

## **Technical Note: NR-Latex & Latex Products**

Rubber Latex is a stable dispersion of polymeric substances in aqueous medium and is essentially a two phase system; 1) Disperse phase (discontinuous phase of rubber molecules) & 2) Dispersion medium (aqueous continuous phase of serum). Basically there are two types of lattices viz. Natural lattices and Synthetic lattices. Natural Rubber Latex (NR Latex) is the most widely used latex for the manufacture of latex based rubber products.

### *Fundamental characteristics of lattices*

Lattices are complex colloid systems containing polymer molecules as major fraction. The polymer may be a homo polymer or co-polymer (random / block / graft). Stereo regularity and the complexity of the polymer molecules (linear / branched / cross linked) is maintained in the latex form. The avg-molecular size, molecular weight & molecular weight distribution of the latex depend on the grade selected. Lattices are rubbery or resinous in nature and the rubber molecules can be cross linked. Lattices can be plasticized or oil extended. Lattices have their own mechanical properties and temperature limits of serviceability. The rubber particle is generally oval having < 5 micron particle size and a typical particle size distribution. The aqueous phase consists of dissolved and suspended matters and knowledge of their concentration, acidic / basic nature (pH) is essential for successful latex compounding. Latex products are subject to degradation and adequate antioxidant protection is necessary.

### *NR-LATEX*

Over 200 species of plants are found to yield NR latex on tapping. Only 'Hevea Brasiliensis' plant is of commercial importance and accounts for 99% of World's NR production. On tapping the Hevea brasiliensis tree, NR-Latex exudes.

### *Composition of field Latex*

:

<u>Material</u>	<u>% By weight</u>
Total solids contents (TSC)	36
Dry rubber contents (DRC)	25-40
Proteins substances	1-1.5
Resinous substances	1-2.5
Ash	Up to 1.0
Sugars	Up to 1.0
Water	Balance

Two surface phases are present in latex viz. air aqueous phase interface (surface free energy of latex) and an aggregate of polymer-aqueous phase (Stability / Change). The manner in which surface-active substances are distributed in the two phases is of great significance for product manufacture.

### *The Dispersed Phase (NR):*

Consists of small (approximately < 5  $\mu$  diameter) polymeric particles dispersed in serum with - ve surface charge (anions). Typical composition of the disperse phase is as follows:

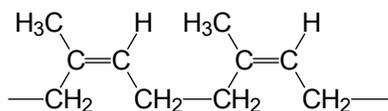


<u>Material</u>	<u>% by weight</u>
Rubber hydrocarbon	86
Water (dispersed in rubber hydrocarbon)	10
Portentous material	1
Lipid substances	3
Trace metals (Mg, K, Cu etc.)	0.05

Density of rubber particles = 0.92 g/cc

Chemical composition : Cis-1, 4 polyisoprene

Chemical structure:



Number avg. mol.wt. : Approx. = 300,000.

Degree of polymerization: Approx. = 5000.

Predominantly a cis configuration (all -CH<sub>3</sub> groups on same side).

Some evidence of presence of oxygen in the form of carbonyl groups, which cause hardening of NR on, prolonged storage. Also contains some peroxides, which form redox systems with other constituents causing cross linking and chain scission.

Protein content is in the form of adsorbed layer, which surrounds the external surface of NR particles (protein is  $\alpha$ -globulin dissolved in the serum). Protein determines the charge (the electrophoresis characterization and coacervation behavior).

Lipids comprise of sterols and sterol esters (approx.0.4%), wax and phospholipids adsorbed on rubber particles through which the proteins are anchored on rubber particles and are dissolved in the rubber hydrocarbon.

The 'gel' content (solvent insoluble rubber) steadily increases, as latex is stored. (After 2 to 3 months the gel content in toluene is as high as 50% (process similar to storage hardening of NR, which takes its Mooney viscosity to 80-100).

#### The Aqueous Phase:

The aqueous phase is a dilute solution of density 1.02 g/cc & contains dissolved chemicals such as:

Carbohydrates = approx. 1% (e.g.) methyl inositol)

Proteins = approx. 1% (  $\alpha$ -globulin, mol.wt. 200,000; Hevein, mol.wt. 10,000 & few others)

Amino acids = approx 0.1% (glycine, tyrosin, & 12 others)

Free nitrogenous bases, e.g. methylamine

Organic acids (other than amino acids)

Metal ions, (K, Mg, Fe, Na, Cu etc.)

Complex enzymes



The predominant CATION present in NR latex is 'Ammonium (NH<sub>4</sub><sup>+</sup>)' although serum also contains significant (25-35%) of Potassium cations. Following table summarizes avg. anion concentrations found in the serum of matured NR latex.

Anions %	HA-Latex	LA-TZ Latex
Carbonate	22.25	22.0
Acetate	12.81	8.74
Malate	9.28	10.14
Succinate	5.45	2.03
Citrate	5.04	6.94
Formate	4.67	3.13
α-glycerophosphate	2.81	4.24
Glucose-t-phosphate	2.24	0.31
Phosphate	2.01	2.22
Oxalate	1.16	1.22
Chloride	1.10	2.01
Sulphate	0.58	0.03
Hydroxide	0.51	0.14
Propionate	-	5.34

Adsorbed non-rubber materials:

Protein-lipid complexes: Lipids hydrolyze releasing fatty acid soaps which improve the mechanical stability of NR-latex.

High proportions of phospholipids & Furanoid acid representing total fatty acids play role in latex stabilization.

Anions of various types behave differently towards zinc-ammine ions, which are major cause of NR latex destabilization.

NR-Latex Properties:

- Whitish fluid, Density = 0.975-0.980
- pH = 6.5-7.0
- Surface free energy = 40-45 ergs/cm<sup>2</sup>
- Rubber particles = 35 % by weight
- Aqueous phase = 55 % by weight
- Lutoid phase = 10 % by weight.
- Rubber phase = 25 – 35 % by weight (typical = 33 %).
- Difference between TSC and DRC = 3 %.
- Rubber particle size between 200-2000<sup>o</sup>A. (10 A<sup>o</sup> = 1mμ = 1/10<sup>3</sup> μ = 1/10<sup>7</sup>cm),
- Rubber particles are negatively (- ve) charged i.e. Anions.

Particle Size Distribution:

Wide range of diameter: 0.01 μ to 5.0 μ (Avg.0.25-0.8 μ)

Particle size distribution is fairly consistent,

Synthetic rubber lattices have much lower particle size than NR-latex.



### Viscosity:

Latex containing more than 25% by volume of disperse phase is a non-Newtonian fluid. Hence the measured viscosity is dependant on the rate of shear rates, e.g.

Brookfield viscosity at 6 rpm :  $\eta = 180$  mPa.s

Brookfield viscosity at 60 rpm :  $\eta = 87.5$  mPa.s

$\eta_{6/60} = 2.1$

### Preservation of NR latex:

#### High Ammonia NR Latex:

NR-Latex coagulates within few hours due to development of acidity through micro-organisms when the pH falls to around 5.0. Ammonia at 0.7-1.0 % is required for long term preservation. Ammonia also acts as a bactericide and sequestering agent for  $Mg^{++}$  and  $PO_4^{---}$  ions.

[The disadvantages of ammonia are that: It has a strong odor, It is expensive, Ammonia preserved latex undergoes marked thickening when compounded with ZnO, It interferes with the gelation of latex foam compound by Sodium Silicofluoride (SSF). (Excess ammonia has to be driven off before the latex is used for compounding.)]

#### Low Ammonia NR-Latex:

- Zinc Dialkyl dithiocarbamates (ZDMC / ZDEC) at 0.1 – 0.2 % along with 0.2 % ammonia and 0.2 % lauric acid enhance the stability of NR-Latex to the level of 0.7% ammonia preserved latex without any significant effect on vulcanization. *However, the latex may give deposits that discolor badly on ageing (copper staining).*
- Boric acid at 0.2% with 0.2%ammonia & 0.05% lauric acid is most popular LA- Preservative system. (Precaution: 0.1% boric acid increases the KOH number by 0.14 units). The deposits are free from discoloration and boric acid is cheap, harmless to human beings, easy to handle and can be estimated accurately. *However the unvulcanized deposits tend to soften faster.*
- Sodium Pentachlorophenate at 0.2% with 0.2% ammonia is used as a stabilizer *but not popular due to toxicity problems associated with pentachlorothiophenol.*

### Creaming of Latex Concentrates:

The density of rubber (= 0.92 g/cc) dispersed in latex is **less than** the density of serum (= 1.02 g/cc) hence the rubber particles move upwards. This '**creaming**' effect is prominent if NR latex is left undisturbed for more than a week.

### Filterability:

Filterability is defined as amount of latex, which will pass through a filter under standard conditions before clogging takes place. Creamed latex gives greater filterability than centrifuged latex .SR Lattices have high filterability due to smaller particle size.

NR Latex Grades:

<u>NR latex Specification ASTM D 1076</u>	<u>Type 1</u>	<u>Type 2</u>	<u>Type 3</u>
Total Solids contents (TSC), min, %	61.5	66.0	61.5
Dry Rubber Content (DRC), min, %	60.0	64.0	60.0
TSC – DRC, max, %	2.0	2.0	2.0
Total alkalinity as ammonia, as % on latex,	0.60 min	0.55 min	0.29 max
Sludge content, max, %	0.10	0.10	0.10
Coagulum content, max, %	0.05	0.05	0.05
KOH number, max,	0.80	0.80	0.80
Mechanical Stability, min, sec	650	650	650
Copper content, max, %	0.0008	0.0008	0.0008
Manganese content, max, %	0.0008	0.0008	0.0008
Color on visual inspection	A	A	A
Odor after neutralization with boric acid	B	B	B
Note: A=No pronounced blue or gray, B=No putrefactive odor, Type 1=Centrifuged NR latex preserved with ammonia, Type 2= Creamed NR latex preserved with ammonia, Type 3= Centrifuged NR latex preserved with ammonia and secondary preservatives.			

Destabilization of latex or Gelation:

NR latex may be destabilized by acidification, addition of salts of polyvalent metals, higher concentration of any salt, dehydration, mechanical agitation or freezing. Important methods of destabilization are those, which produce uniform destabilization (gelation) of a three-dimensional aggregate of rubber particles. The aqueous phase is retained in the interstices of the gel. NR latex has excellent gel strength (hence excellent film forming ability), most suitable for manufacture of dipped goods and foamed products. Gels do not have constant composition or structure and film shrinks due to exudation of aqueous phase. Excessive stabilization results in weaker gels and slower rate of gelation.

Three methods of Gelation:

- Organic acid/acids or acid liberating substances.
- Use of salts of multivalent cations.
- Application of heat.

