of drop in temperatures between these interfaces.

8.5 Design and Fabrication of Lining Supports

In the lining of tanks the important points to be considered are:

- The metal surfaces must be accessible for manual working. Suitable manholes and gateways are to be provided in the structures for movement of operators and for adequate ventilation.
- Weld seams should be continuous, smooth, and free from porosities and blow holes, projections and burrs. These should be smoothened out by grinding.
- Large tanks should be suitably reinforced outside arresting any deflection due to loads applied during application of lining.
- Settling allowances during fabrication and erection of the tank should have been already taken care of before application of the lining.
- Since electrical gadgets like exhaust fans, blowers, spark testers and so on will be used during the application of the tank lining, the tank should be properly earthed.
- The scaffolding inside the tank should be free standing and not supported by the walls of the tank (see Figure 8.1).
- The surface area being large in the huge storage tanks, it must be sand blasted and primer coated in sections.
- Suitable fire fighting devices should be placed inside the tanks, since the solvents handled in the lining application and coating adhesives are highly inflammable.

The fabricator of vessels should be informed in advance that the vessel will be lined and should be asked to follow the standard procedure for fabrication of equipment meant for rubber lining. The standard procedure generally contains the precautions to be taken for obtaining a good surface finish, welding finish and ease of accessibility of the fittings, nozzles, vents and piping. The lining contractor makes detailed guidelines to help the fabricators in the design and fabrication of tanks suitable for rubber lining.

To obtain a good lining, it is necessary that the lining surface either of mid steel, cast iron, stainless steel, aluminium, concrete, wood, should be fabricated/constructed avoiding sharp corners or edges. Sharp corners should be ground to have a radius and the weld seams have to be flush to the adjoining surfaces. There must be accessibility by hand to all the surfaces to be lined. These criteria need not be applied to lining of long pipes. In the case of long pipes, a soft rubber bung of Shore hardness 35 A is used as a tool for lining. However, spiral welded pipes lead to poor quality lining since the travel of the bung through the same will not be uniform and total air elimination cannot be guaranteed.

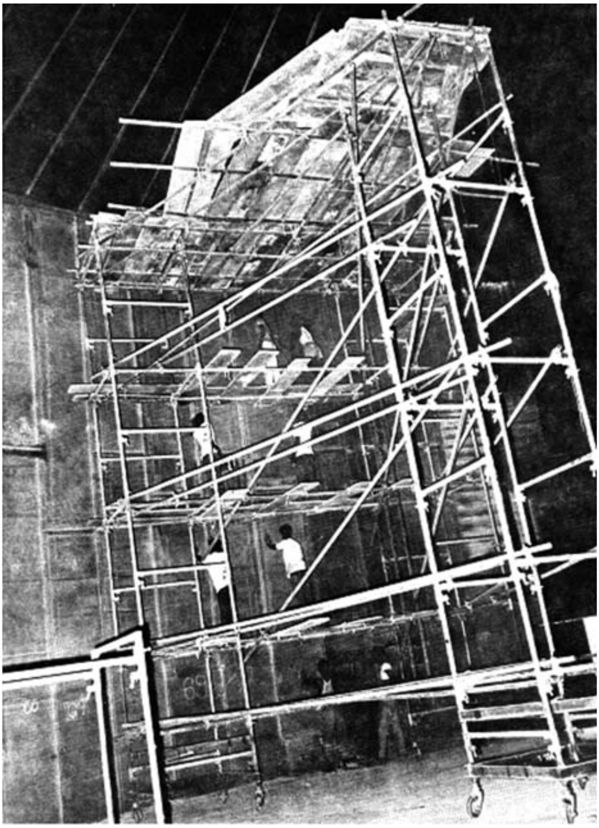


Figure 8.1 Rubber lining of large storage tank in progress with multi-stage scaffolding

The welds should not be porous or should not have any cracks. As the lining is usually subjected to vulcanisation in autoclave at temperatures of 130 °C to 150 °C, the entrapped air inside the weld could expand and blow out the lining thereby necessitating repair work on the lined vessel.

After rubber lining, no welding or earthing should be done on the lined tank and therefore the lugs, hooks, pipe supports, which may be required to be welded on the vessel or piping, should have been planned and completed at the time of fabrication of the vessel. The fabricator is normally informed about this in advance. For concrete tanks, the concrete should be bone dry through the entire thickness and the lining surface should be free of dust, cracks, holes, and so on.

For perfect bonding between lining surface and adhesive, the surface must be absolutely free of oil, grease and contaminants such as: rust, chemical deposits, and so on. In order to eliminate the rust and the scales from old steel vessels meant for relining, sand blasting is carried out twice. This will also provide the required roughness to the surface to be lined.

8.6 Adhesive Coating

Adhesives, prepared in the Sigma mixer, are tested for their viscosity and homogeneity before application onto the surface of the vessel to be lined. It is usual to give a first and primer coat of the adhesive over the blasted surface immediately after sand blasting.

Generally for lining and other interconnected operations, the humidity should not be very high. The preferred humidity is 60–70%. To enhance good adhesion, several primer coats are used on the metal surface. After coating, it is dried before the actual lining process, i.e., the application of calendered sheet. It is necessary to ensure that the solvent in the adhesive has completely evaporated as otherwise, during lining the volatile solvent will ‘blister’ out and thereby make the bonding poor.

8.7 Application of Calendered Sheet

The application of the calendered sheet on to the coated surface is the actual lining. The sheets should be laid on the coated surface without stretching. The air between the rubber sheet and the metal must be rolled out. The rolling is done with different kinds of rolls starting from 10 cm diameter and up to 3.75 cm diameter with a face length of 5 cm. The choice of the rolls depends on the place and the accessibility, like corners, acute angles, and bends. Taper cutting of the jointing edges, which has to be done manually, is a highly skilled job, requiring considerable experience. Very sharp edged knives and blades are used for cutting the sheets as per required profiles and sizes. The taper length should be four times that of the thickness and should be at an angle of 45°.

The lining sequence for each kind of vessel and piping should be planned ahead and the design of sheet to match the contours and shapes of the vessels needs to be done meticulously, to achieve a properly finished, smooth lining with perfect joints. After the vessel is lined, it is ready for vulcanisation either in the autoclave, or by an open steam or by an hot water curing process.

A responsible rubber lining manufacturer or applicator should be able to carry out the lining at any place and at any time. It will only be a question of additional auxiliary equipment and materials, which might be required at times of different climatic conditions. The main base metal surface is mild steel in the form of welded construction. Natural rubber lining is even today is of great importance in acid resistant applications. Natural hard rubber (ebonite) lining, if subjected to high temperatures tends to crack, which is obviously due to the thermal deformation in the tank. The danger of crack development is due to the differing expansion coefficient of steel and ebonite, and while handling thin walled lined structures, i.e., they hit solid beams or other structural elements during handling. In order to combat such a situation which is unavoidable in a project site the ebonite lining has a flexible semi-ebonite bottom layer adhering to the metal to take up the mechanical shocks without passing the shocks to the hard ebonite lining layer above. In other words an ebonite lining will have a 2 mm flexible ebonite bonded intimately with metal surface and 3 mm as a top layer resistant to corrosive media. Soft rubber linings will withstand temperature fluctuation as they are elastic and basically shock absorbing.

In road tankers transporting different chemicals in the same rubber lined tankers is a common practice since it is uneconomical to have the tank lined for each type of acid/chemical. In this case, it is advisable to rinse the tank with water before filling up different chemicals each time. In general, the transportation tankers such as railway tankers, road tankers and ship tankers have dimensions, which can still be vulcanised in autoclaves [4]. The size of the tank is limited by the maximum size of the autoclave and also depends on the feasibility to transport them before and after rubber lining. The author's opinion is that the maximum size of the autoclave can be 5 m diameter x 10 m long which is considered to be a techno-economically viable size for factory operations, which in most cases can accommodate road tankers, railway tankers and ship tankers.

In this kind of ship (tanker) lining there is no limitation concerning the choice of rubber compound type. Due to outside influences such as forces connected to fluid flow and jerkiness in the tank, dynamic stresses occur on all transportation tankers. In addition to this, as stated earlier change of chemicals loaded in the tankers are often made by operators. In general it can be said that the life time of the lined tanker is shortened by frequent change of chemicals. The most handled acids in a single tanker can be hydrochloric acid, phosphoric acid, dilute sulfuric acid, caustic soda lye, hypochlorite, formic acid, dilute hydrofluoric acid, residual acids from prickling tanks, and regenerated acids.

8.8 Autoclave Vulcanisation

An autoclave is a pressure vessel (see Figure 8.2) capable of withstanding an internal pressure generated by steam.

For rubber lining, the working pressure in an autoclave is normally 4–5 kg/cm^2 relative to atmospheric pressure. The equipment selected for this purpose has to accommodate a fairly large proportion of chemical plant equipment, piping and so on. The lined equipment is loaded in a trolley and then pushed into the autoclave with the help of a winch motor. The boiler pressure is maintained at 0.69 MPa and the steam pressure inside the autoclave is kept 0.41 MPa resulting in a constant temperature of 130 to 140 °C, as the case may be, depending upon the type of compounds used for lining. The curing cycle time normally varies between 6 to 16 hours, and is largely dependent on the compound used and the size of the vessel. After vulcanisation is over, the autoclave is opened and the lined equipment and tanks are unloaded for finishing and inspection.

