The different compounding ingredients used in rubber latex can be grouped into curing agents, sulfur, accelerators, antioxidants, fillers, pigments, stabilisers, thickening and wetting agents, and other ingredients such as: heat sensitisers, plasticisers, viscosity modifiers, and so on.

### 3.1 Compounding Ingredients

#### 3.1.1 Curing Agent: Sulfur

Sulfur is the universal vulcanising agent for natural rubber and also for synthetic rubbers, which contain olefinic unsaturation in the polymer chain, whether these polymers are in latex form or in the form of dry rubber. Sulfur is the main vulcanising agent for natural rubber, synthetic polyisoprene, styrene-butadiene rubber, acrylonitrile-butadiene rubber, polybutadiene rubber, and so on. The crosslinks formed during sulfur vulcanisation of olefinically unsaturated rubber are of three types: monosulfidic, disulfidic and polysulfidic. The relative properties of above crosslinks have an implication in the mechanical and ageing behaviour of vulcanisates. Monosulfidic and disulfidic crosslinks give better ageing resistance compared to polysulfidic linkage, whereas the initial tensile properties are better for a rubber vulcanisates with polysulfidic linkage. When the amount of sulfur used is high, a higher percentage of polysulfidic linkage is formed.

Sulfur to be used for latex compound should be of good quality and easily dispersed in water. Colloidal sulfur is preferred for latex compounds, which is obtained by a reaction between hydrogen sulfide and sulfur dioxide in an aqueous medium [1].

Thiurams, for example, tetramethylthiuram disulfide (TMTD) with disulfidic linkage can be used as a vulcanising agent in olefinically unsaturated rubber in the absence of elemental sulfur (sulfurless curing). This type of curing is superior to conventional curing for heat resistance, oxidative aging resistance, and so on.

Butyl xanthogen disulfide (at 4 phr) in presence of zinc oxide can be used for vulcanising rubber latex without elemental sulfur. Vulcanisate properties of this system are inferior to those obtained using the thiuram system.
3.1.2 Accelerators

The rate of sulfur vulcanisation can be increased by the addition of accelerators. The most important class of accelerators used in latex industry are metallic and amine dialkyl dithiocarbamate, thiazoles and thiurams function as secondary accelerators.

Dithiocarbamates are a class of accelerators used as primary accelerators in latex compounds. It can be in the form of alkali metal salts such as sodium diethyl dithiocarbamate (SDC) or zinc salts such as zinc dimethyl dithiocarbamate (ZMDC). An important difference between the ammonia and alkali metal salts compared to the polyvalent metallic ions is that the former are soluble in water, whereas the latter are not. Water insoluble solids are incorporated in latex as dispersions in water. Table 3.1 shows the preparation of a sulfur dispersion.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>100</td>
</tr>
<tr>
<td>Dispersol F Conc</td>
<td>4.0</td>
</tr>
<tr>
<td>Distilled water</td>
<td>96.0</td>
</tr>
</tbody>
</table>

*Ball milled for 72 hours

Commonly used dialkyl dithiocarbamates in latex compounds are zinc diethyl dithiocarbamate (ZEDC), SDC, and piperidinium pentamethylene dithiocarbamate [2].

The accelerating activity of various dithiocarbamates differs considerably. ZDEC is of intermediate activity and it tends to cause gradual thickening in ammonia preserved natural rubber latex (NRL) under normal storage conditions due to the slow liberation of zinc ions. An exception to this rule is zinc pentamethylene dithiocarbamate. Latex films turn brown in the presence of dithiocarbamate and copper due to the formation of copper dithiocarbamate.

Xanthates are very reactive accelerators. They are active even at room temperature. They are somewhat unstable and are invariably accompanied by a bad odour. This may be due to a small amount of carbon disulfide, which is evolved during their decomposition on storage. Alkali metal xanthates are water soluble whereas heavy metal salts are insoluble. Typical examples are zinc isopropyl xanthate, sodium isopropyl xanthate, zinc-\(n\)-butyl xanthate.

Thiazoles are used as secondary accelerators in combination with dithiocarbamates. They impart lower compression set and higher modulus and load bearing capacity. Two thiazoles which are most commonly used in latex compounding are sodium mercaptobenzthiazole (SMBT), and zinc mercaptobenothiazole (ZMBT). SMBT
Latex Compounding Ingredients

are usually prepared by dissolving mercaptobenzothiazoles in a slight excess of sodium hydroxide solution. The most suitable thiazole accelerator for latex work is the water insoluble ZMBT. This may be prepared by a reaction between sodium mercaptobenzthiozole solution and zinc sulfate solution. ZMBT can be used in place of ZDEC to get desirable technological properties such as high modulus, and so on.