Gelation By Acids:

NR latex particles are stabilized due to adsorbed carboxylic anions (from fatty acid soaps and protein molecules on the surface). This net –ve charge produces repulsive forces and ensures absence of aggregation. Reduction in pH by the addition of acids reduces ionization of adsorbed anions and decreases the repulsive forces due to which gelation takes place.

Gelation by Salts:

Calcium nitrate is widely used in the dipping industry to produce gels of compounded latex on the 'formers'. Calcium ions form insoluble salts with all fatty acid soaps & solutions of proteins and destabilize the latex. The Calcium ions also effect high concentration of ions which reduce the colloidal stability of



compounded latex by creating a electrical double layer around rubber particles and thus reducing the strength of –ve electrical potential.

Zinc ions also produce effect similar to Calcium ions. However, Zinc ions react with ammonia to form complex ammine cations that form insoluble salts with fatty acid soaps, but do not react with proteins thus, producing partial destabilization effect.

#### Heat Sensitized gelation:

Latex compounds are specially formulated to give rapid gelation when the temperature is increased (with room temperature stability unaffected). The zinc oxide-ammonium salt process (ZOA) uses the ability of ammonium salts to increase the solubility of Zinc oxide in aqueous ammonia solutions and thus, enhance the effect of Zinc ions. The addition of an ammonium salt also increases the ionic strength of the aqueous phase and contributes to destabilization. The ZOA process is truly not heat sensitive since the gelation occurs at room temperature within a short time. However, heat accelerates the process.

#### Film formation and structure:

Formation of film involves immobilization of free-moving polymer particles when brought into contact. In most of latex-goods manufacturing processes the contact between polymer particles is achieved by 'gelation' process (result of drop in pH as the volatile ammonia stabilizer during the initial stages of drying). Note that if the pH is maintained by using a fixed alkali stabilizer like KOH this process will not proceed. Gelation does not affect the rate of drying of the film or any other characteristics. The film is leached before drying to remove water-soluble serum residues, residual coacervant and other surface-active substances. This improves the feel of the film, eliminates porosity defects and resists water absorption and ageing. Warm / hot water is used for leaching (use of water soluble compounding ingredients e.g. water soluble accelerators is avoided where leaching process is involved). The film thickness per dip varies from 0.1 mm to 0.2 mm depending on the viscosity of the latex compound. Multi-dip systems are used to produce a product of desired film thickness.

#### Chemically Modified Lattices

##### Prevulcanized NR Latex:

PV NR latex is a chemically modified NR latex, which on drying gives a vulcanized film. PV NR Latex is produced in the rubber plantation factory using field latex or concentrates or in the consumer's factory. NR latex compounds containing ZDEC or ZDBC ultra fast accelerators usually achieve some degree of pre-vulcanization during the process of 'maturation' in the dispersed rubber phase. Commercially produced PV NR latex is prepared as follows:

<u>Compounding Ingredients</u>	<u>Dry (pbw)</u>	<u>Wet (pbw)</u>
NR Latex (60 %, Ammonia preserved)	100	167
50 % ZnO dispersion	1	2
50 % ZDEC dispersion	1	2
50 % Sulphur dispersion	2	4
10 % KOH Solution	0.3	3
10 % Stabilizer Solution (Sodium Caseinate)	0.2	2

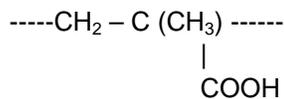


The latex is contained in a stirred and jacketed mixing vessel and the compounding ingredients are added. The vessel is heated by passing hot water through the jacket. After heating for 3 – 5 hr at 50 – 60°C or when the QC tests show that the desired degree of cross linking has been achieved; the latex compound is cooled to room temperature. It is then filtered or clarified centrifugally before use.

The degree of cross-linking is determined by solvent swelling, combined sulphur analysis or by assessment of tensile properties. PV latex is popular in medium/small sector dipped goods industry since further compounding of latex is not necessary or is limited to incorporation of desired pigments (e.g. manufacture of toy-balloons, medical goods, feeding bottle teats, etc). The cross linking can be achieved by reaction with sulphur, sulphur donors (e.g. TMTD, DTDM, TETD) or by gamma radiation. The compounding formulations can vary depending on end applications. If ZDEC / ZDBC is present, ZnO is not necessary. (ZnO reduces the film clarity and may be substituted by ZnCO<sub>3</sub> to improve the same). For peroxide cross-linking, tert-butyl hydro peroxide and tetra ethylene pentamine are used. Maximum film clarity is obtained by using ZDBC alone. The cross-links found in Prevulcanized latex are predominantly polysulphidic (except for Sulfurless /Sulfur donor cures).

#### Heveaplus MG graft polymers:

Grafted side chains of polymethyl-methacrylate on NR molecule



The grades: Polymethyl-methacrylate contents 15 % (MG<sub>15</sub>), 30 % (MG<sub>30</sub>) & 49 % (MG<sub>49</sub>).

The film forming ability of MG lattices decreases as polymethyl methacrylate content increases.

This latex can be blended with unmodified latex in desired proportions. Such blends provide considerable increase in modulus and retention of tensile strength & tear resistance. Film forming properties can be improved if methylacrylate is partially replaced by butyl methacrylate in the grafting reaction.

#### Hydroxyl amine modified latex (HRH latex):

On storage, the viscosity of the rubber in latex concentrates increases due to the molecular cross-linking process. The rate of storage hardening is faster during the first 20 – 30 days (and beyond 100 days the process is completed). When hydroxylamine is added at 0.15 phr at the latex production stage; the hardening effect is inhibited. The vulcanizates show slightly low modulus (thus for latex foam a lower volume shrinkage). Other properties are largely unchanged. This latex is useful for production of latex-foam and latex adhesives (for quick grab strength) used in footwear production.

#### Deproteinized latex:

Latex concentrate contains about 2 % by weight 'protein' of which 50 % is associated with the surface of particles. The protein is largely retained on the surface of the rubber product causing increase in their water absorption and skin allergy on repeated contact, which has been a serious problem with sensitive individuals. Re-centrifuging followed by latex dilution removes high proportions of protein content from the serum. Rest can be removed by treatment with a proteolytic enzyme (e.g. 0.1 phr of Novo SP88 – 24 h at 40°C) or protein displacement by a surfactant (e.g. Sodium dodecyl sulfate). The treated latex has to be



diluted and re-centrifuged. Deproteinized latex produces film containing 0.02 – 0.03 % Nitrogen and is used for dipped goods requiring special electrical properties.

#### Latex Compounding Ingredients:

The conversion of NR-Latex into finished products is accomplished using different processes. The processes are based on the criteria of minimum energy consumption during various stages. (Higher energy consumption during drying has been a major concern).

In all the processes, a stable colloidal system is maintained for a desired time after which the system is made unstable to convert the same to a solid product. Maintaining the balance between too much and too little stability is the major challenge.

The latex compounds contain four or more distinct disperse phases and are highly polydisperse with several different surface-active agents. The aqueous phase of high ionic strength gives the NR-latex compounds a relatively low colloid stability but facilitate conversion to solid products. For dipped goods, the latex compounds used must produce continuous films on the former and maintain film integrity during drying and vulcanizing stage.

#### Latex compounding ingredients:

1. Vulcanizing agents:	Sulphur, Sulfur donors & others.
2. Accelerators:	Dithiocarbamates, Thiazoles, Thiurams, Xanthates
3. Antioxidants:	Amine datives, Phenolic derivatives.
4. Fillers & pigments:	Inorganic, Organic.
5. Surface-active agents:	Anionic, Cationic, Amphoteric, Nonionogenic.
6. Viscosity modifiers:	Plant hydrocolloids, Proteins, Polyvinyl alcohols, Cellulose derivatives, Starches, Polyacrylates, Carboxylate polymers, Colloid clays, etc.)
7. Other ingredients:	Mineral oils, Waxes, Resins, Antifoaming agents, Antiwebbing agents, corrosion inhibitors, etc.

#### 1. Vulcanizing Agents:

##### Sulfur:

Sulfur is the universal vulcanizing agent for all diene lattices. Fine particle size Rubber grade sulfur powder is used. Sulfur dosage 0.3 to 2.5 phr on dry basis in the form of 50% dispersion in water.

The dosage of sulfur depends on the rate and state of cure desired and the amounts of other compounding ingredients used. For the best heat resistant vulcanizates the sulfur dosages are kept at minimum and consistent with the 'modulus' requirements.

With low sulfur contents, very fast accelerator combinations are necessary to achieve sufficiently rapid rate of cure.

Sulfur Donors:

Used where a 'sulfur less' vulcanizate is required for optimum heat resistance or for use in contact with metals or for excellent resistance to copper catalyzed oxidative degradation. Vulcanization by TMTD and Zinc Oxide (without sulfur) is slow at 100°C. Thiourea activates TMTD vulcanization at 100°C when used at TMTD: Thiourea ratio = 1:2 pbw. Excess of either would produce a retarding effect. Use of sulfur donors other than TMTD is very rare.

TMTD cured NR-Latex vulcanizates give excellent heat and ageing resistance, which is further enhanced by the conventional antioxidants and dithiocarbamate accelerators. Sulfenamide accelerators e.g. CBS are also activated by Thiourea to produce acceptable cure rates without addition of sulfur and give vulcanizates which are not stained by copper. Butyl xantogen disulphide at 6.0 phr and accelerator ZDEC at 4.0 phr with 5.0 phr ZnO are used to vulcanize NR-Latex films in the absence of additional sulphur.

C) Other curatives:

Organic peroxides and hydro peroxides may be used to vulcanize NR-Latex products with higher translucency.

Metal Oxide cures e.g. Zinc Oxide are used for polychloroprene latex.

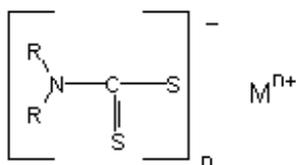
2. ACCELERATORS

Wide range of accelerators is available. Only those with highest activity are of importance for latex products since the vulcanization is carried out at low temperatures of 90-120°C in aqueous medium.

Important classes are Metallic dithiocarbamates.

Thiazoles and Thiurams are used as secondary accelerators with dithiocarbamates for obtaining modified vulcanizate properties. The Metal xanthates also find limited applications.

Specialized accelerators such as DPG and Thiocarbanilide find applications in latex compounds based on polychloroprene latex.

Dithiocarbamates:

The CATION is a Metal ion or a derivative of Ammonium ion. Amine and Alkali metal salts are water-soluble. Metal salts e.g. Zn salts of dialkyl dithiocarbamic acid are not water-soluble. ZnDEC is the most widely used accelerator for latex compounding. Amongst others are (ZnDMC), (ZnDBC), Zinc pentamethylene dithiocarbamate (ZnPDCC).

Sodium diethyl dithiocarbamate (Na - DEC), Sodium dibutyl dithiocarbamate (NaDBC), Sodium pentamethylene dithiocarbamate (NaPDCC) and Piperidinium pentamethylene dithiocarbamate (PPDC) are water-soluble accelerators.