Figure 8.2 A 3-metre by 8-metre autoclave

8.9 Inspection

Pinholes in a rubber lined tank will expose the underlying metal surface to corrosive chemicals, which are handled by the tank. Continuity of rubber lining is checked with a spark tester with a voltage varying from 6000 V to 20,000 V, depending on the thickness of rubber and also the conductive property of the lining compound. While using the spark tester, it is necessary to ensure that the spark does not remain continuously in one spot, to ensure that a burnt hole may not occur through the lining material, because of the continuous sparking.

8.10 Adhesive Manufacture

Sigma blade mixture/kneader is used for preparing the adhesives used for lining. Warmed stocks in the mill are charged into the mixer, along with solvent and other ingredients and then the mixer is run for a cycle time, which can vary between 4 hours and 16 hours. When the adhesive made is homogenous, it is tested and packed in barrels to be used later for lining. Furthermore, before lining, the adhesives are tested for any degradation in their properties, such as viscosity, as a precaution.

As the choice of raw materials is steadily becoming a complex task with new polymers and compounding ingredients fighting for a place among the already established ones, critical evaluation is essential before their worth is assessed.

It should be recognised that appreciable shifts in properties are sometimes made possible by special compounding variations for example, the heat resistance of NR vulcanisates may be improved considerably by varying of the vulcanising system. The normal sulfur vulcanisation system is capable of many variants, which will govern the chemical nature of the sulfur crosslink, i.e., whether it is essentially a mono, di, or polysulfide type. The nature of the sulfur crosslink can have considerable influence on the heat resistance of the vulcanisate.

For a particular application, the base polymer, or polymer blend, has first to be selected according to the broad pattern of final properties required and the curing method used. This must then be combined with an appropriate crosslinking system, and whether carbon black or non carbon black. the reinforcement, if any, has to be decided on next, sufficient processing aids being included to ensure satisfactory mixing and processing. It should be remembered that reinforcing fillers of finer particle size are, as a rule, generally expensive and so excessive reinforcement should therefore be avoided when not critical. Any permissible diluents or special additives for specific effects are then added to the formulation list.

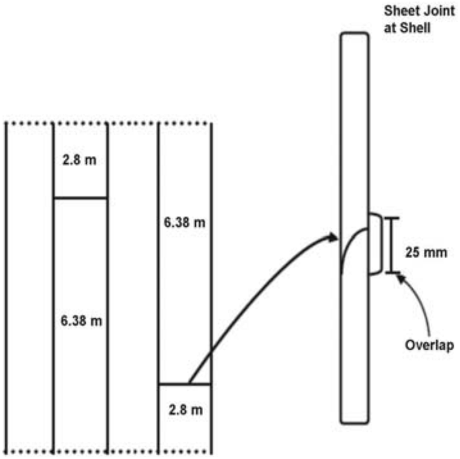
Protective antidegradents are selected according to the severity and type of service exposure and to their relative effectiveness in the particular base polymer used. The stages in which the ingredients are mixed in production must also be borne in mind, and the appropriate ingredients grouped accordingly. For example, protective agents are commonly added early and crosslinking agents added last.

8.11 Rubber Lining of Large Storage Tanks

Rubber lining of large storage tanks is a challenging job and the procedure involved embraces all aspects of multi disciplinary engineering practices such as chemical, mechanical and electrical. A typical rubber lining procedure for a phosphoric acid storage tank situated in a receiving port terminal is described next.

Huge circular storage tanks are normally rubber lined with precured rubber sheets using selfcuring bonding adhesives at the tank site. The site humidity is checked so that is not more than 65%, since a high humidity will interfere in the effective bonding of the lining with the metal surface. The lining operation is stopped if rain prevails. In the case of phosphoric acid storage tank, either a natural soft rubber, Neoprene rubber or butyl rubber of durometer hardness 50 – 55 A, is used depending on the defoaming agents or any additives in low concentration in the bulk acid. The adhesive used will be a Neoprene-based one with an isocynate-based accelerating agent for selfcuring. The tanks installed in terminals will normally have a diameter ranging from 20 m to 30 m and height from 9 m to 15 m. The lining thickness normally used in practice is 3 mm for the roof, 5 mm for the shell and 10 mm for the floor. For tanks with a height above 20 mm, a multistage, normally six stage scaffolding of approximately 1 – 1.5 to 2 m height between stages is erected inside the tank as shown in Figures 8.1 and 8.3.

In such huge tanks since the area to be rubber lined is more than 2000 m^2 including pipes and fittings, manhole flanges and blind flanges and other accessories, the total area is sand blasted, primer coated and rubber lined in stages. Before sand blasting the tank is inspected to check for a good metal surface free of pittings and weld projections which are to be ground smooth especially at joints. The various steps of lining involve: sheet cutting, sand blasting, adhesive coating and sheet laying. The sheets are cut to the required size with taper cuttings at the ends of the joints. On the blasted surface, three coats of the adhesive bonding solution are applied with adequate drying time between coats. The final coat will have the isocynate accelerator admixed with the Neoprene-based adhesive. After drying, the sheets are laid and rolled down with a roller eliminating the air. The rubber lining sheet layout and the joint details are shown in Figure 8.3.



Sheet Dimension

1. If the sheet is 9 m long, the stretch of the sheet is approx. 1 cm/m of length of the sheet ie 9 cm, when the sheets are vertically lined on the shell.
2. The stretch is not applicable for 1 m long sheet (i.e., sheets of short lengths)
3. Width of the sheet is 1.25 m approx.
4. The above is applicable for a 52 ° Shore A natural rubber compound

   For case to case (i.e., for each sheet) the length of sheet is determined taking into consideration the stretch as well as the overlap joints (Stretch is overhanging due to self weight and rolling)

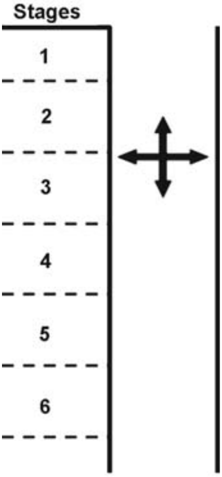
Figure 8.3a Sheet layout of lining in a storage tank

In the tank, the sheet joints at the roof and at the floor level should be as shown in Figure 8.3c, i.e., at the floor. The sheet end from the shell should be laid below the floor sheets, and not *vice versa* and the sheet end at the roof should be laid beneath the shell sheet. A 1 mm security strip of 50 mm wide should be laid on the joints.

8.12 Sheet Dimensions

When the sheets are laid vertically on the tank shell, there is a stretch of about one centimetre per meter length of the sheet. This is due to self weight and tension stress due to hanging. For example, for a 9 m sheet the stretch will be 9 cm.

The stretch in a shorter sheet less than 2 m long is not significant. The stretch of the sheet is more for low hardness compounds (Shore 45 A to 50 A). However, the practical hardness of sheet for such a precured lining should not be more than Shore 60 A. Each length of sheet for cutting to size is determined by taking into consideration the stretch, as well as the overlap joints which are staggered. This stretch factor should be taken into consideration before laying to avoid undersize or oversize.



Sheet Laying and Rolling

1. Mark the horizontal reference line
2. Lift the sheet to the 1st stage in scaffolding
3. Roll down, fixing one end lengthwise on the horizontal line simultaneously fixing the other end also
4. The coated sheet should also have a liner cloth which is removed before rolling with the roller (i.e., after temporarily fixing the sheet on all the three side (i.e., top and 2 sides)
5. Then roll with a roller as follows:

   Rolling should be started from the centre sideways and downwards, eliminating the air sideways and downward. The joints, i.e., the edges should be re-rolled finally. The sheet should be marked into segments to follow rolling as follows (with a chalk).

✓	✓
✓	✓

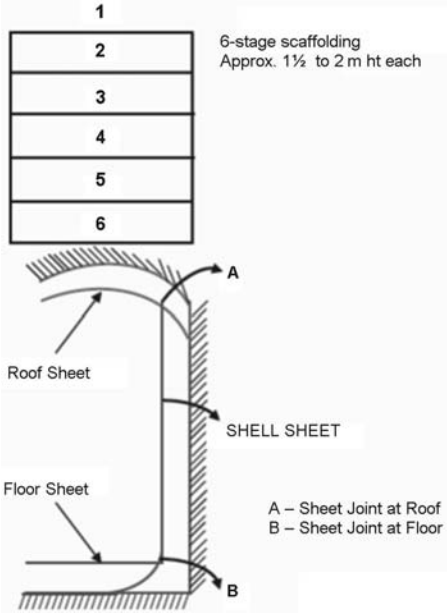
   Each segment to be marked after rolling to differentiate rolled as well as unrolled surface.

Figure 8.3b Procedure for sheet laying and rolling while lining a large storage tank

8.13 Sheet Laying and Rolling

The following procedure is normally followed:

- Mark the horizontal reference line on the tank surface.
- Lift the sheet to the first stage in the scaffolding.
- Fix one end, lengthwise on the horizontal reference line simultaneously fixing the other end also.
- The rubber sheets are coated and dried prior to laying with the primer coat of the adhesive solution.
- Roll down from the top reference line with a 5 cm roller, eliminating the air between the metal and the sheet.