Thiurams are used as a secondary accelerator along with dithiocarbamates. Some typical examples are tetramethylthiuram monosulfide (TMTM), tetraethylthiuram disulfide, dipentamethylenethiuram disulfide (DPTD), dipentamethylenethiuram tetra sulfide. All these accelerators are insoluble in water and so they are incorporated in latex as dispersions. The cure with these accelerators is comparatively slow but their activity can be improved by incorporating sulfur bearing compounds such as thiourea in the compound.

3.1.3 Antioxidants

The ageing characteristic of rubber latex vulcanisates is better compared to dry rubber, since it is not subjected to any degradation during processing (in latex processing there is no mastication or exposure to high temperatures). For NRL products the aging resistance is further improved by the presence of naturally occurring rubber constituents which function as antioxidants. Similarly some of the vulcanisation chemicals such as ZDEC/zinc mercaptoimidazole, and so on, also improves aging resistance.

Two types of antioxidants are used in rubber compounding: the amine type and the phenolic type.

Amine type antioxidants cause discoloration/staining on ageing and because they are resinous in nature it is difficult to disperse them in the rubber latex.

Phenolic antioxidants are the most commonly used in latex, compounding examples are styrenated phenol (SP), substituted cresols, and so on. Water insoluble liquid antioxidants are incorporated in to the latex as an emulsion in water. The emulsified antioxidant droplets are adsorbed on to the rubber particles as the compound matures. Even if this does not occur they will be expected to disperse rapidly in the rubber phase when the latex is dried down to form a solid deposit.

3.1.4 Fillers and Pigments

Inorganic fillers and pigments are added to the latex in order to make it less expensive and to stiffen the product or to colour it. These fillers don’t have any reinforcing effect when they are added to latex as they do in dry rubber. If the compounded latex with
carbon black as filler is subjected to irradiation by high-energy radiation this causes some reinforcement. This study was conducted by A and G Lamm [3].

The next sections discuss the important inorganic fillers used in the latex compounding.

3.1.4.1 Kaolinite Clays

Kaolinite clays are a class of inorganic fillers, which are commonly incorporated into latex compounds. The kaolinite clays form an important group of fillers, which are an inexpensive material of fine particle size and they are readily dispersed in water with the aid of small amounts of dispersing agents. Some grades of kaolinite clays can be added directly in dry form. The pH of an aqueous clay slurry is usually in the range of 7 to 8. In some cases the pH is lower and in range of 4.0 to 4.5. The acidity may be readily corrected by the addition of a small amount of potassium hydroxide (KOH).

Kaolinite clay is sometimes added to NRL at a level of 400 phr. At these levels the products are very hard and show virtually no rubbery properties.

3.1.4.2 Calcium Carbonate

Naturally occurring forms of calcium carbonate are whiting, chalk, limestone, and so on. All of these are very inexpensive and give poor quality products with a marked tendency to discoloration. Precipitated calcium carbonate is widely used in latex compounds. It may contain small quantities of water-soluble calcium salts, which tend to reduce the stability of the latex. One method of detecting the presence of soluble calcium salts is by the addition of a small amount of sodium carbonate prior to the addition to the latex.

3.1.4.3 Titanium Dioxide

The most effective white pigment used in latex compounding is rutile (titanium dioxide). For regular application five parts (phr) is used in latex paints.

3.1.4.4 Lithopone

Lithopone is a mixture of barium sulfate and zinc sulfide, and it may be used as filler. It is used as an inexpensive alternative for titanium dioxide.
3.1.4.5 Barytes

Barytes is precipitated barium sulfate, which has been used with NRL to give filled compounds with good extensibility and elongation at break. The main disadvantage of this pigment is its tendency to sediment rapidly. This is because of its high specific gravity.

3.1.4.6 Carbon Black

Carbon black is used as black pigment in latex compounding. The carbon blacks are added to latex in the form of dispersion or slurries after adjustment of the pH to alkaline. Wet ground mica is also used as a filler in latex compounding.

3.1.5 Stabilisers

Surfactants: These are substances which lower the surface free energy against air and aqueous media, along with interfacial free energy against immiscible organic liquids. One method to classify these agents is based on function:

- Wetting agent
- Dispersing agent
- Dispersion stabilisers
- Emulsifiers
- Foam promoters and foam stabilisers

The disadvantage of this classification is that there exists a considerable degree of overlap among different categories. For example, potassium oleate is classified as a foam promoter for latex foam and as a stabiliser for synthetic and NRL. Most surfactants are tolerably efficient in the majority of functions but may be outstandingly efficient in just one respect.