The cure time and temperature have marked effect on the tensile strength and 600% modulus of NR-Latex vulcanizates. *The optimum values are obtained by curing for 20 minutes in hot air at 100°C.*



A wide range of ZnO, Sulphur and Accelerator dosages are used e.g.

ZnO:	0.5 to 5.0 phr
Sulfur:	1.0 to 1.5 phr
Dithiocarbamate Accelerator:	0.5 to 1.5 phr.

Increasing the proportion of any one of the components increases the rate and state of cure without any significant change in the value of % elongation at break. Although ZnO is not necessary when Zn-diethyl dithiocarbamates are used as accelerators, the presence of ZnO improves the tensile properties and reversion resistance of the vulcanizates.

When transparency is desired for the finished product, ZnO is used at 0.5 phr max. ZnCO<sub>3</sub> or Zn-Stearate are difficult to disperse but when used, the latex compounds are less prone to thickening.

ZnDMC is slower than ZnDEC and ZnDBC is faster than ZnDEC. ZnPDC is highly active in NR-latex Compounds but not necessarily in SR-latex compounds.

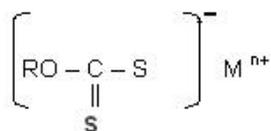
Zn-dialkyl dithiocarbamates cause gradual thickening of ammonia preserved latex under normal storage conditions due to slow liberation of zinc ions. Dithiocarbamates with no Zn contents do not cause any thickening.

Water-soluble dithiocarbamates are easier to add to latex compounds but also are less active. Water-insoluble dithiocarbamates have to be used if water leaching of the product is necessary. (Although water soluble accelerators are not easily leached in hot water wash.)

With only 0.5 phr of water-soluble dithiocarbamates, the NR-Latex compound films cure rapidly at 70°C. Increase in accelerator dosages does not influence the cure rate; however, the state of cure increases (higher modulus & lower permanent set).

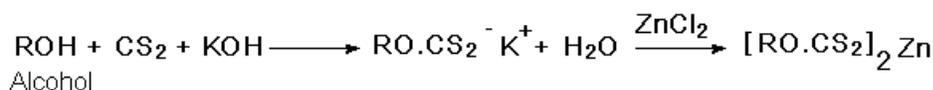
Zinc dibenzyl dithiocarbamate (ZnBzDC) is used as nitrosamine free Dithiocarbamate accelerator for Latex compounds. ZnBzDC produces high stability latex compounds in the presence of ammonia. If Ammonia is removed (with formaldehyde or air blowing) then NR-latex prevulcanization is possible with a combination of ZnBzDC & ZnMBT at elevated temperatures. ZnBzDC is slower curing accelerator as compared to ZnDEC or ZnDBC.

### Xanthates:



Xanthates are very reactive and very labile accelerators. These are active even at room temperature. Unstable and have bad odor (CS<sub>2</sub> evolved during decomposition). Alkali metal xanthates are water soluble while heavy metal salts are insoluble. Only Na and Zn salts are commonly used.

Xanthates can also be formed in-situ using desired alcohol, CS<sub>2</sub> and KOH.

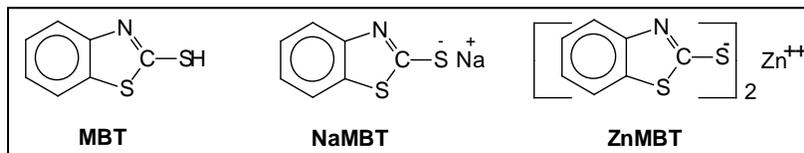




Di isopropyl xanthogen polysulphide an FDA approved xanthate is used as accelerator in industrial glove manufacture based on carboxylated NBR latex at 0.75 to 1.0 phr with 0.3 – 0.5 phr sulphur and 3.0 phr ZnO. Xanthates are also used as sulphur donors with TB<sub>2</sub>TD, MBTS. For PV latex xanthates are used at 0.5 – 0.75 phr with SDBC as a booster at 0.1 – 0.12 phr and sulphur at 1.0 – 1.5 phr.

### Thiazoles:

Function as secondary accelerators for dithiocarbamates giving vulcanizates of higher modulus. Commonly used thiazole accelerators are:



Dosage of thiazoles can be varied over wide limits. Typical combinations for :

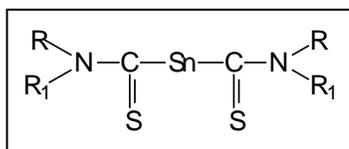
<u>NR – Latex</u>	<u>SBR- Latex</u>
ZDC – 1.0 phr	ZDC – 0.5 phr
ZMBT – 0.25 – 0.5 phr,	ZMBT – 1.0 phr

MBT itself is slightly acidic and neutralizes alkali (ammonia or KOH added as latex stabilizer) and gradually causes latex thickening or even coagulation! Mechanical stability of latex compound is considerably reduced. MBT is useful in foam compounds to reduce the pH of gelation by reacting with alkali (SSF gelation). NaMBT has a tendency to enhance the latex compound stability to undesirable extent because of its high pH (over 11.0).

ZMBT is the most suitable accelerator for latex compounding and is insoluble in water (and latex serum). It has almost no effect on latex compound viscosity. Partial replacement of ZDEC by ZMBT has different effects depending upon the dosages.

Replacement of 25% to 50% ZDEC by ZMBT results in very high modulus without any extension of cure cycle. While the tensile strength is marginally affected, the EB% is reduced 100% from its original value. The combination of ZDC and ZMBT is more 'peaky' than ZDEC alone. When combination of ZDC – 0.75 + ZMBT – 0.25 phr is used; the modulus is sensitive to over cure and under cure.

### Thiurams:



Not active enough in latex compounds and hence used as secondary accelerators with Dithiocarbamates (e.g. ZDEC). When n >1, the thiurams act as sulfur donors and 'sulfur less' cures are possible (thus TMTM is not a sulfur donor).



Thiurams most commonly used are TMTM, TMTD, TETD, and DPTD, DPTT (Di pentamethylene disulfide and tetra sulfide).

All thiurams are insoluble in water. Incorporating sulfur-bearing compound such as Thiourea markedly increases accelerating efficiency of thiurams including TMTM. The combination of TMTD and ethylene thiourea (ETU) is faster than ZDEC (with or without Thiourea). Tetra butyl thiuram disulfide is used in the latex products requiring heat and copper staining resistance with following recommended dosages.

Accelerator /Sulfur	Heat Resistance, pbw (dry)	Copper Staining Resistance Pbw (dry)
TBuTD	1.0	1.0
DTDM	-	1.5
ZMBT	0.6	0.6
DPTT	1.5	-
Heptaldehyde aniline reaction product	0.15	0.15
Sulfur	0.2	0.2

DPTT finds applications in heat resistant latex threads based on sulfur less cure with good color and heat ageing properties. The cure system and antioxidant dosages recommended are:

DPTT	2.0 phr (dry)
ZMBT	1.5 phr
ZDBC	0.5 phr
Phenolic antioxidant	1.5 phr

### 3. ANTIOXIDANTS

Antioxidants act as protective agents in latex compounds depending on the nature of the product and the service conditions envisaged. Latex vulcanizates compounded using about 1.0 phr of Zn-dialkyl dithiocarbamate accelerators may not need further antioxidant protection unless the products are very thin or the service conditions are very severe.

The incorporation of many antioxidants in latex compound is often difficult. The choice of antioxidant is particularly important where the product will be subjected to detergent washing (e.g. gloves).

As received from the latex suppliers, NR latex and many synthetic lattices contain substances, which function as polymer antioxidants. Amine derivatives (e.g. TMQ, PBNA) are generally more powerful antioxidants against the effect of heat, light and trace metals but these tend to cause discoloration during rubber product ageing. However, TMQ can be used for dark / black colored products. Phenolic antioxidants are generally weaker against degradative forces but do not cause any discoloration and hence widely used in all latex compounds.

The type and dosages of various phenolic antioxidants used for latex compounding may vary depending upon the end rubber product/application.

The phenolic antioxidants are classified as:



Monophenols: e.g. BHT, Styrenated Phenol, Alkylated hindered phenols.

Bisphenols: e.g. A/O 2246 – 2,2' Methylene bis (4 methyl-6-t butyl phenol),  
Polybutylated bis phenols, thio bis phenols.

Polyphenols: e.g. Wingstay L – Butylated reaction product of p-cresol and dicyclopentadiene,  
Irganox 1010 – Tetrakis (methylene 3-(3,5-dibutyl-4 hydroxyphenyl) propionate) methane.

Latex foam products/carpet backings require antioxidants (at 1.0/1.5 phr dosages). This is because the product demands longer service life (10 – 15 years), retention of cushioning effect (to ensure long life for fibers), non staining - but can be slightly discoloring characteristics (since dark/black colored finished products), resistance to dyes (metal ions) and detergents (strong oxidizing agents), resistant to UV light and heat (longer drying conditions at high temperatures etc.)

Latex dipped goods are thin walled articles and hence need adequate protection.

Latex threads require highly non-staining and persistent antioxidants along with resistance to detergents.

Recommended antioxidant dosages for various applications are as follows:

Latex foam products: 0.5 – 1.0 phr Polyphenol for non staining applications

0.5 phr TMQ for dark colored products

Dipped goods: 0.5 – 1.0 phr Polyphenol

1.0– 2.0 phr Styrenated phenol

0.5 phr TMQ for dark colored products

Rubber threads: 0.5 – 1.0 phr Polyphenol

Other goods: 1.0 phr Styrenated phenol

The lifetime and effectiveness of the antioxidants can be greatly enhanced by the addition of an UV absorber such as benzothiazole derivative (Tinuvin P) or hydroxybenzophenones, which are colorless.

Conventional amine or phenolic antioxidants are used with sodium-EDTA salt for the protection of Unvulcanized latex compounds. The Na-EDTA salt acts as a metal ion-chelating agent for copper and manganese ions.

#### 4. FILLERS AND PIGMENTS:

Inorganic fillers are added to reduce cost, stiffen the products and influence the compound flow behavior.

The typical reinforcement effects of fillers as observed in dry rubber compounds are not observed in latex compounds. For example, carbon blacks or fine particle size clays do not enhance the tensile strength or tear strength since there is no mastication step involved in latex compounds and thus no free radicals are created to interact with reactive sites on the fillers.

Kaolinite clays of fine particle size are used in the form of dispersion in water. It is necessary to check the pH of aqueous clay slurries is 7.0 – 8.0. Any acidity may be corrected by addition of dilute KOH solution. Clay loadings from 30 – 100 phr produce soft vulcanizates with higher tension set. Loadings between 100 – 400 phr produce very hard products without any rubbery properties, but only increase in modulus values.