Lining Thickness

Roof Thickness 3 mm
Shell Thickness 5 mm
Floor Thickness 5 + 5 = 10 mm
Shell 2nd layer up to 1 m ht 5 + 5 = 10 mm

Figure 8.3c Thickness of rubber lining at different places in a phosphoric acid storage tank

From any point the rolling should be started from the centre, to the side and then downwards, eliminating the air. The overlap joints should finally be rerolled. The sheets should be segmented by marking with a chalk stick, each segment being marked after rolling to differentiate rolled as well as unrolled surfaces.

8.14 Procedure of Tank Inspection before Undertaking the Lining Operation

After the fabrication of the tank, the metal surface should be inspected for any pittings or projections and the same is to be levelled out by grinding. This visual inspection should be done before the tank is hydraulically tested since rusting formed immediately after the hydraulic test will camouflage the defects on the surface. Any leaks at the metal joints found during hydraulic testing should be repaired before start of rubber lining and not during the operation. Before the start of rubber lining the tank should be earthed properly. The lining operator should check the earthing beforehand.

8.15 Rubber Lining of Pipes

For pipes the sand blasted inner surfaces are coated by pouring of the adhesive solutions. For this purpose the pipes are laid obliquely on two ‘A’ frame stands of different height say 1 m and/or 0.75 m.The adhesive solution is then poured through the pipe, which during this operation is rotated slowly and the excess is collected in a container at the opposite end. This operation is repeated twice. In each case the coating of the adhesive solution is allowed to dry. Then a previously formed tube of rubber having length of at least 50 cm longer than that of the pipe, is closed at both ends. At one end a small opening is made by pinching and the tube is inflated with air. The tube is then drawn into the coated pipe with the aid of a rope made of Nylon or cotton duck (heavy, plain or woven cotton). The air pressure is then increased by additional pumping of air through the pinched hole to allow the tube to be pressed well on the wall of the pipe. The two closed ends of the tube are then cut open and one of the protruding ends is folded and pressed into contact with the whole area of the flange of the mild steel pipe, see Figures 8.4 and 8.5.

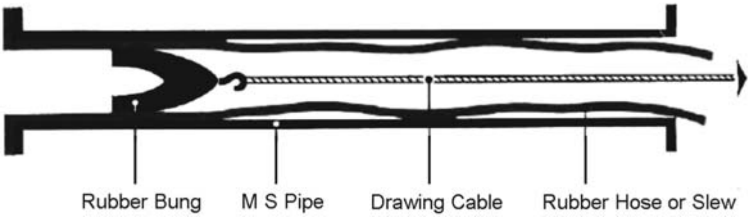
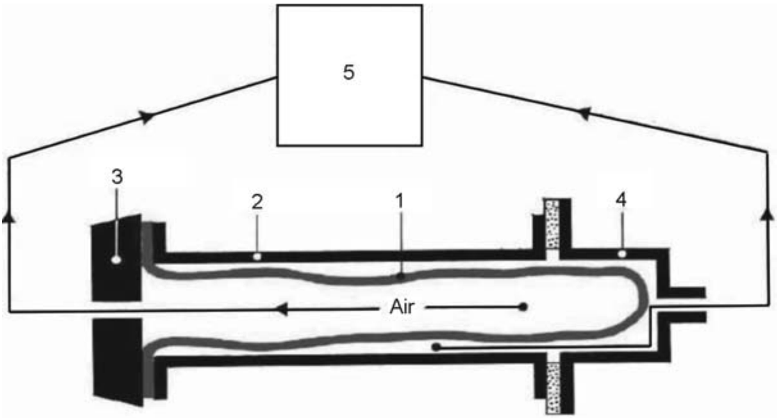


Figure 8.4 Rubber lining of a long pipe using a bung (ms : milled steel)

The other end of the pipe remains free when the mild steel pipe is firmly clamped. A bell shaped rubber bung of low hardness (Shore 45 A) is slowly drawn into the pipe from the end where the rubber is folded and fixed on to the flange, by means of a cable attached to an electric pulling winch motor. The diameter of this rubber bung is about 10% greater than the inside diameter of the pipe to be lined and is coated with lubricants such as talc, or soft soap to reduce the friction when it is drawn through. When the bung moves it presses the rubber tube against the wall of mild steel pipe and expels the air trapped between the tube and the mild steel pipe. Finally the free end of the tube is then pressed on to the other flange with a roller and stitched well. The lined pipe is now ready for autoclave vulcanisation. Recommended maximum lengths of straight pipe for satisfactory lining are shown in Table 8.3. There is no standard norm for the maximum length of straight pipes of various diameters for lining. Since lengthy pipes with smaller diameters cannot be accessed for inspection and testing, the maximum lengths of straight pipes are recommended based on normal and convenient industrial practice.



1. Hose made from ebonite compound, closed at one end
2. Iron pipe
3. Soft rubber cover with hose connection to the pump
4. Iron bell with hose connection to the pump
5. Vacuum pump

Figure 8.5 Rubber lining of a short pipe using a vacuum

Table 8.3 Recommended maximum lengths of straight pipe for satisfactory lining

Nominal bore (mm)	Maximum length between flanges (mm)
25	1000
40	2000
50	3000
65	4000
80	5000
100 and above	6000

The conventional method of lining pipes involves the use of rubber bungs, in this method, the green (unvulcanised) rubber sheet is made in the form of a tube called a 'slew' and the same is drawn into the coated pipe. The tube length is longer than the length of the pipe. The bung diameter is also larger than that of pipe. The rubber bung is drawn from one end of the tube towards the other end using a winch. The travel of the bung presses the tube against the wall of the pipe and expels the air trapped between the rubber and the pipe. After this process, the lined pipe is cured.

The disadvantages of the above process are:

1) Folding of the 'slew' during the passage of the bung
2) Air entrapment, and
3) Low productivity.

To overcome the above disadvantages, a special process using a vacuum technique can be adopted. In western countries this process is popular.

The tube or 'slew' is closed at one end and drawn into the coated pipe. The open end of the tube is struck to the flange of the pipe and closed with a soft rubber cover, which is connected to a vacuum pump by a hose. A metallic cover, which is also connected to the pump, is put over the other end of the pipe. The air inside the tube is sucked out through the soft rubber cover at one end and at the same time the air between the tube and the pipe is removed via the metallic cover. The vacuum thus created should be adjusted in such a fashion that the tube is kept balanced and at a suitable point of time the vacuum inside the tube is released. On release of the vacuum, air flows into the tube at controlled, gradual rate and presses against the wall of the pipe. This process, ensures that no air remains trapped. This procedure is suitable for pipes of smaller lengths. For a long distance piping system such small pipes need to be flange joined.

8.16 Storage of Rubber Lined Pipes

The following precautions are to be taken while storing rubber lined pipes prior to erection and commissioning:

- The outside surfaces of the rubber lined pipes should be protected against atmospheric corrosion, such as rusting with an anti-corrosive weather resistant coating, based on chlorosulfonated polyethylene or Neoprene. A primer coat of red oxide is given. In many installations, epoxy coating or chlorinated rubber-based coating is also applied if cost considerations are not significant. It is, however, recommended that a suitable white paint is applied on the outer surface as this will reduce the heat transmitted on the rubber lining and the adhesive bonding beneath it.
- The pipes should be stored in stands at least about 1 metre above ground level for handling without damage.
- It is advisable to avoid direct exposure to sun and other climatic conditions should be avoided. However, in huge tanks in port terminals, this is not possible and therefore a weather resistant coating is given.
- The pipes should be covered with tarpaulin if stacked outdoors and free air flow should be ensured to avoid hot air packets, to prevent premature oxidation.
- The ideal measure will be that the rubber lined surface is always kept wet with water in order to arrest the likely deterioration from ultraviolet rays and ozone attack during storage.

8.17 Surface Preparation for Rubber Lining

The advent of the sophisticated protective rubber lining has brought about the necessity of acquiring a wider knowledge of precise surface-finishing conditions that must be fulfilled at the metal surface in order to achieve the utmost adhesion and bonding of the lining material to the metal. The performance of any type of lining is very much dependent on the cleanliness of the surface. The environment in which the equipment, storage tanks or road tankers are located determine to a greater extent the type of lining that should be specified, for example, a tank that is located in a harbour terminal will have to be rubber lined, adopting precured rubber sheets with a self curing adhesive bonding solution. If maximum life expectancy of a rubber lining is expected, it should be firmly adhered to the metal. The key to the life and effectiveness of lined equipment exposed to a corrosive environment is its design and construction. The design and construction not only includes the structural design enabling manoeuvrability during the lining operation, but also the surface preparation. Proper surface preparation plays a vital role in the ultimate protection against corrosion. For film formation of the adhesive coating of even thickness all over and for uniform wetting and drying, removal of surface contaminants is all that is required.