Chemically surfactants are classified as amphoteric, anionic, cationic, and non-ionic, and so on, depending upon the active entity present.

Anionic surfactants: In this case the surface activity is attributed to the anion – examples are carboxylates, sulfates, sulfonates, and so on.
Unsaturated straight chain aliphatic carboxylates derived from oleic acid find application as colloidal electrolytes in emulsion polymerisation. The oleates are also used as an emulsifier in water immiscible oils, and as a foam promoter in the manufacture of latex foams.

**Fugitive soaps:** These are ammonium soaps. They lose free amines by vulcanisation. Ammonia is the most volatile base but is rather too volatile for some applications, alternatives include morpholine and triethanolamine. Rosin acid soaps also find applications as emulsifiers, colloidal electrolytes and foam promoters.

**Sulfonates:** are much more sensitive to acids and heavy metal ions than are the carboxylates. They mainly function as wetting agents and examples of this group are sodium diisopropyl naphthalene sulfonate, sodium dibutyl naphthalene sulfonate, and so on. A well-known compound sodium naphthalene formaldehyde sulfoxylate is prepared by reacting two molecules of sodium naphthanate sulfonate with formaldehyde. This substance is a deflocculating and dispersing agent and it finds application in preparing dispersions of insoluble powder. Sodium salts or esters of sulfonic acid are another group and they find application as wetting and dispersion stabilisers.

**Sulfate:** In general, substances of this class are all strongly surface active and find application as wetting agents and dispersion stabilisers. The typical examples of straight chain alkyl sulfonates include sodium dodecyl sulfate, sodium hexadecyl sulfate and a mixture of them.

### 3.1.6 Thickening and Wetting Agents

**Thickening agent:** It is frequently necessary to increase the viscosity of latex compounds. Thus, dipping mixes may require to be thickened so that thicker deposits of rubber are obtained or spreading mixes are thickened to prevent the latex from striking through the fabric.

Latex compounds may be thickened in two ways: (i) by filling the mix or (ii) by adding thickening agents. The tolerance of latex for these fillers is limited and their addition may produce undesirable effects in the rubber. It may prove necessary, therefore to add thickening agents, among which a wide range of natural products are available, e.g., gums, casein, glue and gelatine. These are all somewhat unpredictable in effect, are subject to bacterial attack and although they may cause high initial increase in viscosity, this effect decreases on prolonged storage. Furthermore, they have marked effects on the ‘handle’ of the rubber article and on its resistance to water.
Commonly used thickening agents are sodium carboxymethyl cellulose, polyvinyl alcohol, and so on.

**Wetting agent:** Sometimes the addition of a wetting agent to the latex mix is necessary for successful impregnation of fabrics or fibres with latex. Though a medium speed wetting agent, Calsolene oil HS has been found to assist in obtaining a complete penetration between textile fibres without any danger of destabilising the latex.

**Calsolene oil HS:** Calsolene oil HS, a highly sulfonated oil, is available as a clear, amber coloured liquid, readily soluble in water. Unlike some high speed wetting agents, Calsolene oil HS does not give rise to viscosity changes of the latex compounds.

### 3.1.7 Other Compounding Ingredients

**High styrene resin latex** can be used as a reinforcing resin. High styrene-butadiene co-polymer lattices enhance the stiffness and hardness of the deposits.

There is a progressive increase of modulus and a progressive reduction in elongation at break as the proportion of resin in the vulcanisate is increased. Tensile strength increases at first as the level of resin is increased and then passes through an optimum and falls off, which may be due to the breakdown of resin particles and the rubber matrix interface. High styrene resin lattices may be used in conjunction with lattices of polychloroprene/acrylonitrile-butadiene and co-polymers of styrene-butadiene and natural rubber.

**Resorcinol formaldehyde resin:** The direct condensation of resorcinol and formaldehyde in natural rubber is not easy to effect. Formaldehyde tends to destabilise the latex. Excess ammonia is added to prevent coagulation. Formaldehyde reacts with ammonia and prevents the resin formation. If excess of a fixed alkali is added to prevent coagulation, difficulty may arise because of the faster rate of resorcinol formaldehyde resin formation.