Calcium carbonates (whiting, chalks etc.) give poor quality products with marked tendency to discoloration. The water-soluble salts in calcium carbonates (e.g. chlorides, sulphate s etc.) tend to reduce latex stability. To avoid this small amount of sodium carbonate is added to the whiting slurry prior to addition to latex to ensure **that the pH is alkaline.**



Rutile titanium dioxide - white inorganic pigment in latex compound. Anatase can also be used. Usually 5 phr is used on dry basis and incorporated as 50% or 30% dispersion slurry. For latex paints even over 100 phr loadings may be used.

Lithophone (a mixture of zinc sulphide and barium sulphate) is also used as a cheap alternative for titanium dioxide.

White pigments are used to impart whiteness and to provide white background for pastel shades. Blanc fixe (Ppt. Barium Sulphate) filler is used to get smooth and strong deposits of white color on the products. However, it causes loss of extensibility and elongation and sedimentation.

Carbon black is sometimes used as a black pigment. Care has to be taken to adjust the pH of the slurry towards alkalinity.

Organic fillers like high styrene resins enhance the stiffness and strength of the deposits based on latex compounds. There is a progressive increase in the modulus values of latex compounds without much loss in elongation at break when high styrene resins are used. These resin lattices are available for blending with NR latex and the proportions used are in the range of 10 – 25 phr.

Lignin – a cheap by-product of paper making industry is soluble in NaOH solution and can be added into latex as an organic filler.

#### 5. SURFACE ACTIVE AGENTS:

Surface-active agents or surfactants are the chemicals; when present at low concentration in a system, have the property of adsorbing onto the surface or interfaces of a system and altering the surface or interfacial free energy to a marked degree.

The term surface denotes an interface where one phase is a gas (usually air). The interfacial free energy is the minimum amount of work required to be done to create that interface. The molecules at a surface have higher potential energies than those in the interior. This is because they interact more strongly with the molecules in the interior of the substance than they do with the widely spaced gas molecules above it. Work is therefore required to be done to bring a molecule from the interior to the surface.

The surfactants usually act to reduce the interfacial free energy by expanding the interfaces significantly so that the energy/unit area is reduced and the two phases merge easily. The dosages of surface-active agents are very small, e.g. ppm level to 1%.

Utilization of surfactants is more of an art than a science. Surface-active agents have a characteristic (called amphipathic) structure consisting of a structural group that has a very little attraction for the solvent (lyophobic group) together with a group that has a strong attraction for the solvent (lyophilic group).

When a surface-active agent is dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent causes a distortion of the solvent-liquid structure by increasing the free energy of the system.

In an aqueous solution of a surfactant, the distortion of the water by the lyophobic (hydrophobic) group of the surfactant and the resulting increase in the free energy of the system when it is dissolved means that less work is needed to bring a surfactant molecule than a water molecule to the surface. The surfactant therefore concentrates at the surface and the hydrophilic group prevents the surfactant from being



expelled out from the water, resulting in the reduction of the surface tension and orientation of the molecule at the surface with its hydrophilic group in aqueous phase and hydrophobic group away from it.

The chemical structures of groups suitable as lyophilic or lyophobic portions of a surfactant molecule depend on the nature of the solvent. For surface activity in a particular system, the surfactant molecule must have a chemical structure that is amphipathic in that solvent under the conditions of use.

The hydrophobic group is usually a long-chain hydrocarbon residue. The hydrophilic group is an ionic or highly polar group.

Although surfactants are sometimes classified as wetting agents/dispersing agents/dispersion stabilizers/emulsifiers/foam promoters/foam stabilizers etc., this classification has disadvantages that the groups are not mutually exclusive!. (Not all wetting agents are good dispersing agents and some may flocculate aqueous dispersion of fine powders!).

The classification of surfactants by their chemical nature.

Anionic surfactants	The surface active portion of the molecule bears a -ve charge e.g. $\begin{array}{c} \text{O} \\    \\ \text{R} - \text{C} - \text{O}^- \cdot \text{Na}^+ \end{array}$ (A soap) or $\text{RC}_6\text{H}_4\text{SO}_3^- \cdot \text{Na}^+$ (Alkyl benzene sulfonate)
Cationic Surfactants	The surface active portion of the molecule bears a +ve charge e.g. $\text{RNH}_3^+ \cdot \text{Cl}^-$ (Salt of long-chain amine) or $\text{RN}(\text{CH}_3)_3^+ \cdot \text{Cl}^-$ (Quaternary ammonium chloride)
Zwitter ionic Surfactants	Both +ve and -ve charges may be present in the surface active portion. e.g. $\text{RNH}_2\text{CH}_2^+ \cdot \text{COO}^-$ (Long chain amino acid) or $\text{RN}(\text{CH}_3)_2\text{CH}_2\text{CH}_2^+ \cdot \text{SO}_3^-$ (Sulfobetaine)
Non-ionic Surfactants	The surface active portion bears no apparent ionic charge, e.g. $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (mono-glyceride) or long-chain fatty acid), or $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (Polyoxyethylenated alkyl phenol)

The nature of hydrophilic group is usually different for different molecules whereas hydrophobic groups are usually of similar nature. The hydrophobic groups include:

- Straight-chain long alkyl groups ( $\text{C}_8 - \text{C}_{20}$ )
- Branched-chain long alkyl groups ( $\text{C}_8 - \text{H}_{20}$ )
- Long-chain alkyl benzene residues ( $\text{C}_8 - \text{H}_{15}$ )
- Alkyl naphthalene residues ( $\text{C}_3$  and greater length alkyl groups)
- Rosin derivatives
- High molecular weight propylene oxide polymers (polyoxypropylene glycol derivatives)
- Long chain perfluoroalkyl groups
- Polysiloxane groups

Selection of a surfactant for a particular system requires knowledge of:

The characteristic features of currently available surfactants (physical and chemical properties).  
The interfacial phenomena involved in the job to be done and the role of surfactant.  
The surface chemical properties of the surfactant and the relationship of the surfactant structure to its behavior in various interfacial phenomena.

PROPERTIES AND USES OF COMMERCIALY AVAILABLE SURFACTANTS

Anionic Surface-active Agents

The surface activity is attributed to an anion

e.g. Sodium Stearate:  $[C_{17}H_{35}CO_2]^- Na^+$

The anion is  $[C_{17}H_{35}CO_2]^-$

The mostly used anionic surface active agents are carboxylates, sulphonates and sulphates.

Carboxylates ( $R.CO_2^-$ )

R is long chain aliphatic hydrocarbon (e.g. Stearate, Oleate) or complex hydrocarbon ring system (e.g. Rosin acid soaps). Always the R-group is the non-polar and hydrophobic component of the anion while the ionized carboxylates group is the polar hydrophilic component.

These are sensitive to acids and to dissolved heavy metal ions, which destroy their surface activity. The important members of carboxylates have odd number of carbon atoms in the alkyl group (e.g. dodecanates C=12, stearates C=17, palmitates C=15 etc.)

The oleates are very powerful surface-active agents and emulsifiers for oils and also as foam promoters. The oleates are thus not used as general dispersion agents as the foam generated during ball milling is so much as to interfere seriously with the efficiency of the grinding process.

As far as the nature of R group is concerned, increasing the length of hydrocarbon chain decreases its stability, whereas introduction of unsaturation and the substitution of hydroxyl group increase the solubility. Potassium soaps are more soluble than sodium soaps. Rosin (wood rosin) dissolves in strong alkalis to give rosin soaps or resinates from which heavy metal rosin-soaps are precipitated which contain 90% resin acids and 10% non acidic material. These are used as emulsifiers for most SR lattices production.

Sulphonates (Active ion:  $R.SO_3^-$ )

In these anionic surface-active agents group, the active ion is  $R.SO_3^-$ , where R is long-chain aliphatic hydrocarbon radical or an aromatic nucleus. Sulphonates are very less sensitive to acids and heavy metal ions hence the surface activity is retained over a very wide range of pH and metal ion concentration.

The alkyl-aryl sulphonates increase the hydrophobic character of the non-polar part of the anion. These are very powerful wetting agents and do not promote foam formation. These are mostly used for the preparation of dispersions of insoluble powder along with efficient stabilizers.



C3 or C4 alkyl groups achieve the optimum wetting. Many commercially available wetting agents are derivatives of  $\beta$ -naphthalene sulphonic acid, e.g. sodium di isopropyl naphthalene sulphonate, sodium dibutyl naphthalene sulphonate, sodium naphthalene formaldehyde sulphonate (Dispersol L and LN, Belloid TD). Fatty acid ester and amide sulphonates, e.g. Vulcastab LS (sodium salt of ester sulphonic acid) are strong wetting agents and dispersion stabilizers.

*Sulphates*  $(R.SO_4)^-$  or  $(R.SO_3)^-$

These chemicals include sodium dodecyl (or laurel) sulphate, sodium hexadecyl sulphate, which are strongly surface-active dispersing agents and dispersion stabilizers and are more water-soluble.

#### Inorganic Polysulphates

The alkali polyphosphates (e.g. tetra sodium pyrosulphate) in addition to their ability to function as dispersing agents, they are very good sequestering agents and hence can be used with hard water also.

#### *Cationic Surface Active Agents*

Surface activity is due to cation. The chemicals where cation is derived from the ammonium ion by replacement of one or more hydrogen atoms with organic molecules (e.g. salts of primary/secondary/tertiary amines and those which are quaternary ammonium salts).

These are used as colloidal electrolytes for cationic synthetic lattices and as foam stabilizers where foaming has been done using cationic soaps.

#### *Amphoteric Surface Active Agents*

In these surface-active agents, the surface active component is either a dipolar ion or either anion or cation according to the prevailing conditions of pH. Most used members of this group are water soluble proteins but these are very mild surface active agents and used only as stabilizers.

#### *Non Ionic Surface Active Agents* $R[(CH_2.CH_2.O)_nH]_m$

These groups of chemicals do not produce ions under normal conditions. These are condensation products of ethylene oxide with fatty acids, fatty alcohols or phenols. R is a hydrophobic radical derived from fatty acid and polyethenoxy chains provide the hydrophilic component. Because of wide variation in chain length, these condensates are specified by molar ratio of ethylene oxide to hydrophobic material.

These are excellent emulsifiers (e.g. Vulcastab LW) and also dispersion stabilizers.

### GENERAL NOTES ON SURFACTANTS APPLICATIONS

Anionics are generally not compatible with cationics.

Non ionic and Zwitter ionics are compatible with all other types.

Carboxylic acid salts are more sensitive to low pH, polyvalent cations and inert electrolyte in aqueous phase than the salts of organic phosphoric acids and these are more sensitive than organic sulfonates and sulfates.

Branched-chain or ring containing surfactants are more soluble and show lower viscosity in aqueous media than straight chain materials with same number of carbon atoms.