8.18 Methods of Surface Preparation

Several methods are used in practice for preparing the metal surfaces before rubber lining such as:

- Cleaning with hand tools
- Cleaning with power tools
- Cleaning by sand blasting
- Cleaning by water blasting
- Cleaning with steam, high pressure water and chemicals, and
- Pickling with acid.

Cleaning by hand tools is the oldest process [4]. Today this is used only when power tools are not available and where the surface is inaccessible to power tools and too small. The hand tools generally used are wire brush, scraper blades and chipping hammer and emery or sand paper. Handheld electric or pneumatic power tools for cleaning include sanders, pneumatic scalers, needle gun and rotary steel brushes.

Sand blasting is by far the best and most practical method and for large areas, this is the method followed. For outdoor blasting operations, coarse river sand is used for the blasting operation. For indoor blasting, steel shot are used. Sand blasting is the cheapest method and widely used. Sand blasting is done using compressed air at an output pressure of 6 kg/cm^2. Low pressure reduces blasting efficiency considerably.

The high and the low points of the blasted surface called the ‘peaks and valleys’, are an important factor for anchoring of the adhesive coating. The sand blasting nozzles generally in use will have either 6.4 mm, 7.9 mm or 9.5 mm diameter. Where sufficient air is available at the correct uniform pressure, the larger sized nozzles are preferred to smaller ones for more area coverage.

The sand blasting operation can be continuous or intermittent. For continuous sand blasting, the flow of sand should be continuous. For rubber lining of large storage tanks, sand blasting is done intermittently, simultaneously followed by primer coats. For productivity, the sand blasting equipment may have double hopper arrangements, at some places.

Blasted surface qualities are often specified by users of rubber lined equipment. A white surface finish after blasting, corresponds to a Swedish standard SIS 05 59 00 [5], grade SA3 or BS 7079 [6] and to first quality [7, 8]. This white finish is defined as a surface with a grey white, uniform metallic colour slightly roughened to form a suitable anchor pattern (peaks and valleys) for primer coat and subsequent lining. The finished surface should be free of all oil, grease, dirt, visible mill scale, rust corrosion products, oxides or remaining adhesive or paint coatings or any other foreign matter.

A near white surface finish corresponds to grade Sa2.5 of the Swedish Standard SIS 05 59 00 for blast cleaning [5] (see Table 8.4 for the Swedish grades) or BS 7079 [6–8] second quality. This finish is defined as one from which all oil, grease, dirt, mill scale, rust, corrosion products, oxides remaining coatings, except for a very light shadows of light streak discoloration. At least 95% of the surface has the appearance of a white metal surface finish and the reminder is limited to light discoloration.

A commercial blasted surface finish corresponds to Swedish Standard SIS 05 59 00, grade SA2 third quality [5] (see Table 8.4). The finish is defined as one from which oil, grease, dirt, rust scale and foreign matter have been completely removed form the surface, except for slight shadows streaks or discoloration and pitting. For old tanks, the surface might have been pitted, allowing slight residues settling at the bottom of the pits. These should be removed by brushing.

Table 8.4 Swedish Standard SIS 05 59 00, 1967 [5]

Sa1	Light blast cleaning to remove mill scale, rust and paint
Sa2	Widely known as commercial blast. Inferior to Sa2.5
Sa2.5	Very thorough blast cleaning to achieve near white metal. Inferior to Sa3
Sa3	Blast cleaning to visually clean steel. Surface should be completely free from oil, grease, mill scale and rust

Water blasting will remove substances such as loose and blistered paints, loose rust, grease and other accumulated residue. Since water blasting will not produce a surface equivalent to that produced by sand blasting, it is nevertheless an economical method of cleaning for lining application.

A piece of rubber lined equipment at the end of its service life is re-lined if the metal is not badly damaged due to mechanical abuse or/and spillover of acids and so on. For re-lining the remnants of rubber sticking to the metal surface are removed by hot water or steam with chemical additives before sand blasting is done.

This method is known as ‘sweating’. For example, preparatory to relining of a tank handling caustic soda for its service life, it is good practice to first thoroughly clean with steam or high pressure hot water before sand blasting. Phosphoric acid solution (5% by weight in water) is added to the steam or high pressure water, will neutralise any alkali residues. Care, however, should be taken by the operator, to avoid exposure to fumes and spillage, and standard precautionary methods and measures should be strictly followed. At times authentic information as to the use of acidic water handling in cleaning operation are not provided by the equipment suppliers. In this case without seeking expert advise such cleaning operation should not be resorted to. Pickling is done for cleaning the surface of small metal parts using dilute hydrochloric or sulfuric acids in pickling tanks, which are rubber lined. The acid pickling process will yield a fresh metal surface suitable for bonding with rubber for manufacturing metal rubber bonded components. This process is followed mainly in the manufacture of rubber bonded components.

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9

Testing of Rubber Lining

For many years, treating rubber with chemicals was considered to be a test for rubber. The aim of this testing was to understand the characteristics of the rubber to enable further supplies to be manufactured when there was an inadequate supply of the natural rubber. The extraordinary properties of rubber, like its stickiness, elasticity and elongation encouraged researchers to conduct various tests to explore its then unknown characteristics, such as strength, reactivity with other chemicals, swelling in solvents, oxidisability, stability, and so on. The chemical analysis of rubber provided the chief means of measuring the changes in rubber brought about by vulcanisation.

Even before the discovery of vulcanisation by Goodyear [1], the effects on rubber of heat, light, acids and alkalies were studied. Testing became necessary when early investigators faced problems with rubber and its vulcanisates. Possibly the earliest chemical resistance test on rubber was undertaken by Goodyear when he treated rubber with nitric acid and this yielded a hardened mass [2, 3]. He mistakenly called this phenomenon vulcanisation, before he accidentally discovered vulcanisation with sulfur at a later point.

Though efforts towards conducting tests and designing testing devices were being made, early investigations were seriously limited by a lack of knowledge about rubber and the absence of suitable facilities for assessment and interpretation of the results. Since the composition of the rubber being tested was sometimes not known, the results were misleading and investigation could not correlate the results of tests with the actual service life of the rubber.

A few decades ago, Carpenter grouped the physical tests conducted on rubber into two classes [4]. The first group included measurement of dimensions, specific gravity, density, tensile strength and ultimate elongation, the relationship between stress and strain, compression strength, hardness and resilience. These tests characterise the rubber vulcanisate and the test data usually represent a specification for the given rubber product. In the case of anticorrosive and anti-abrasive rubber linings, these tests are quoted as the technical data. These tests are quite useful for compounding studies.

The second class of tests focused on ageing, oxygen and ozone attack, adhesion, resistance to wear and tear, and general fatigue. This class also includes tests under simulated service condition in laboratory environments. These two classes of tests are conducted on vulcanised rubber. For assessing the processibility of the compounded unvulcanised rubber stocks, tests such as Mooney viscosity, plasticity, scorch time and plasticity retention index are carried out.

For rubber linings a visual check of the appearance is done in the first instance, to find any air blisters or cracks on the cured rubber lining. A visibly good surface may still have a loose bond with metal; this can be arbitrarily tested by giving small hits on the surface with a wooden mallet and comparing the sounds. A clear and well-bonded lining may produce a clear defined sound. Surfaces with air blisters or loose bonds will give a clapping sound. Spark testing is used to check for the continuity of lining.

Chemical tests such as acetone extraction, chloroform extraction, potassium hydroxide extraction, free sulfur, total sulfur and combined sulfur are done to find out the ingredients mixed in the rubber. Most of the physical and chemical tests and their methods are given in standard specifications, such as those published by the American Society for Testing and Materials (ASTM) and the British Standards Institution (BSI), in addition to other national and international specifications.

9.1 Density of Solids

Densities of engineering materials reflect the mass and diameter of the atoms that make them up and the efficiency with which they are packed to fill the space. Most metals have high densities because the atoms are heavy and closely packed. Polymers are much less dense because the atoms of which they are made (carbon, hydrogen and oxygen) are light and because they generally adopt structures which are not closely packed. Ceramics – even the ones in which atoms are packed closely – are on average a little less dense than metals, because most of them contain light atoms like oxygen, nitrogen and carbon. The density of compounded rubbers is based on the densities of the ingredients that make up the compound. Density or specific gravity measurements are important tests on compounded rubbers, especially those used for lining applications because volume cost is an important factor in these compounds.

9.2 Hardness

The most practical tests for rubber lining are hardness tests, spark tests and immersion tests. The hardness test is invariably the most used test for rubber lining quality by clients, although as a single measurement it is somewhat inadequate.

The term hardness is a vague one, as illustrated by the different concepts of hardness reflected by expressions such as ‘scratch hardness’, ‘inundation hardness’, ‘cutting hardness’ and ‘abrasion hardness’.

Mohs did not define hardness when he developed his scale of hardness ranging from talc to diamond with the state of liquidity as the zero of the scale [5]. This hardness is indicative of the abrasive nature of the material when in contact with rubber.

In rubber testing the elastic structure is not damaged and the original shape is restored, since the deforming forces are lower than the recovery forces exerted by the elastic nature of rubber. In this respect, rubber test methods differ from those applied to metals, bitumens, waxes, greases and ceramics where measurements of permanent deformation are made.