### 3.2 Preparation of Aqueous Dispersions and Emulsions

All dispersions or solutions, which are to be added to latex should be prepared with distilled water or soft water. The degree of dispersion required depends upon the quality of the rubber article to be made. Thus, for thin articles, in which high strength is necessary, finely dispersed compounding ingredients are essential. Poor dispersions may also adversely affect the transparency and colour of the product. It is sometimes more convenient to mill all the solid ingredients together as a single batch. It should
be realised, however, that if this procedure is adopted it will be found that the time required to produce a reasonable dispersion of the most difficult ingredient, is the same as that required to reduce the particle size of the most intractable component. For example it is difficult to prepare a sulfur dispersion and so it is given 72 hours of ball milling so if sulfur is also mixed together with other chemicals then at least 72 hours has to be given so that a good dispersion of sulfur together with other ingredients is obtained. For the production of high quality ‘pure gum’ rubber articles, it is recommended that all dispersions be prepared individually.

Dispersions prepared individually should be mixed together prior to addition of latex since, even though no obvious flocculation is apparent, the particles may aggregate and the quality of the mix be impaired.

3.2.1 Dispersion of Water Insoluble Solids

The treatment required to produce high-quality dispersions of water-insoluble solids depends on the physical nature of the materials. Those which have been prepared by drying from a colloidal state (e.g., clays) do not usually require prolonged milling. Their primary particles are small but have aggregated and can sometimes be re-dispersed merely by stirring with water containing a dispersing agent, followed by passing the paste through a colloid mill or by brief ball milling.

Other materials, however, require actual grinding of the particles and for this purpose ball or gravel milling is necessary, the later being reserved for difficult materials such as sulfur.

**Ball milling:** The container is rotated about its cylindrical axis in a horizontal plane at such a speed that the charge is tumbled. In this example of the ball mill (Figure 3.1), the grinding charge consists of unglazed porcelain or glass balls, their size being governed by the diameter of the container. A small laboratory mill may use balls of 1.2–1.5 cm diameter. Larger mills require balls of an average diameter of about 2.5 cm.

The rate of grinding by the mill is related to the diameter of the container. If the mill rotates too rapidly, centrifugal force will cause the charge to adhere to the container walls and no grinding results.

Large mills must rotate more slowly than small ones and the following table of optimum speeds assists the operator in arranging the milling operation. Slower speeds may be used but the time of milling will be extended since the grinding is achieved by a definite number of rotations of the mill. **Table 3.2** shows the ball mill size and suggested speed of operation.
Colloid mill: A colloid mill essentially consists of two circular plates, one of which is stationary and the other is rotating at a very high speed (1,000 to 20,000 rpm). The clearance between the two plates is generally adjusted to within 0.025 to 0.200 mm. Most colloidal mills are provided with water cooling devices to prevent overheating of the material being dispersed.

The solid powder is first made into a slurry with the required amount of water and dispersing agent and fed into the space near the axis of the mill and is carried outwards between the discs by the centrifugal pressure set up. Besides its use in the preparation of aqueous dispersions of soft materials (e.g., china clay), the colloid mill is also used to wet the powders before ball milling. The powder is made into slurry and then passed through the colloid mill. By this treatment, the material will be wetted properly and after ball milling will produce a satisfactory dispersion.

Dispersing agents: The selection and amount of dispersing agent are determined by the physical properties of the material to be dispersed. The functions of these agents
are to wet the powder, to prevent or reduce frothing and to obviate re-aggregation of the particles. The concentration of the dispersing agent should be maintained at the minimum required to produce the desired effect and need rarely exceed 2% except in special circumstances.

Dispersol F Conc: Dispersol F Conc is a very effective dispersing agent recommended for use in the preparation of aqueous dispersions of the water insoluble solid ingredients used in the various types of latex compounds. By using a sufficient quantity of this dispersing agent, the water insoluble compounding ingredients in powder form can be dispersed in water by an appropriate mechanical milling process, e.g., ball milling. The mechanical action necessary to secure good dispersions depends on the physical nature of the material to be dispersed. Sulfur for example, which is a hard material and occurs in relatively large ultimate particles requires actual grinding in a ball mill for a long period. For materials such as accelerators and zinc oxide, ball milling for a shorter period or colloid mill may be used. When re-aggregation of the ultimate particles is very weak, for example, in the case of good quality china clay, simple mechanical stirring in the presence of Dispersol F Conc will suffice. For resinous materials such as Accinox B, there is a tendancy for it to adhere to things and so the addition of an inert material, such as China clay is necessary to prevent this.

Tables 3.3–3.6 show the formulae and methods for the preparation of the aqueous dispersions of the common compounding ingredients used in latex.