Hot acids easily hydrolyze organic sulfates and esters are readily hydrolyzed by hot alkali (or hot acids). Amides are more resistant to hydrolysis.

Non-quaternary cationics are generally sensitive to high pH, polyvalent anions and inert electrolyte in aqueous phase. Quaternary ammonium salts, on the other hand, are generally not sensitive to such additives.

Oxyethylenation of any surfactant results in increase in its solubility in water and decrease in sensitivity to pH changes.

## 6. VISCOSITY MODIFIERS

These are hydrocolloids soluble in water and increase the viscosity of water. Sometimes these substances are known as thickeners. Broadly these are classified on the basis of their origin viz. plant origin or animal origin.

### Alginates

Alginic acid is polymerized 1, 4'- $\beta$ -anhydromannuronic acid. Found as a calcium salt in marine algae. Its sodium salt is obtained by dissolving in sodium carbonate solution and is used as a viscosity modifier although the usage is limited due to handling difficulties and hygroscopic nature.

### Gum Arabic

Gum (resin) collected from *acacia tree* and is a mixture of Ca, Mg & K salts of Arabic acid. The equivalent weight of Arabic acid is 1000 and the mol. wt. of gum Arabic is 240000.

It dissolves in water and the solution is reasonably acidic and the acidity varies from sample to sample. Maximum viscosity is obtained at pH 6 to 8 and can be used as thickener for latex compounds.

### Proteins

Proteins are linear high molecular weight polyamides and are classified in several ways. The latex compounds are concerned with simple proteins, which are water-soluble.

Proteins are Amphoteric polyelectrolytes and at pH 5.0 they have no overall electric charge and thus can be used as viscosity modifiers for latex compounding.

### Casein

Casein is the most widely used protein. It is a phosphoprotein obtained from the raw protein of milk by acid precipitation (by mineral acid or allowing lactic acid to develop).

Casein has a mol. wt. of 40000 and is a pale buff colored powder with approx. 10% moisture.

A solution of casein in water in the region of pH 4.5 – 5.0 acts as a protective colloid, dispersion stabilizer and thickener.

It forms useful combination with alkyl-aryl sulphonate of dispersing agents for preparation of dispersions of insoluble powders in water.

Casein solution in dilute alkali is used in latex based adhesives for rubber to textile bonding adhesives.

Casein is easily attacked by micro-organisms giving foul odor and has to be protected using pentachlorothiophenate.



### Glue

Glue is a protein derivative obtained from animal connective tissues by hydrolysis with steam/hot water. Glue pre-swollen with mild acid treatment and having solution pH at 4.7 – 5.0 is used as a protective colloid and foam stabilizer.

### Gelatin

Gelatin is refined glue and can substitute glue. It consists of water-soluble proteins of high molecular weight, which swell in cold water and completely dissolve in hot water.

### Polyvinyl Alcohols

PVA is markedly surface active and shows a very little tendency to foam. PVA solution in water is an effective emulsion and dispersion stabilizer. However, it tends to precipitate out in the presence of borates.

### Cellulose Derivatives

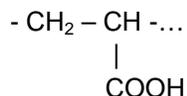
Cellulose-alkyl ethers, hydroxyalkyl ethers, carboxyalkyl ethers etc. are used as thickeners in latex compounds.

### Starches

Starches are mixtures of polysaccharides – amylose and amylopectin. Amylose is water-soluble and is used as a thickener in latex adhesives. Sago and maize starches are preferred, which are rich in amylose.

### Polyacrylates and Polymethylacrylates

Polyacrylonitrile is hydrolyzed to obtain polyacrylic acid..



Under alkaline conditions, corresponding alkali-polyacrylate is obtained which is water-soluble and its viscosity depends on the degree of alkalinity.

## 7. OTHER COMPOUNDING INGREDIENTS

Mineral oils and ester plasticizers find applications in latex compounds. The choice is determined on the type of latex (e.g. mineral oils for NR, SBR and other general purpose lattices and ester plasticizers for NBR, CR, PVC, PVA lattices).

Waxes and petroleum jellies are used in latex compounds for obtaining certain specific properties/ effects (e.g. petroleum jelly as cell-wall lubricant for latex foam products).

Varieties of viscous and resinous ingredients are used to impart tack to latex-adhesive films.



Antifoaming and Antiwebbing surfactants are used in latex compounds intended for the production of dipped goods (e.g. medium chain length aliphatic alcohols like 2-ethylhexy alcohol or silicone greases).

### SOLUTIONS, DISPERSIONS & EMULSIONS

The compounding ingredients are added to lattices as aqueous solutions, dispersions or emulsions depending on their solubility or insolubility in water. (A few ingredients may be directly added to latex e.g. dry fillers to certain latex foam compounds or ester plasticizer to PVA latex.)

The particle size of dispersion or the droplet size of emulsion should be close to the latex.

The stability of dispersions and emulsions should be comparable with the latex. The stabilizing systems should be similar for the ingredient preparation and the latex.

Care should be taken to ensure the compatibility of latex and the ingredient added in solution form.

As far as possible, the pH of solutions, dispersions and emulsions should be adjusted to match the pH of the latex.

#### SOLUTIONS:

Solutions of highly water-soluble ingredients are prepared in soft water to desired concentration and then added to the latex compound.

Solubility of some water-soluble compounding ingredients (e.g. accelerators) may be temperature dependent. Hence, either more dilute solution has to be prepared or appropriate temperature has to be maintained.

Casein solution is best prepared in dilute alkaline medium as a caseinate solution (e.g. ammonium hydroxide alkali will give ammonium caseinate solution). Casein is allowed to swell in warm water for few hours and the alkali is added with constant stirring. The concentration of casein solution may be adjusted to 10 – 15% by weight. Sodium pentachlorophenate is added as a preservative.

Water-soluble cellulose solution is prepared by dissolving cellulose in boiling water.

#### DISPERSIONS:

To start with, coarse slurry of powdered ingredient is made in water along with dispersing agents and dispersion stabilizers and then it is ground in a suitable mill to desired average particle e.g. 5 micron or lowers to produce a stable dispersion.

The mills, which only break down particle aggregates of, fine particles but do not affect any particle size reduction, are known as colloid mills.

The mills, which do effect reduction to ultimate particle size as well as disperse any agglomerates, are ball mills, pebble mills, ultrasonic mills, attrition mills etc.

The colloid mills are used for fillers such as zinc oxide, china clay, ppt. calcium carbonate that are of much finer particle size and only the breaking of loose aggregates is necessary.

Ingredients which are in coarse crystalline form (e.g. sulphur, accelerators, and antioxidants) are ball milled for reduction to ultimate particle size desired.

#### Colloid Mills

Several types of colloidal mills are available. The main principle is that the slurry of powder is subjected to a high rate of shear, thereby causing the agglomerates to break down.



Some mills have higher throughput but are not very effective in terms of agglomerate breakdown and others would effectively break down agglomerates but throughput may be comparatively lower. The

selection is done on the requirement of extent of breakdown and one has to evaluate the performance of available options to suit the need.

### Ball Mills

Ball mills consist of cylindrical containers in which slurry of the ingredient, dispersing agent / wetting agent in water is placed together with charge of balls/pebbles.

The quantity of charge is adjusted in such a way that an empty air space (approx. 40-50 % of the total volume) is left free.

The cylindrical containers are revolved slowly about their axis horizontally. When the mill is working properly, the balls get carried round with the container for a short distance and then cascade.

The process of cascading causes grinding of the particles in the slurry.

The container rpm is rather slow to avoid centrifuging of the balls.

Frothing in the free empty space prevents grinding action!

The ball mills are lined with steel and pebble mills are generally of ceramic cylinders.

The critical speed in rpm for a ball mill is  $= 54.2 / \sqrt{R}$  ; where R is the radius of the container in ft.

The balls used may be distributed in various sizes (diameters).

Steel balls grind faster than pebbles of similar size due to higher impact.

The efficiency of the ball mill is roughly proportional to its diameter.

As a guideline, approx. 50% of the volume in a jar is filled with balls and the slurry is just above the level of the balls to ensure sufficient empty space availability.

The rpm at which the jar should rotate is calculated as given above.

Generally 15 to 20 cm diameter jars rotate at 65 – 75 rpm, 25 to 50 cm diameter jars rotate at 50 – 60 rpm and 50 – 60 cm diameter jars rotate at 40 rpm.

The ball milling time is usually 24 – 48 hours depending on the slurry material and the extent of grinding desired. Smaller size jars use 10 – 12.5 mm dia. balls and larger mills require 25 mm dia. balls.

### Attrition Mills

A mixture of slurry and grinding medium (glass beads) is agitated at high speeds by means of reciprocating paddle and circulated by a pump to accelerate the grinding action. The pump is also used for charging the material and discharging the mill.

Attrition mills rapidly produce fine and high concentration dispersions. (Typical cycle few minutes to one hour.)

Attrition mills have low power consumption and are very economical and yet produce excellent dispersions.

### Formulations for Dispersion

The active ingredient content is always a simple integral multiple/sub multiple (e.g. 25%, 33%, 50%, 66% etc.).

Generally, the solutions of dispersing agent and stabilizers with water are combined and added to water and then dry powder is added with high speed stirring.

Preparation of sulphur dispersion is relatively difficult as it tends to flocculate and sediment. It generally requires higher proportions of dispersing agents (2.0 – 2.5 phr) and at least 1.0 phr stabilizer like caseinate/ethylene oxide condensates. Sulphur dispersion preparation also takes more ball milling time, e.g. 72 hrs. as compared to 24 hr. or even lower for other ingredients. Thickeners are often used for sulphur dispersions to retard sedimentation (but not at the ball milling stage!).

Accelerator dispersions are prepared at 50% active content.

ZDEC tends to flocculate at 50% and hence one may consider 33% dispersion for ZDEC. Sometimes 1% methylcellulose is added to enhance the stability of the dispersion and discourage sedimentation.

Zinc oxide dispersions can be prepared by ball milling or by colloid mill depending on particle size desired.

One can make a single dispersion of all possible ingredients in the proportions desired in the compounding formulation, and can include antioxidants and other minor ingredients in such recipe.

Resinous antioxidants/other ingredients are difficult to grind and hence Kaolinite clays are used as inert carriers. Equal weights of antioxidant (e.g. TMQ) and Kaolinite clay are combined to get 50% dispersion with higher proportions of dispersing agents and stabilizers. The active antioxidant content thus will be 25%. The clay particles coat the coarser antioxidant as disintegration takes place thereby preventing the latter from sticking together again.

Fillers such as calcium carbonates, china clays are added to latex as 67% - 75% dispersions using dispersing agents (and thickeners if necessary to adjust the viscosity). Sometimes marked increase in viscosity of the dispersion is observed due to build up of a second layer of surface-active agent on top of the initially adsorbed layer. The orientation of the second layer prevents essentially hydrophobic surface to aqueous phase encouraging flocculation. In case of ZnO, enhanced hydration of ZnO particles due to excess dispersing agent can also cause such problems.