As the rubber hardness is a measurement of almost completely elastic deformation, it could be expected that attempts would be made to relate hardness to elastic modulus. Most rubber hardness tests measure the depth of penetration of an indentor under either a fixed weight or a spring load and when rubber is assumed to be an elastic isotropic medium the indentation obtained at small deformation depends on the elastic modulus, the load applied and the dimensions of the indentor. It is recognised that with a spherical ball indentor the relationship between the indenting force 'D' and the Young's modulus E_i given by:

$$D = ER^2 f\,(H/R)$$

where R is the radius of the ball, H the depth of indentation and f (H/R) is the function of the shape factor H/R which is characteristic of the shape of the indentor.

The standard test method for measuring the durometer hardness of rubbers according to ASTM D2240–05 [6] is based on the penetration of a specified indentor forced into the material under specified conditions. The indentation hardness is inversely related to the penetration and is dependent on the elastic modulus and viscoelastic behaviour of the material. This method is an empirical test intended primarily for control purposes. No simple relationship exists between indentation hardness determined by this method and any fundamental property of the material tested.

The real objective in conducting hardness tests is to measure the elastic modulus under small strain. In almost all hardness measuring instruments, the time at which the reading is taken is important, since for a particular set of conditions the usual hardness test imposes a constant load on the specimen, the test becomes a creep test if readings are taken at different time intervals after application of the load. This factor is responsible for the failure of exact correlation between different instruments requiring different time intervals for reading. The correlation is particularly poor when materials having varying creep rates are compared. The hardness of rubber vulcanisates changes with temperature and therefore it is important that tests for specification purposes, or in different laboratories, should be made at the same temperatures.

During a study of natural rubber and chloroprene rubber stocks containing various carbon blacks, Buist pointed out that certain properties are closely related [7]. For example, for natural rubber the following groups are highly correlated:

1. Shore hardness and abrasion resistance

2. Swelling in benzene, elongation and modulus at 300%

3. All tests of hardness

4. Plasticity, compression, resilience and modulus

5. Shore hardness tests with all other tests, and

6. Tensile strength is not highly correlated with any other properties.

9.3 Spark Testing

Before an item of equipment lined with ebonite or any soft rubber leaves the workshop it is tested for nonporosity. According to regular practice, the only reliable method of determining this is using a spark tester or inductor at a test voltage of 20,000–25,000 volts.

Spark testing is an important test conducted for continuity of rubber lining, as any faults at joints or pinholes in the sheets are detected with the spark testers. The adhesive strength to the metal can only be tested on counter samples lined and cured along with the rubber lined tanks. Destructive testing is not normally done with cut samples from the lined tank except for substantially aged tanks, for example after 10 years service. Since rubber lining is a manual job, a large surface area, such as a ship's tank of more than 5000 m^2, can take about two months for completion under normal conditions. The shipyard (or the client's site) needs to supply electricity, transport facilities, storage facilities, air, water and steam supply facilities from a nearby source. It is preferable that the rubber lining applicators arrange their own scaffolding since this is a specialist operation.

The principle of the spark tester depends on the transformation of the primary voltage of 42 volts to one of 20,000 to 25,000 volts.

9.4 Description of Apparatus

The spark test equipment tests rubber linings for the presence of pin holes and it consists of a main or direct current (DC) operated generator or interrupter, to which a Tesla coil is added within a tuned circuit. The coil operates best at a fairly high frequency and is capable of generating a very high peak alternating current (AC) voltage.

Rubber linings are tested for the presence of any pin holes which could potentially allow acid flow to the metal surface below and result in corrosion. An AC high voltage and high frequency spark discharge of 150 to 30,000 cycles should be used. The adjustment of the test output voltage is achieved by measuring the length of the spark in air by means of a spark gap of 20–25 mm. It is advisable to avoid excessively large electrodes due to the AC inductive loss through the thin anticorrosive coating of film thickness 300–400 μm. So, the larger the electrode, the more diminished is the initial preset applied voltage. This inductive loss is not too critical when testing large joint-free lining surfaces. For this type of application, an excessively large voltage is unnecessary for any porosity or faults present would be directly through the thickness of the lining material such as 2 mm, 3 mm or 5 mm. A straight or 'T-shaped' electrode with at least a 150–200 mm wide working probe edge is recommended for this type of testing.

For testing overlap joints, a pointed or tipped electrode should be used to ensure a minimum loss of applied voltage and thus maximum effective test concentration. It is important when testing joints to use a sweeping, downwards movement, continually moving, never stopping too long in one position. Otherwise too much strain will be applied to the dielectric strength of the rubber joints and adjacent areas of the joint thus increasing the risk of dielectric breakdown. For pipes, an electrode of circular wire is used. Electrodes are available having both a flat section for flat surface and tips for joints. With surfaces having no faults or pinholes a bluish corona discharge will be observed in the electrode. Faults, porosity or pinholes will be recognised by the passage of bright spark and the dying out of the corona discharge. In addition an audible change of note will be heard from a buzzing corona to a crackling noise with each spark drawn to the fault.

While using the spark tester, it is necessary to ensure that the probing brush or tip does not remain continuously in one spot, so that a burnt hole many not be formed through the lining materials, because of the continuous sparking. The test voltage has to be adjusted to levels of lower than 10,000 while testing compounds with high loadings of carbon black and or graphite.

9.5 Swelling Test

Guidance about the chemical resistant nature of rubber compounds can generally be obtained from the change that the rubber undergoes after immersion in liquids of various kinds. During immersion in a given liquid, the surface layer of the rubber is attacked in the initial stages.

The action of corrosive liquids such as acids, alkalies, water, fumes and gases basically involves: absorption, diffusion, permeation, extraction and chemical reaction. Absorption leads to swelling and an increase in weight. Diffusion leads to percolation through pores. Permeation leads to leakage of fumes and gases. Extraction leads to reduction in weight. Chemical reaction either adds to the weight or degrades rubber depending upon the intensity and vigour of the reaction and also the conditions to which the reaction product is exposed. With swelling, the rubber is strained and the physical properties change. The leaching or extraction of certain chemical ingredients, especially the antioxidising agents, from rubber has a significant influence on the useful life of the lining.

9.6 Specifications and Codes of Practice

A number of specifications and codes of practice are followed throughout the world for rubber lining, the major ones being from the ASTM, the BS Specifications, the German Institute for Standardisation (DIN) and the Japanese Industrial Standards (JIS) which give exhaustive information on rubber lining procedures, testing methods and code of practice.

There are other standard specifications from various countries. The British Standard Institution (BSI) BS ISO 4880 [8] deals with the specification for lining with rubber. It also specifies design, fabrication and surface finish of equipment to be lined; quality and methods of lining; inspection and testing; storage, handling, transportation and installation of lined equipment; and testing continuity of lining with correction methods for faulty linings.

The international standards for immersion testing of rubber deal with the change in weight and volume of rubber samples when they are immersed in various corrosive liquids. The details of these specifications are given in Table 9.1.

Table 9.1 International standards for immersion testing of rubber

Specification Code	Title
ASTM D471 (American) [9]	Standard Test Method for Rubber Property – Effect of Liquids
BS ISO 1817 (British) [10]	Rubber, Vulcanised – Determination of the Effect of Liquids
DIN ISO 1817 (German) [11]	Rubber, Vulcanised – Determination of the Effect of Liquids
JIS-K 6258 (Japan) [12]	Dipping test for rubber

The chemical reaction of rubber lining with the corrosive chemicals and acids causes deterioration, resulting in progressive damage to the lining unless the reaction is not allowed to continue further. With an increase in temperature the changes described previously take place at a faster rate. In all the above standard methods, the changes in weight of rubber after immersion in a liquid media over a period of time and in different temperature conditions can be considered to be an indication for assessing its suitability for use in those particular conditions.

Though an absolute reference value is not available for comparison in any of the international standard specifications, the technical publications about the chemical resistance properties of rubber by liquid immersion tests certainly provide relative and useful data with which the suitability of anticorrosive rubber lining compound can be assessed with a fair degree of accuracy. For this reason manufacturers and applicators of rubber lining resort to tests under simulated conditions instead of accelerated ageing, immersion or swelling tests.

The previous specifications give different temperature conditions for the liquid immersion test as follows:

BS	25 ± 1 °C to 150 ± 1 °C
ASTM	–75 ± 1 °C to 250 ± 2 °C
ISO	–75 ± 1 °C to 250 ± 2 °C
DIN	20 ± 2 °C to 130 ± 2 °C

If temperatures are not specified, the immersion tests have to be carried out at room temperature. The volume of the immersion liquids should be adequate to immerse the sample of rubber. The test should be carried out in the absence of direct sunlight to avoid atmospheric oxidation. Test pieces from cut samples or counter samples from the finished rubber lining compound have to be buffed smooth.

The duration of the tests in the above standards vary as follows:

BS	24 hours, 18 hours, 96 hours, 168 hours, up to 30 days
ASTM	22 hours, 70 hours, 166 hours, 670 hours
ISO	22 hours, 70 hours, 7 days, 14 days, 28 days

The change in volume as well as weight of the test piece after immersion, with respect to time, is recorded. The test chemicals and reagents used in immersion test and the nature of attacks are as given in Table 9.2.