<table>
<thead>
<tr>
<th>Table 3.3 Preparation of sulfur* dispersion (50%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredient</td>
</tr>
<tr>
<td>Sulfur</td>
</tr>
<tr>
<td>Dispersol F Conc</td>
</tr>
<tr>
<td>Distilled water</td>
</tr>
</tbody>
</table>

*Ball milled for 72 hours

<table>
<thead>
<tr>
<th>Table 3.4 Preparation of Accicure ZDC* dispersion (50%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredient</td>
</tr>
<tr>
<td>Accicure ZDC</td>
</tr>
<tr>
<td>Dispersol F Conc</td>
</tr>
<tr>
<td>Distilled water</td>
</tr>
</tbody>
</table>

*Ball milled for 24 hours
### Table 3.5 Preparation of zinc oxide* dispersion (40%)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc oxide</td>
<td>100</td>
</tr>
<tr>
<td>Dispersol F</td>
<td>3.0</td>
</tr>
<tr>
<td>Distilled water</td>
<td>147.0</td>
</tr>
</tbody>
</table>

*Ball milled for 24 hours

### Table 3.6 Preparation of Accinox B* Dispersion (20%)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accinox B</td>
<td>50.0</td>
</tr>
<tr>
<td>China Clay</td>
<td>50.0</td>
</tr>
<tr>
<td>Dispersol F Conc</td>
<td>3.0</td>
</tr>
<tr>
<td>Distilled water</td>
<td>147.0</td>
</tr>
</tbody>
</table>

*Ball milled for 24 hours

### 3.2.2 Evaluation of the Quality of Dispersion

Consistency in quality and stability of the dispersions are highly desirable. Suitable tests should be done to assess the quality of the dispersion before addition to the latex. In doubtful cases it is advisable to carry out a small-scale test also with the compounded latex prepared by using the dispersions under test.

A drop of the dispersion is allowed to fall on the surface of the water taken in a tall glass cylinder. The drop must not fall to the bottom, but should disperse well in the water phase, leaving a cloudy trail.

### 3.3 Preparation of Emulsions

As for dispersions, distilled or softened water should also be used for the preparation of emulsions of the water immiscible liquids, which are used in latex compounds. An emulsion is defined as a system in which a liquid is colloidally dispersed in another liquid. The emulsions for latex use should be of the oil-in-water type, in which the water is the continuous phase and the suspended droplets carry a negative charge.
Equipment used for the preparation of an emulsion consists of a tank and a high speed stirrer. Very fine and stable emulsions can be prepared by a device, which imparts a shearing action, e.g., a colloidal mill or a homogeniser. In an homogeniser the liquid is mixed with the required amounts of water and the emulsifying agent is forced through a fine orifice under high pressure (6.9 MPa to 34 MPa). Thus, liquid mix is subjected to a high shearing force, which breaks down the particles to the required size.

Various synthetic emulsifying agents are available on the market, but for latex use, soaps have been found to be quite satisfactory. Often the addition of the ingredients to the soap solution with stirring will produce a satisfactory emulsion. However, a better and more effective method of emulsification, is to produce the soap in situ during the mixing of the components. In this method, the cationic part of the soap (ammonia, KOH or amine) is dissolved in water and the anionic part (oleic, stearic or rosin acid) is dissolved in the liquid to be emulsified. Soap is formed when these solutions are mixed. Often this technique is modified in that the water solution is added in small amounts to the non-aqueous phase, producing at first a ‘water-in-oil’ emulsion, which undergoes an inversion to an ‘oil-in-water’ emulsion on further addition of the water-solution. Table 3.7 and Table 3.8 give the formulations used for the preparation of liquid paraffin and SP emulsions.

In the formulation in Table 3.7, oleic acid is mixed with liquid paraffin and the mixture added to the water containing the concentrated ammonia solution. The two phases are mixed by agitation and the stability and dispersion of the emulsion is improved by being passed through a homogeniser. A further improvement in quality is obtained by replacing one part of water in the formulation by one part of Vulcastab VL.

In the formulation in Table 3.8, Part A is heated to about 60 °C and then added with high speed stirring to part B also at the same temperature. The stirring is continued until the emulsion attains the required temperature.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid paraffin</td>
<td>50.0</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>2.5</td>
</tr>
<tr>
<td>Concentrated ammonia solution</td>
<td>2.5</td>
</tr>
<tr>
<td>Water</td>
<td>45.0</td>
</tr>
</tbody>
</table>
Table 3.8 Preparation of SP (50% emulsion)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Part A</strong></td>
<td></td>
</tr>
<tr>
<td>SP</td>
<td>50.0</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Part B</strong></td>
<td></td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>1.5</td>
</tr>
<tr>
<td>Water</td>
<td>46.5</td>
</tr>
</tbody>
</table>

References