A high degree of dispersion results in low viscosity and low sedimentation rate. On the other hand, partially flocculated dispersions have high viscosity and sediment rapidly.

The aqueous pigment dispersions contain water (to desired viscosity), wetting agents, dispersing agents and colloid stabilizers/viscosity modifiers.

These dispersions are formulated to contain a balance of anionic and non-ionic compounds, which together form efficient wetting and dispersing and stabilizing system (e.g. sodium polymethacrylate plus sodium polymeta sulphate plus a non ionic wetting agent or methyl cellulose plus anionic dispersing agent like sodium polymeta phosphate plus tetra sodium pyrophosphate etc.).

EMULSIONS:

Emulsions of the type oil-in-water are used for latex compounding. First a coarse suspension of oil droplets is made in water and then this is subjected to high speed intense shearing and impact using a specially designed emulsifier.

Colloidal mills, ultrasonic mills or specially designed emulsifiers are used for refining purpose. The coarse emulsions are prepared by using one of the two techniques given below. :

Dissolving the dispersing aids, stabilizers, thickeners etc. in water and then adding the oil under high speed stirring.

Soap-in-Situe: The fatty acid component of the soap is dissolved in the oil and the alkali component is dissolved in water together with any stabilizer. The oil phase is then poured into aqueous phase with high-speed stirring whereupon emulsification takes place spontaneously.

The soap is formed just at the locations where it is required and where it is most effective. The overall ratio of alkali to acid determines the pH of emulsion, which should be mildly alkaline (e.g. pH = 9) for which 5% extra alkali over acid is needed.

By using slight excess of fatty acid, it is possible to produce very stable emulsions, which are neutral in nature. Such emulsions will reduce overall alkalinity of any latex and yet enhance its stability due to soap contents.

Oil Emulsion by Soap-in-Situe Method

Ingredients	Dry (pbw)	Wet (pbw)
Part A : Oil Phase		
Oil	80	5
Oleic acid	5	5
Part B :Aqueous Phase		
Morpholine	1.75	1.75
5% sodium carboxy methylcellulose	1	20
Water	-	93.25
Active ingredient = 40%		

Styrenated Phenol (SP) antioxidant can be emulsified using above method. Slight excess alkali must be added since phenols themselves tend to interact with the alkali.

Waxes and petroleum jelly can be dispersed by melting them and then emulsifying in hot water. The emulsion is stirred vigorously until the temperature falls below the melting point of wax.

Antioxidants like TMQ are melted with an equal weight of oil and then emulsified in hot water. It is necessary to agitate the emulsion until the temperature has fallen sufficiently to allow the disperse phase to solidify.

One should always explore new techniques for the preparation of emulsions. For example, it is preferable to add aqueous phase to oil phase with stirring to produce water-in-oil emulsion first and then add more water so that phase inversion takes place when soap-in-situe technique is used.

TYPICAL FORMULATIONS: DISPERSIONS & EMULSIONS

i) 50% Sulphur Dispersion

Ingredients	Dry (pbw)	Wet (pbw)
Sulphur	100	100
* 10% dispersing agent solution	2.5	25
** 15% dispersion stabilizer solution	1.0	7
5% betonies clay dispersion	1.0	20
Water	-	48
*Sodium naphthalene formaldehyde sulfonate	--Ball mill for 72 hours	
**Ammonium caseinate	--Total solids = 52.25%	
--Total active ingredient = 50%		

ii) 33% Accelerator Dispersion

Ingredients	Dry (pbw)	Wet (pbw)
Accelerator	67	67
* 10% dispersing agent solution	1	10
** 20% wetting agent solution	1	5
Water	-	118
*Sodium naphthalene formaldehyde sulfonate	-Ball mill for 24 hours	
**Polyethylene oxide condensate	-Total solids content = 34.5%	
-Total active ingredient = 33%		

iii) 50% Zinc Oxide Dispersion

Ingredients	Dry (pbw)	Wet (pbw)
Zinc oxide	100	100
* 10% dispersing agent solution	1	10
** 20% wetting agent solution	1	5
Water	-	85
* Sodium naphthalene formaldehyde sulfonate	-Ball mill for 16 - 18 hours	
**Polyethylene oxide condensate	-Total solids content = 51%	
-Total active ingredient = 50%		



## iv) 25% Antioxidant Dispersion

<u>Ingredients</u>	<u>Dry (pbw)</u>	<u>Wet (pbw)</u>
Antioxidant	50	50
* 10% dispersing agent solution	1.5	15
** 20% wetting agent solution	1.5	7.5
Kaolinite clay	50	50
Water	-	77.5
*Sodium naphthalene formaldehyde sulfonate	-Ball mill for 24 hours	
**Polyethylene oxide condensate	-Total solids content = 51.5%	
-Total active ingredient = 25%		

## v) 67% Filler Dispersions

<u>Ingredients</u>	<u>Dry (pbw)</u>	<u>Wet (pbw)</u>
Filler	133	133
* 10% dispersing agent solution	1	10
** 20% wetting agent solution	0.5	2.5
Water	-	54.5
* Sodium naphthalene formaldehyde sulfonate	-Colloid mill or ultrasonic mill	
**Polyethylene oxide condensate	-Solids content = 67.5%	
-Active content = 67%		

## vi) 50% Antioxidant SP Emulsion

<u>Ingredients</u>	<u>Dry (pbw)</u>	<u>Wet (pbw)</u>
Antioxidant SP	100	100
Oleic acid	2	2
Triethanol amine	0.5	0.5
Ammonia	0.5	0.5
Water	-	97
Triethanol amine, ammonia and water are mixed and added to a mixture of Antioxidant SP and oleic acid with high speed stirring. The resultant mixture is cooled and passed through a colloid mill twice.		

*16% Stearic Acid Emulsion*

Stearic acid, 10 pbw is melted with 2.5 pbw of oleic acid and added to 490 pbw of hot water (70°C) containing 2.5 pbw of KOH. Ammonia 2.5 pbw is then added and the mixture is cooled with continuous stirring.

General

All dispersions are prepared using soft water.

The degree of dispersion depends on the finished product quality or process requirements (e.g. for high strength films very fine particle size dispersions are necessary, for good product color or transparency very fine particle size dispersions are necessary).

For high quality rubber goods dispersions of each ingredient should be prepared separately and also added separately (rather than making a single dispersion of all the compounding ingredients).

The quality of dispersion is easily checked by allowing a drop of the dispersion to fall on the surface of water taken in a 1000 ml glass cylinder. The drop must not fall to the bottom but should disperse well in water phase.

For production of articles like latex thread, ultra thin dipped goods; the average particle size of dispersion should be 5 microns or lower in diameter (similar to rubber particles in latex).

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**LATEX PRODUCTS MANUFACTURE**

<u>Manufacturing Process</u>	<u>Products</u>
1. Dipped latex products	Surgical gloves, House hold gloves, Industrial gloves, Contraceptives, Feeding Bottle teats, Toy balloons etc.
2. Foamed latex products	Mattresses, Pillows, Upholstery, Carpet Backings, Packaging materials etc.
3. Latex extrusions	Latex thread.
4. Latex spreading	Carpet backing, Textile treatment, Paper Coatings
5. Latex castings	Toys, Bulbs
6. Miscellaneous	Rubberized coir /fiber products, Battery Separators, Adhesives and PV-latex.

1. DIPPED LATEX PRODUCTS

Dipping process is described as ‘ Immersion of a former into a suitable latex compound followed by a slow withdrawal in such a way so that a uniform deposit of latex compound film is formed around the outside of the former which is subsequently dried , leached , vulcanized and stripped to obtain a finished product.

The dipping methods are classified as Straight dip, Single dip, Multi dip, Wet coacervant dip, Dry coacervant dip, Heat sensitized dip and Electro deposition dip.

### Straight- Dip ( or Simple Dip )

In this method dipping of the former is done without any other dipping aids like coacervants. Deposits on the former are formed due to the viscosity of the latex compound and its tendency to wet the former. The deposits are very thin and suffer from several defects.

### Single- Dip

Assistance of some dipping aid is taken for the treatment of the former before dipping but the former is dipped only once in the latex compound and hence the films are very thin and prone to defects.

### Multi- Dip

The process operations are similar to single dip but multi dips are given allowing partial or complete drying after each dip.

A large number of dips may be necessary to achieve desired product thickness (each dip would correspond to 0.125mm to 0.250mm thickness depending upon the viscosity of the latex compound). The products are generally free from defects.

### Wet-Coacervant Dipping

A liquid coacervant such as acetic acid is used to assist the build-up of latex film deposit. The former is dipped first into acetic acid (or sometimes first into latex compound and then into acetic acid followed again by a dip into latex compound.)

The former is first dipped into acetic acid; the excess of acetic acid is allowed to drain-off. It is then immersed into the latex compound and allowed to dwell for a predetermined time. The thickness of the deposit depends on the dwell time and the stability of the latex compound towards the coacervant.

This process is not widely used due to the non-uniformity of the deposits and the tendency of the deposits to slip-off the former during withdrawal.

When the former is first dipped into latex compound followed by a dip in the coacervant and then again into latex compound, the deposits tend to be little thicker. Thus two latex dipping are involved and the initial latex dip and the coacervant dip may not knit satisfactorily causing delamination during product service. However, this technique is very useful for producing fabric-supported products.

### Dry-Coacervant Dipping ( Coagulant Dipping )

The most widely used dipping method, involves use of dry coacervants such as calcium chloride, calcium nitrate, cyclohexyl ammonium acetate & a few other salts.

The coacervants are dissolved in a volatile solvent at optimized concentrations and the formers are first dipped in this solution and allowed to dry to obtain a deposit of dry or very viscous coacervant coating.

The former is then dipped into latex compound and allowed to dwell for optimum time to build-up desired thickness. The dwell time depends on the type & concentration of the coacervant and the stability of latex compound towards the coacervant.

Examples of dry coacervant solutions are given below:

Anhydrous calcium chloride	15 pbw
Calcium Nitrate tetra hydrate	15 pbw
Methyl / Ethyl alcohol	50 pbw
Water	20 pbw

*A small dosage of quaternary ammonium salt soap assists the wetting of former and also partially destabilizes latex layer in the vicinity of the former. Small proportions of clay & talc are also added to increase the quantity of solution pick-up and to facilitate removal of rubber deposit after drying.*

Calcium Nitrate tetra hydrate	60 pbw
Distilled Water	30 pbw
Acetone	5 pbw
Non-ionic wetting agent	1 pbw

*Generally, very viscous deposits are obtained on the former. If dry deposits are desired, the former temperature has to be raised.*

Cyclohexyl ammonium acetate Used as coacervant when products of optimum clarity are desired. This also provides superior bead adhesion and mild antioxidant action.