Table 9.2 Immersion test and the nature of attacks

Name of chemical	Nature	Density	Main type of attack on rubber
Water	Neutral	1	Diffusion
Hydrochloric acid	Acidic	1.18	Diffusion and formation of reaction products
Sulfuric acid	Acidic	1.84	Diffusion
Phosphoric acid	Acidic	Depends on concentration	Diffusion
Nitric acid	Acidic	1.42	Diffusion
Sodium hydroxide solution	Alkaline	Depends on concentration	Diffusion

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11. DIN ISO 1817, *Rubber, Vulcanised – Determination of the Effect of Liquids*, 2004.
12. JIS K6258, *Rubber, Vulcanised or Thermoplastic – Determination of the Effect of Liquids*, 2003.

10

Specification and Codes of Practice for Rubber Lining

It has long been recognised that rubber lining is one of the most effective means of protecting chemical plant and equipment against corrosion and abrasion. However, a universally acceptable guide for users, equipment fabricators, rubber lining contractors and applicators on materials and methods of application and testing, inspection and design and finish of vessels, tanks and pipes is not available. Every country has its own specifications and codes of practice. Every client in the process industries requiring rubber lining specifies their own chosen test methods and specifications in their tender documents. Valuable technical information which can be used as guidelines is also available from raw material suppliers as well as lining contractors such as Blair Rubber Company (USA), Olin Rubber Lining Service (USA), Gerland (France), Clouth (Germany), and the Yorkshire Rubber Linings Ltd., (UK) and many other major contractors in Europe, North America and Japan.

Many industries faced the challenge of a loss of millions of dollars, incurred every year due to corrosion. Unfortunately, even though they were using rubber as a protective material they were not guided by any specification of materials, testing procedures and application methods for several years. The phenomenal losses compelled the industry to consider corrosion prevention as an important issue from the very early stages of design and fabrication, through to installation of chemical plant and equipment.

Despite this awareness there was little sharing of information across industries on corrosion and its protection. This was primarily fuelled by a fear of losing the trade secrets of their respective technologies, and the associated loss of business and revenue due to this. This attitude was prevalent throughout the world between fertiliser, chlor-alkali and many other giant chemical facilities. As a result of this no laboratory could fully assist the plant operator with corrosion-based issues, other than to offer some laboratory scale test data on chemical resistance. This information mostly took the form of bar charts and graphs provided by the technical service departments of the raw rubber and material manufacturers like Dupont, Bayer, Dow Chemicals, Exxon, Polysar and so on. This was, without doubt, useful as a starting point for operational and in-house research and development in the compounding technology, but did not provide a standard norm or code of practice for rubber lining which could be followed universally. Expertise and knowledge about corrosion and the related issues was high in several countries, but this was restricted to certain companies and industries.

International seminars and conferences have been held in various countries to address this critical issue, and enabled the participants to share their experiences in corrosion and its protection [1, 2]. Motivated by the knowledge sharing, acceptable specifications and code of practice were drafted by many institutions in the developing and developed nations and subsequently followed by industry.

A number of specifications were developed by the American Society for Testing and Materials (ASTM), British Standard Institution (BSI) and many others in Germany, Japan and India, in addition to the International Standard Organisation (ISO). These specifications give exhaustive information on rubber lining. BSI is the independent body responsible for preparing British Standards. It presents the UK view on standards in Europe. Specifications and standards of different countries though based on general concepts differ marginally in application and approvals. For example, in the high voltage spark testing of highly carbon filled compounds the ASTM prescribes a lower voltage and spark length when compared with the BS which does not deviate their norm of spark length and voltage for compounding variations. This necessitates low carbon filled compounding to be developed for achieving optimum results.

The BSI's BS6374-5 [3], deals with specifications for lining with rubbers. It includes information on design, fabrication and surface finish of equipment to be rubber lined, quality, methods of lining, inspection and testing, storage, handling, transportation and installation of lined equipment, testing continuity of lining and rectification methods for faulty linings.

ASTM D2240-05 [4] deals with the procedure for rubber lining and equipment. ASTM D429-03e1 [5] deals with adhesion to rigid substrates. The Annual Book of ASTM Standards Part 38: Section: 09 [6, 7] is a useful reference for rubber products, industrial specifications and related test methods.

ISO 8501-1 [8] deals with the preparation of steel substrates before application of paint and related products and the visual assessment of surface cleanliness.

Based on wide experience, The Plant Lining Group of the former Federation of British Rubber and Allied Manufacturers (FBRAM) had prepared a code of practice to be followed by industry to ensure satisfactory standards of lining materials, polymers and workmanship [9]. The leading members of this Federation were BTR Industries Ltd., Dunlop Rubber Ltd., Dexine Rubber Ltd., Nordac Ltd., and Redfern's Bredbury Ltd. This code sets out the advice of the Plant Lining Group for vessels to be lined with compounds of natural and synthetic rubbers:

- Part I is concerned with the design and preparation of vessels of mild steel, cast iron, steel alloys, aluminium alloys, concrete and of pipes and fittings.
- Part II covers the procedure for efficient lining.
- Part III deals with materials and their properties.
- Part IV focuses on testing and inspection.
- Part V deals with resistances of natural and synthetic rubber compounds to corrosive chemicals.

The FBRAM, now The British Rubber Manufacturers' Association (BRMA), specifies that all users of rubber lined equipment should familiarise themselves with BS 6374 Parts 1-5 [10–14]. They also give advisory guidelines on the use and handling of rubber lined equipment.

The Verein Deutscher Ingenieure (VDI) 2539 [15] relates to the surface protection coatings with organic materials. It deals exclusively with the testing of finished surface protective films made from organic materials and in this, only nondestructive testing procedures are described. The composition, properties and suitability of the protective material do not fall within these guidelines.

DIN EN 14879-4 (supersedes VDI 2537) [16] deals with surface protection with organic materials; surface protection with strips made from natural and synthetic rubber.

VDI guideline 2531 [17] is intended to give the planning and design engineer a survey of the applicability of materials for relevant stresses and how they can be stressed.

DIN EN 14879-1 (supersedes VDI 2532) [18] applies to the design and execution of metal constructions to be protected against corrosion. For buildings of reinforced concrete, or concrete and brickwork, VDI 2533 [19] are valid. DIN EN 14879-4 (supersedes VDI 2537[20]) [16] deals with surface protection with layers of natural and synthetic rubber. VDI Guidelines should be referred to in the selection and treatment of the material base for the process industries such as metal and concrete structures and fabrications, as well as in the selection and properties of the protective material, namely rubbers).

The technical practice committee of the National Association of Corrosion Engineers (NACE) standard SP 01.78 [21] specifies design, fabrication and surface finish of mild steel tanks and vessels to be lined for chemical immersion service. This standard stipulates that in the design of tanks for chemical service, consideration must be given not only to chemical resistant rubber linings but also to prevent contamination. To obtain high performance of these linings special consideration must be taken during the tank design and fabrication stage itself. This standard was prepared by the Task Group T6 of NACE on protective coatings and linings, presenting the recommended practices for the design, fabrication and surface finish of tanks and vessels that are to be lined for corrosion resistance and to product contamination showing good and bad design practices too. These recommendations are essential to the lining suppliers, applicators and users of such tanks. This code supersedes NACE RP 01 78.

The Indian Standard for lining of vessels and equipment for chemical processes, IS 4682-1 [22], mentions that the use of linings with rubber for protection against corrosion has been the normal industrial practice for more than half a century. The lined vessels and tanks are quite suitable for use either under vacuum condition or high pressure conditions. The appropriate thicknesses for rubber linings are recommended in this standard for various corrosive and abrasive conditions as follows:

1. Storage vessels of chemicals with moderate corrosion effect such as acidic water (water containing up to 5,000 ppm free acidity) at ambient temperature: 3 to 4 mm thickness.
2. Alum solution up to 10% at ambient temperatures: 3 to 4 mm thickness.
3. (10%) Sulfuric acid at temperatures up to 40 °C: 3 to 4 mm thickness.
4. Brine (30%) and caustic lye solution (15%) at ambient temperatures: 3 to 4 mm thickness.
5. Oxidising chemicals at temperatures up to 90 °C to 100 °C: 5 to 6 mm thickness.
6. Slurry application: 5 to 10 mm thickness.

For piping, the minimum thickness of 3 mm is satisfactory. The maximum single ply thickness recommended for application is 5 mm and all thicknesses more than 5 mm should be in two or more plies having a maximum thickness per ply of 4 mm. While the thickness specification is for application of lining, the calendering sheet thickness standard used is 1 mm, which is doubled with several plies of 1 mm to obtain the required lining thickness, to ensure pinhole free sheet.

This standard stipulates the minimum adhesion values of the various types of rubbers used in different methods of vulcanisation, determined in accordance with the specified method B in IS 3400-5 [23] as shown in Table 10.1.