Cyclohexyl amine	12.4 pbw
Glacial acetic acid	7.6 pbw
Methyl Alcohol	80 pbw

For Synthetic Rubber Lattices the coacervant solutions have to be modified to suit their compounding chemistry.

*For CR-Latex*

Calcium nitrate tetrahydrate	10 pbw
Anhydrous Calcium chloride	10 pbw
Methyl alcohol	60 pbw
Acetone	20 pbw

*For NBR-Latex*

15% Calcium Nitrate in Methyl Alcohol  
 1% Non-ionogenic Surface active agent  
 10% Calcium nitrate in Isopropyl Alcohol

### HEAT SENSITIZED DIPPING

Heat sensitive latex compound is prepared and hot formers are used to produce dipped goods. The deposits are built up around the former and the heat is conducted to surrounding latex compound.

The deposit thickness depends on the temperature of the former, heat sensitivity of the latex compound and the heat capacity of the former. Very thick deposits can be obtained.

Heat sensitivity obtained by compounding latex with polyvinyl methyl ether method is the most suitable which enhances the room temperature stability of the latex compound.



This method is used only for products which require thick or foamed deposits. The tank containing latex compound has to be kept cool.

### ELECTRO DEPOSITION

Latex particles carry a -ve charge and hence can migrate to the former which is +vely charged. This method is not very popular since several other mechanisms also take place simultaneously e.g. oxygen is evolved at the anode, the surfactants may migrate depending on the charge they carry, conductivity of the batch may change, etc.

### MANUFACTURING PROCESS – LATEX DIPPED GOODS

#### FORMERS

Formers are made from porcelain (glazed / unglazed), glass (hollow), aluminum / aluminum alloys, wood (varnished / unvarnished), plaster of Paris, paper (disposable formers), plastics, etc.

Formers may be solid or hollow, collapsible, etc. but must have smooth surface and easily cleaning properties without affecting the material or surface of the former.

The metallic formers should be dent-free.

The greatest 'cleaning problem' is faced with aluminum formers.

One must be careful while selecting formers and their material of construction keeping in view the handling and cleaning requirements.

#### DIPPING TANKS

The laboratory dipping tanks could be of glass or stainless steel but the factory size tanks are mild steel lined with lead or an alkali resistant resin coating or from aluminum, coated wood or enameled iron. The dipping tanks also could be rubber or plastic lined.

The tanks have to be jacketed for maintaining desired temperature to control the viscosity of the latex compound.

The tanks have to be designed for slow agitation of latex compound from top to the bottom to prevent skinning effect, creaming and sedimentation.

The tanks should be provided with lids to retard evaporation of latex compound when the tank is not in use.

Jacket cooling is absolutely essential when heat sensitized latex is used since the temperature tends to increase through repeated immersion of the heated formers.

#### DIPPING MACHINES

Two types of dipping machines are used.

The first type, in which the formers move downwards into the latex compound tank and the second type in which the latex compound tank is brought up to the formers.

The second type dipping machine gives a closer control of dipping speed. Motion tends to be more uniform and any vibrations are easily eliminated (but this machine is expensive and higher energy consuming).

Movements of formers are effected by cables and pulleys which are activated by hydraulic ram or wind-up gears.

The formers are held in jigs which are placed on moving rails or platform.

### SEQUENCE OF OPERATIONS

Sequences of operations are generally product dependant but involves following steps (manual / automatic)

1. Compounding of Latex
2. Pretreatment of formers (cleaning, washing, heating, dipping into coacervant solution).
3. Immersion of formers (rate, quality, deposit thickness)
4. Dwell time (in the presence of coacervant for the thickness required)
5. Withdrawal (two stage for bead formation)
6. Inversion 180° (for dispersal of drops at the bottom followed by rotation)
7. Drying, leaching, beading (drying temperature, period, leaching by hot water)
8. Dusting (Zinc Stearate, Starch, and lycopodium powder).
9. Vulcanization (can be combined with drying, 100°C live steam).
10. Stripping (manual / air blast / rollers)
11. Inspection (as required for the product)
12. After treatments (Roughening, Halogenation, Flocking, Jazzing, etc).

### LATEX COMPOUND DESIGN FOR DIPPED GOODS

**POLYMER:** NR/SR, Unvulcanized / Prevulcanized (but not their blends!) SR lattices have very low wet gel strength. Products with high oil / heat resistance made from CR, NBR latices.

**FILLERS:** Only small quantities for cost-reduction (max. 20 phr). Fine particle size clays are generally used. Fillers stiffen products considerably.

**SOFTENERS:** Are used when fillers are used. Mineral Oil 5 – 10 phr can be added to lower the modulus (and offset filler effect). Softeners are added as Emulsions.

**STABILISERS:** Polyethylene oxide condensates or protenous chemicals are added as stabilizers. Over stable latex may cause difficulties in dipping process. Small amount of KOH is added as a replacement of volatile ammonia to maintain the alkalinity . No stabilizers are required for PV Latex.

**ANTIOXIDANTS:** The dipped goods are generally thin-walled articles and hence antioxidants must be used in dipped latex products. It is important that antioxidants must be finely ground and well dispersed. Liquid antioxidants like styrenated phenol are very good with this respect since its emulsion disperses very well in the rubber film.

**VISCOSITY MODIFIERS:** These are necessary for the adjustment of latex compound viscosity in the dipping tank where thickness of the dip depends on latex compound viscosity. Sodium carboxy methyl cellulose is recommended. Alginates and quaternary ammonium salts are also very effective but these promote rapid creaming.

**OTHER ADDITIVES** Curatives will be as per base polymer of the latex. In case of PV Latex, curatives may be omitted. Addition of 5 phr polyethylene dispersion improves the filler texture considerably.

*All dipped goods should be thoroughly leached in hot water before vulcanization for obtaining the best possible tensile properties. (Tensile strength and Elongation at break).*

*Deproteinized NR Latex should be used for the manufacture of surgical gloves.*



The ISO / ASTM / DIN / BS specifications should be referred for the manufacture of gloves and other medical / FDA approval seeking latex goods before formulating the latex compound or finalizing subsequent manufacturing process.

TYPICAL COMPOUNDING FORMULATIONS FOR DIPPED LATEX PRODUCTS

SURGICAL GLOVES

<u>INGREDIENTS</u>	<u>DISPOSABLE (PBW)</u>	<u>STERILIZABLE (PBW)</u>
60 % NR Latex (LA)	167	167
20 % Polyethylene oxide fatty alcohol condensate solution	1.0	1.0
10 % KOH Solution	4.0	4.0
50 % Antioxidant Dispersion/Emulsion	1.0	2.0
50 % Zinc Oxide Dispersion	1.0	2.0
50 % Sulphur Dispersion	3.0	0.5
50 % ZDEC Dispersion	1.0	-
50 % ZDBC Dispersion	1.0	2.0
50 % TMTD Dispersion	-	1.0

Drying + Cure time: 30 minutes at 105°C.

EXAMINATION GLOVES

<u>INGREDIENTS</u>	<u>PBW</u>
60 % NR Latex (deammoniated)	167
10 % KOH Solution	4.0
10 % Potassium Caseinate Solution	2.5
20 % Anionic Surfactant (sulphated fatty alcohol)	1.0
50 % ZDEC Dispersion	2.0
50 % Zinc oxide Dispersion	1.5
50 % Sulphur Dispersion	2.0
50 % Antioxidant Dispersion	2.0
Water	to adjust viscosity
Antifoaming Agent	as required

Drying + Cure time: 20 min at 105°C.

HOUSEHOLD GLOVES

<u>Ingredients</u>	<u>General Purpose</u>	<u>Detergent Resistant</u>
60 % NR Latex (LA)	167	167
10 % KOH Solution	4	2
20 % Potassium Laurate Solution	2	1.5
50 % Sulphur Dispersion	2.5	2.5
50 % Zinc oxide Dispersion	2.0	3.0
50 % ZDEC Dispersion	2.0	1.0
50 % ZMBT Dispersion	-	1.5
50 % DTDM Dispersion	-	2.0
20 % DPG Dispersion	-	6.0
50 % Antioxidant Dispersion	2.0	3.0

Drying + Cure time: At 120°C for 40 min.

INDUSTRIAL GLOVES

<u>INGREDIENTS</u>	<u>PBW</u>
60 % N R Latex (LA)	167
20 % Potassium Laurate Solution	4
10 % KOH Solution	4
50 % Sulphur Dispersion	4
50 % ZDEC Dispersion	2
50 % Zinc oxide Dispersion	4
50 % China clay Dispersion	40
20 % Antioxidant Dispersion	5
20 % Carbon Black Dispersion	As required

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Drying + Cure time: 30 min – 110°C

ELECTRICIAN'S GLOVES

<u>INGREDIENTS</u>	<u>PBW</u>
60 % NR Latex (LA)	167
20 % Potassium Laurate Solution	1
10 % KOH Solution	2
50 % Sulphur Dispersion	2.5
50 % ZDEC Dispersion	2
50 % ZMBT Dispersion	1
50 % Antioxidant Dispersion	2
50 % Zinc Oxide Dispersion	3
40 % Formaldehyde	to give pH=9.5

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Drying + Cure time: 60 min – 120°C

CONDOMS

<u>INGREDIENTS</u>	<u>LOW MODULUS (PBW)</u>	<u>HIGH MODULUS (pbw)</u>
60 % NR Latex (LA)	167	167
10 % KOH Solution	2	2
20 % Potassium Laurate Solution	1	1
50 % Sulphur Dispersion	2	4
50 % ZDBC Dispersion	0.5	1
50 % ZMBT Dispersion	0.5	1
50 % Zinc oxide Dispersion	1	2.5
50 % Antioxidant SP Emulsion	1	1

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Cure: 20 min at 110°C

FEEDING BOTTLE TEATS

<u>INGREDIENTS</u>	<u>PBW</u>
60 % NR Latex	167
20 % Polyethylene oxide fatty alcohol Condensate Solution	1
50 % Sulphur Dispersion	2
50 % Zinc oxide Dispersion	0.5
50 % ZDEC Dispersion	2
50 % Antioxidant SP Emulsion	2

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Cure: 20 min at 110°C

TOY BALLOONS

<u>INGREDIENTS</u>	<u>PBW</u>
60 % NR Latex	167
10 % KOH Solution	4
20 % Potassium Laurate	2
50 % Sulphur Dispersion	1
50 % ZDEC Dispersion	1.5
50 % Antioxidant SP Emulsion	2
50 % Zinc oxide Dispersion	5
33 % Color Dispersion	As required

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Dry & Cure: 30 min at 100 – 110°C

DIPPED LATEX PRODUCTS BASED ON PV LATEX (PV LATEX)

<u>INGREDIENTS</u>	<u>HOUSEHOLD GLOVES (PBW)</u>	<u>TOY BALLOONS (PBW)</u>
60 % PV Latex (LA)	167	167
50 % Antioxidant SP Emulsion	1	2
67 % Ppt Calcium Carbonate Slurry	37.5	-
50 % Clay Slurry	-	10
50 % Mineral Oil Emulsion	25	20

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Dry & Cure: 20 min at 110°C

DIPPED GOODS BASED ON NBR LATEX

<u>INGREDIENTS</u>	<u>PBW</u>
40 % NBR Latex (Carboxylated)	250
50 % Sulphur Dispersion	3
50 % ZDEC Dispersion	2
50 % Zinc Oxide Dispersion	10
12.5 % Ammonium Caseinate Solution	8
67 % DBP Emulsion	10
10 % Styrene – Ammonium Carboxylate copolymer	3

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Cure 30 min at 120°C



*Notes* :Suitable for coacervant dipping process. Oil resistance will depend on ACN content. High state of cure is required. Styrene ammonium carboxylate gives smooth Coacervant dipping and prevents premature coagulation of the latex compound. pH of the compound should be at 10.3 – 10.5 and adjusted by ammonia addition. Each dwell time is 5 min. Deposits should be leached by hot water (50°C)

## 2. LATEX FOAM PRODUCTS

Latex foam products are cellular (open cell, closed cell or a combination of open cell and close cell structures) products directly produced from liquid latex compounds. The skin is a smooth surface formed by contact with the mould surface.