Table 10.1 Minimum adhesion values of rubber lining* used in different methods of vulcanisation

Types of rubbers	Pressure vulcanisation (kg/cm)	Vulcanisation by hot water or steam at atmospheric pressure (kg/cm)
Natural soft rubber	3.6	2.7
Polychloroprene	3.6	2.7
Butyl rubber	3.6	2.7
Chlorosulfonated polyethylene	2.7	2.7

* The thickness tolerance is ±10%

Apart from the previously mentioned standards and codes, the user industry considers additional specifications for the norm of swelling and hardness tolerance values, which ranges from ± 5 A to 10 A for the rubber lining. In swelling, there is no universally acceptable standard value for the guidance of the rubber lining manufacturers. Lining contracting companies may provide standards for the gradation of their various rubber lining compounds for chemical resistance, based on their experience correlated with swelling data values. The practice involves immersion of the vulcanised rubber sample in various chemicals and recording the data such as weight variation, thickness variation and hardness variation. These variations are yardsticks for grading the rubber lining compounds, as shown in Table 10.2.

Table 10.2 Percentage weight variation of rubber samples over 28 days immersion in liquid media

No.	Variation of weight (%)	Grade	Remarks
1	< 1	A	This compound is eminently suitable.
2	> 1 to < 3	B	This compound also is suitable and serves the purpose reasonably.
3	> 3 to < 4	C	This compound is suitable only when the lining is protected over with brick lining.
4	> 4	D	Cannot be recommended for rubber lining at all even with brick lining.

One chemical consulting company, Andritz-Ruthner in Vienna (*www.andritz.com*), has stipulated a method in which the percentage weight is not considered alone but it is combined with the area of the sample as well as the number of days of immersion. According to this procedure, vulcanised rubber sheets completely covered over steel plate samples of 5 cm x 5 cm are kept dipped in the chemical media and the weight of the sample in grams during the periods of immersion (of 12 days, 40 days or 80 days) are recorded and referred as ‘g’. The days are recorded as ‘D’. The surface areas of the samples are noted before commencing the test and this is referred as M^2.

From the data collected a graph is plotted as follows:

- g/m^2 against D
- g/m^2 square root of D, against D

For a good quality rubber lining compound to be used with 20% hydrochloric acid, the curve (of item 1) should be as near to the X axis as possible, i.e., it should have a low slope. Similarly, for the same quality of rubber lining (of item 2) the curve will exhibit a rise in the beginning but later on, it should fall off rapidly. It can be noted here that Ruthner has not specified any absolute reference value, so that one could compare compounds on the same basis.

Swelling of elastomers by liquid is known to be a diffusion controlled process and up to the equilibrium swelling ratio, the volume of liquid absorbed is proportional to the square root of the time during which the elastomer has been immersed in the liquid. For most liquids, the rate of penetration depends also upon the viscosity of the swelling liquid rather than its chemical nature.

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22. IS 4682-1, *Code of Practice for Lining of Vessels and Equipment for Chemical Processes – Part 1 Rubber Lining*, 1994.

23. IS 3400-5, *Methods of Test for Vulcanised Rubbers: Part 5 Adhesion of Rubbers to Textile Fabrics*, 1987.

Useful Websites

Australian Corrosion Association:
www.corrosion.com.au.

National Association of Corrosion Engineers, USA:
www.nace.org.

Advances in Materials and Processing Technologies (AMPT), Bahrain:
www.ampt2008.com.

KCH Group UK Ltd:
www.kchgroup.com.

Abbreviations

AC	Alternating current
AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
BIIR	Bromobutyl
BR	Butadiene rubber
BRMA	British Rubber Manufacturers' Association
BS	British Standard
BSI	British Standard Institution
CIIR	Chlorobutyl rubber
CR	Chloroprene rubber
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSM	Chlorosulfonated polyethylene rubber
DC	Direct current
DIN	German Institute for Standardisation
DVGW	The German Technical and Scientific Association on Gas and Water
EPDM	Ethylene-propylene diene terpolymer(s)
EPM	Ethylene-propylene monomer
EPT	Ethylene propylene terpolymer
FBRAM	Federation of British Rubber and Allied Manufacturers

FDA	Food and Drug Administration
FEF	Fast extrusion furnace
HCl	Hydrochloric acid
IR	Isoprene rubber
IIR	Isobutylene/Isoprene Copolymer (butyl rubber)
IS	Indian Standard
ISO	International Standard Organisation
JIS	Japanese Industrial Standards
ML	Mooney viscosity with a large rotor
MS	Mooney viscosity with a small rotor
NACE	National Association of Corrosion Engineers
NMR	Nuclear magnetic resonance
NR	Natural rubber
phr	Parts per hundred rubber
pphm	Parts per hundred million
ppm	Parts per million
PRI	Plasticity retention index
PTFE	Polytetrafluoroethylene
PV	Prevulcanisation
rpm	Revolutions per minute
SBR	Styrene-butadiene rubber
SRF	Semi-reinforcing carbon black
T_g	Glass transition temperature
UV	Ultraviolet
VDI	Verein Deutscher Ingenieure
WRAS	Water Regulation Advisory Scheme

Appendix 1
Swelling of chloroprene rubber (CR) in various solvents

	Medium	Volume increase %	
		Without carbon black	With 50 phr (semi reinforcing furnace black (SRF)
1	Acetone	55	40
2	Benzaldehyde	365	140
3	Carbon tetrachloride	350	170
4	Cyclohexane	119	75
5	Dibutylphthalate	200	110
6	Ethyl alcohol	10	0
7	Isopropyl ether	80	35
8	Kerosene	60	45
9	Oleic acid	80	40
10	Tetraethyl lead	75	35
11	Turpentine	215	100

Appendix 2

Greek alphabet used to denote engineering quantities of materials

Name	Symbol (capital)	Symbol (lower case)	Used for
Alpha	Α	α	Angle, angular acceleration
Beta	Β	β	Angle, coefficients
Gamma	Γ	γ	Shear strain, kinematic viscosity
Delta	Δ	δ	Differences
Epsilon	Ε	ε	Linear strain
Eta	Η	η	Efficiency
Theta	θ	θ	Angles
Kappa	Κ	κ	Fluid compressibility
Lambda	λ	λ	Wavelength
Mu	Μ	Μ	Thermal conductivity coefficient of friction
Nu	Ν	ν	Kinematic viscosity
Xi	Ξ	ξ	Mathematical constant
Pi	π	π	Mathematical constant
Rho	R	ρ	Density
Sigma	Σ	σ	Normal stress, standard deviation
Phi	Φ	Φ	Angles, potential energy
Psi	Ψ	ψ	Helical angles
Omega	Ω	Ω	Angular velocity solid angle
C. Matthews, IMechE Engineer's Data Book, 3rd Edition, John Wiley and Sons, 2005, Section 2.1, page10 Reprinted with permission from John Wiley and Sons			

Appendix 3
Chemical resistant properties and hardness ranges of both natural and synthetic rubbers

Notes to table overleaf

* The higher hardness of 100 A in natural rubber and nitrile rubber indicates ebonite that can be made with about 50% of sulfur addition.

Ebonite cannot be made from butyl, EPDM, chloroprene, silicone and chlorosulfonated polyethylene.

Silicone rubber has higher temperature resistance.

At room temperature natural rubber can be used for road tankers to handle 70% sulfuric acid.

Neoprene and chlorosulfonated polyethylene can resist pure and strong sodium hydroxide.

Chlorosulfonated polyethylene possesses superior resistance to oxidising environments such as 90% sulfuric acid and 40% nitric acid at room temperature for short duration.

Property	**Natural Rubber**	**Butyl Rubber**	**EPDM rubber**	**Chloroprene rubber**	**Nitrile rubber**	**Silicone rubber**	**Chlorosulfonated polyethylene rubber**
*Hardness A	40–100	40–90	40–90	30–90	45–100	40–80	40–80
Abrasive Resistance	Excellent	Good	Good	Very good	Excellent	Poor	Fair
Room temperature ageing	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Resistance to diffusion of gases	Fair	Excellent	Good	Excellent	Fair	Poor	Poor
Resistance to flexing	Excellent	Excellent	Good	Excellent	Fair	Poor	Poor
Resistance to Petrochemicals and greases	Poor	Poor	Poor	Good	Excellent	Fair	Good
Resistance to Vegetable oils	Good	Good	Good	Fair	Very good	Good	Good
Resistance to Water and anti-freezers	Good	Good	Very good	Fair	Good	Poor	Poor
Resistance to Dilute acids	Good	Good	Good	Good	Fair	–	Good
Resistance to Oxidising agents	Poor	Fair	Fair	Poor	Poor	Poor	Very good
Resistance to Alkalis	Fair	Fair	Fair	Good	Fair	–	Good
Processing characteristics	Excellent	Good	Good	Good	Good	–	Poor
Tear Resistance	Excellent	Excellent	Excellent	Good	Good	Poor	Good

Appendix 4
Useful data for calculating dimension of a steel tank and weight of rubber lining

Circumference of a circle	π x diameter or 3.146 x diameter
Diameter of a circle	Circumference x 0.31831
Area of a square	Length x width
Area of a rectangle	Length x width
Area of a parallelogram	Base x perpendicular height
Area of a triangle	½ base x perpendicular height
Area of a circle	π radius squared or diameter squared x 0.7854
Area of an ellipse	Length x width x 0.7854
Volume of a cube or rectangular prism	Length x width x height
Volume of a triangular prism	Area of triangle x length
Volume of a sphere	diameter cubed x 0.5236 (diameter x diameter x diameter x 0.5236)
Volume of a cone	π x radius squared x 1/3 height
Volume of a cylinder	π x radius squared x height
The diameter of an equal circle	Length of one side of a square x 1.128
Doubling the diameter of a pipe or cylinder increases its volume 4 times.	
The pressure (in lb/in2) of a column of water = height of the column (in feet) x 0.434	
The weight of rubber (in kilograms) for 1 m^2 of lining is calculated as follows: Area (in m^2) x thickness (in mm) x specific gravity of the compound. For example: weight for 5 m^2 of rubber lining is: 5 x 5 x 1.2 = 30 kg	

Appendix 5
Area of Circle

Diameter (in)	Area (in^2)	Diameter (in)	Area (in^2)	Diameter (in)	Area (in^2)
⅛	0.0123	4	12.566	16	201.06
¼	0.0491	4½	15.904	16½	213.82
⅜	0.1104	5	19.635	17	226.98
½	0.1963	5½	23.758	17½	240.52
⅝	0.3068	6	28.274	18	254.46
¾	0.4418	6½	33.183	18½	268.80
⅞	0.6013	7	38.484	19	283.52
1	0.7854	7½	44.178	19½	298.60
1⅛	0.9940	8	50.265	20	314.16
1¼	1.227	8½	56.745	20½	330.06
1⅜	1.484	9	63.617	21	346.36
1½	1.767	9½	70.882	21½	363.05
1⅝	2.073	10	78.54	22	380.13
1¾	2.405	10½	86.59	22½	397.60
1⅞	2.761	11	95.03	23	415.47
2	3.141	11½	103.86	23½	433.73
2¼	3.976	12	113.09	24	452.39
2½	4.908	12½	122.71	24½	471.43
2¾	5.939	13	132.73	25	490.87
3	7.068	13½	143.13	26	530.93
3¼	8.295	14	153.93	27	572.55
3½	9.621	14½	165.13	28	615.75
3¾	11.044	15	176.71	29	660.52
		15½	188.69	30	706.86

Note: This table for area of a circle can be used for any chosen units since π is a constant.

Appendix 6
Circumference of Circle

Diameter (in)	Circumference (in)	Diameter (in)	Circumference (in)	Diameter (in)	Circumference (in)
⅛	0.3927	4	12.56	16	50.26
¼	0.7854	4½	14.13	16½	51.83
⅜	1.178	5	15.70	17	53.40
½	1.570	5½	17.27	17½	54.97
⅝	1.963	6	18.84	18	56.54
¾	2.356	6½	20.42	18½	58.11
⅞	2.748	7	21.99	19	56.69
1	3.141	7½	23.56	19½	61.26
1⅛	3.534	8	25.13	20	62.83
1¼	3.927	8½	26.70	20½	64.40
1⅜	4.319	9	28.27	21	65.97
1½	4.712	9½	29.84	21½	67.54
1⅝	5.105	10	31.41	22	69.11
1¾	5.497	10½	32.98	22½	70.68
1⅞	5.890	11	34.55	23	72.25
2	6.283	11½	36.12	23½	73.82
2¼	7.068	12	37.69	24	75.39
2½	7.854	12½	39.27	24½	76.96
2¾	8.639	13	13	25	78.54
3	9.424	13½	42.41	26	81.68
3¼	10.21	14	43.98	27	84.82
3½	10.99	14½	45.55	28	87.96
3¾	11.78	15	47.12	29	91.10
		15½	48.69	30	94.24

Note: This table for circumference of a circle can be used for any chosen units since π is a constant.

Appendix 7
Conversion of Square Feet to Square Metres

Square Feet	Square Metres	Square Feet	Square Metres
1	0.0925	8	0.7400
2	0.1850	9	0.8325
3	0.2775	10	0.9250
4	0.3700	25	2.315
5	0.4650	50	4.65
6	0.5550	100	9.25
7	0.6475		

Appendix 8
Calculation of the area of different geometric shapes

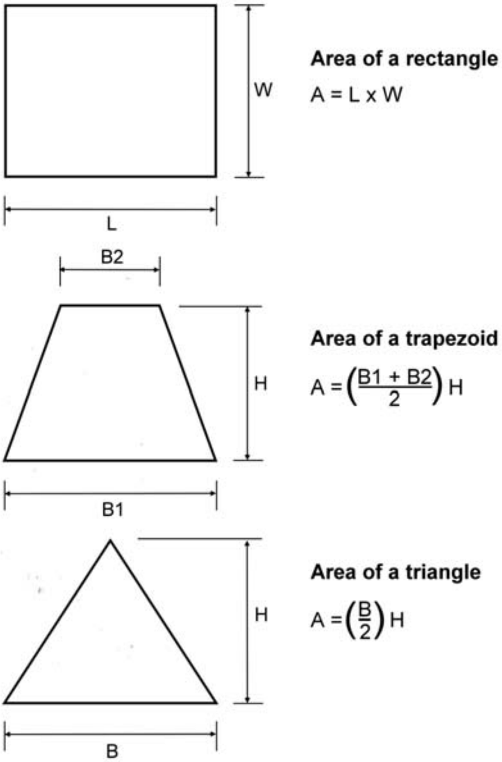
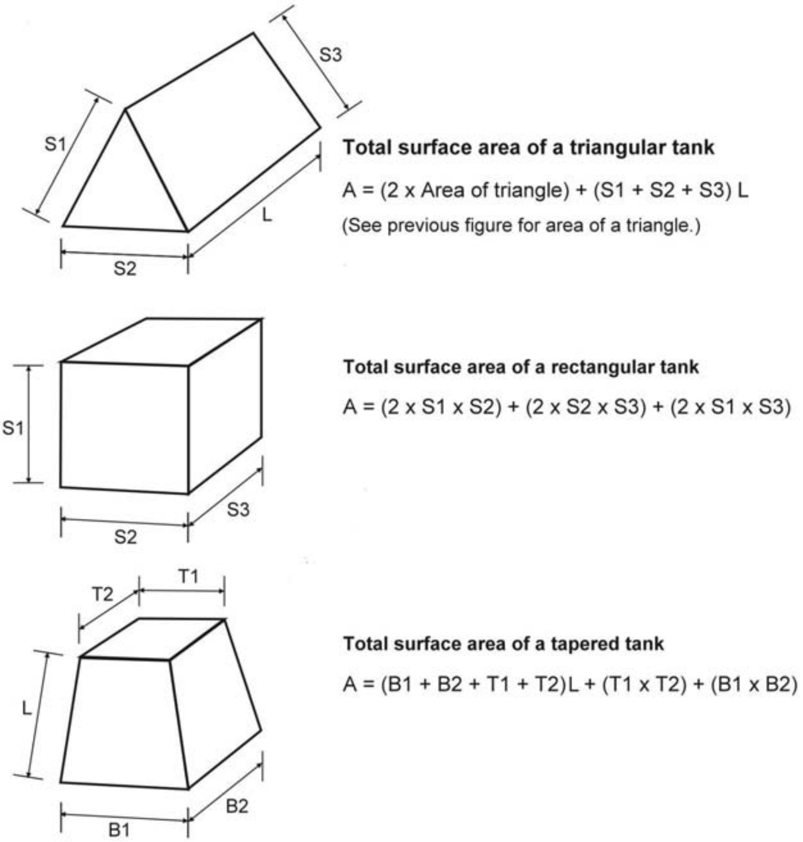


Figure A8.1 Area calculation for two-dimensional shapes



Total surface area of a triangular tank

$A = (2 \times \text{Area of triangle}) + (S1 + S2 + S3)\,L$

(See previous figure for area of a triangle.)

Total surface area of a rectangular tank

$A = (2 \times S1 \times S2) + (2 \times S2 \times S3) + (2 \times S1 \times S3)$

Total surface area of a tapered tank

$A = (B1 + B2 + T1 + T2)L + (T1 \times T2) + (B1 \times B2)$

Figure A8.2 Area calculation for three-dimensional shapes

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Rubber linings can be used as passive protection against the corrosion of plant and equipment in the chemical process industries. Rubbers act as sacrificial materials reacting or un-reacting with the corrosive media, diffusing the liquids or not diffusing, swelling by itself or not swelling, permeating or not permeating gases or fumes, abrading or wearing by the slurry particles, getting ozonised or oxidised; but still protecting the metal surface beneath it, during its considerable life cycle under those severe and stressed conditions. Rubbers age but their life cycle is good enough to protect the metals against corrosion and erosion.

The raw material bases are natural or synthetic rubbers. Rubber is used for corrosion/abrasion proof linings, more than any other material because of its proven superiority in this service at a relatively low cost. Fertilizer, electroplating, ore-refining, petrochemicals, chlor-alkali and paper industries invariably turn to rubber linings, in preference to other types of linings for their high resistance to corrosion and abrasion. Moreover the variety of rubbers, both natural and man-made, available and its flexibility to serve under wide temperature and pressure ranges, made rubber linings as the world-wide accepted anti-corrosive and anti-abrasive media.

This book describes exactly how to use rubber as a lining in tanks and how to overcome problems associated with this technique.

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