### GENERAL PRINCIPLES

The basic steps in the latex-foam product manufacture are :

Foaming of compounded latex by introduction of air (or other gases).

Gelling of foamed latex in the suitable mould.

Vulcanization of foam.

Foam latex compound is a three-phase colloid system (two disperse phases – rubber & air and third continuous phase of modified latex serum). Two principle interfaces are serum-rubber & serum-air. Successful manufacture of latex foam depends on the manipulation of these interfaces.

The gelation of foamed latex destabilizes the serum-rubber interface so that rubber particles come together to form a uniform structure, which makes the foam structure rigid.

The conditions which help destabilization of serum-rubber interface also lead to destabilization of serum-air interface.

If the serum-air interface destabilizes first, the foam will collapse. Hence the gelling of serum-rubber interface must occur first to form rigid foam which will resist collapse due to destabilization of serum-air interface. These sequences are controlled by type of gelling agent, time and temperature adjustments in the process.

When a limited collapse is intentionally allowed; a closed-cell structure will result.

### DUNLOP PROCESS OF LATEX FOAM MANUFACTURE (BATCH PROCESS)

The ammonia content in NR Latex is brought down to 0.1 – 0.12 % from 0.7 % by stirring or addition of formaldehyde. (This prevents premature gelling of latex foam compound and poor foam structure).

The latex is then compounded by adding stabilizers, foam promoters and other ingredients except foam stabilizers zinc oxide and delayed action gelling agent.

The compound is allowed to mature slightly above the room temperature with slow stirring and an air current across the surface to remove remainder ammonia. The maturation temperature is approx. 50°C and the period is between 12 – 24 hr. Half the quantity of sulphur and accelerator is withheld some times during compounding stage.



After the maturation period (during which some prevulcanization may take place which helps in reducing the shrinkage of the final product and also improves modulus and general feel of the product) the compound is stored in cool rooms.

Before the compound is taken for foaming, reminder sulphur and accelerators, if any are added, the compound is brought to room temperature and subjected to foaming process.

Foaming is done either by Batch Process or by Continuous Process.

Batch Process uses 'Hobart' Mixer in which a wire-cage type stirrer rotates at 200 – 225 rpm in a planetary motion. This subjects the latex compound to a whipping action entrapping air inside the compound.

The volume increase of the latex foam compound is controlled by adjusting the foaming time to get desired volume (e.g. the volume increases by 6 – 8 times within 15 – 20 minutes which is suitable for latex foam pillows and about 14 times in 30 – 35 minutes which is typical of very soft density sponge). After the desired volume is reached; Zinc oxide and secondary gelling agent like DPG are added with reduction in beating speed.

This is followed by the addition of the gelling agent.

The beating at reduced speed controls the size of the cells and is continued for 2 – 3 minutes to ensure uniform distribution of the additives and the foamed latex compound is poured into the moulds where gelling takes place within 8 – 10 minutes and the mould is kept in the vulcanizer.

The vulcanization is carried out by open steam at atmospheric pressure for 30 – 45 minutes. Care is taken to avoid over cure and the vulcanization time depends on the thickness of the product. After vulcanization the product is stripped from the mould, trimmed to remove flash and then thoroughly washed in water by passing through rollers under water.

The product is squeezed to remove water and dried at 60 – 70°C in hot air.

### PRECAUTIONS

Ammonia from latex has to be removed completely before Zinc oxide is added. Foam stabilizer to be added when the foam has been refined to desired degree.

Zinc oxide and secondary gelling agent to be added separately.

Sodium silico fluoride gelling agent should be added as 20 % dispersion after adjusting its pH between 6 & 7.

When ZnO & Sodium Silicofluoride are present in the latex compound; it must be rapidly transferred to the mould which has been treated with diluted mould release agent and is at 40°C. It will take about 5 minutes to complete gelling of the foam hence only 5 minutes max. are available for transferring the compound to the mould after addition of Sodium Silicofluoride

Allow the moulds to stand for 10 minutes to complete gelling process before vulcanization  
Polyethylene glycol is a better mold release agent. Avoid excessive use of mould release agent.  
The lids of the mould should be kept in position after the mould has been filled.

## COMPOUNDING FOR LATEX FOAM

### *POLYMERS*

60 % Centrifuged NR latex (high ammonia / low ammonia preserved).

PV latex not used due to poor wet-hot strength and gives a weak finished product when dried due to weak inter-particle integration.

Initial ammonia content should be higher because ammonia is lost during prolonged beating for foaming. Ammonia content prior to gelling should be around 0.13 % max. and corresponding pH = 9.0 for the Batch process.

Low ammonia NR Latex is suitable for Continuous foaming process where foaming is done within seconds.

Control of KOH number is necessary (lower KOH number means lower pH and gelation by Sodium Silicofluoride takes place quickly at lower pH).

SBR lattices can be blended only for cost reduction purpose.

### *FOAM PROMOTERS*

Foam promoters promote rapid foaming and compensate for impurities, which have defoaming effects.

Carboxylate soaps, Castor oil soaps, oleates are foam promoters and are used at 0.5 to 2.0 phr.

Foaming tendency depends on pH and should be maintained at approx 9.0

Although surfactants like polyethylene oxide condensates or alkylated naphthalene sodium sulfonate increase foaming tendency, they cannot be used as foam promoters as they stabilize rubber particles as well as air bubbles against the effect of gelling agent.

### *FOAM STABILIZERS*

Quaternary ammonium soaps, amines and proteins are good foam stabilizers (e.g. cetyl trimethyl ammonium bromide, DPG, triamine base-triethyl trimethylene triamine, glue, casein, etc.)

The foam stabilizers allow the latex to gel before it collapses by sensitizing serum-rubber interface.

Proteins, casein, etc. increase the serum viscosity thus helping foam stabilization.

### *CURATIVES*

Selection depends on the type of polymer

For NR latex 2.0 phr Sulphur + 1.0 phr ZDEC + 0.5 Phr ZMBT is optimum cure system.

Presence of ZMBT increases the compression modulus and reduces compression set at the expense of elongation at break.

Presence of DPG & triamine base used for other purposes like gel sensitization also tend to behave as secondary accelerators causing increase in the rate and state of cure.

For SBR latex higher ZMBT is used along with ZDC (e.g. ZDC –0 .75 Phr + ZMBT – 1.0 Phr)

## FILLERS

Fillers are used to increase the stiffening effect of rubber phase in the latex foam.

Fillers also reduce shrinkage during washing and drying.

Use of fillers affects elongation at break and resistance to cyclic compression. It also results in weak cell structure.

Clays or Calcium carbonates can be used up to 30 phr and can be added dry during whipping stage if the latex is properly stabilized.

Organic fillers like starches, resins are added up to 5 phr. The starch swells and gets gelatinized under the influence of heat; starches should not be used if the products are intended for heavy-duty use or for use under humid conditions.

When starch is used, tannin is used at 5 % of starch weight to insolubilize starch during washing.

High styrene resins can also be used to stiffen latex foam.

Softeners such as Mineral oil have limited usage in latex foam but can be added to offset the effect of fillers.

Waxes & Jelly are added as cell wall lubricants to prevent cells sticking during repeated compression.

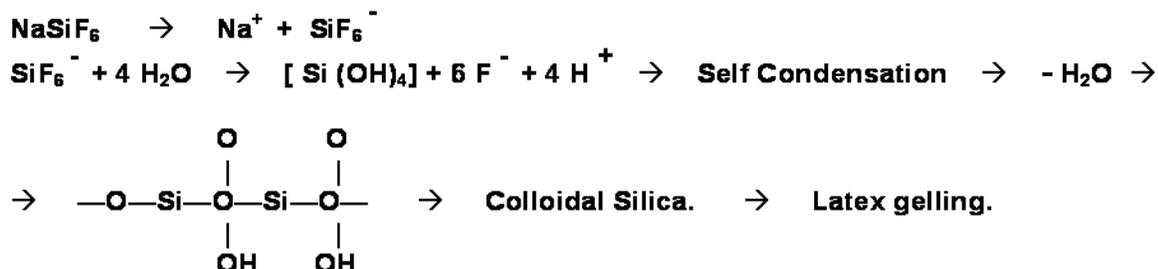
## GELLING AGENTS

1.5 Phr Sodium Silicofluoride (in combination with Zinc oxide – 3 to 5 phr) is the primary gelling agent used for NR Latex foam.

The actual dosage may vary depending on type of latex, alkalinity, amount of soap used, the temperature of latex compound and the speed of gelation required.

Exact quantity must be determined for each batch experimentally.

Sodium Silicofluoride, a delayed action coacervant is a salt of  $H_2 SiF_6$  (Hydrofluorosilic acid). The mechanism is as follows :



The pH of aqs. phase is gradually lowered by titration of hydrogen ions. The latex particles are entrapped in colloid silica, and the latex stabilizers are adsorbed on the silica

Lowering pH permits dissolution of Zinc and encourage formulation of Insoluble soaps of rubber particles.

All above chemical reactions cause delayed action gelling of latex foam.

### OTHER ADDITIVES

Antioxidants like Styrenated phenol, Antioxidant 2246 are added to get optimum aging resistance. Latex foam mattresses, cushions, pillows are traditionally manufactured as light grey or golden or white colour.

Pigments such as carbon black or other colours are added as dispersions.

### PHYSICAL PROPERTIES OF LATEX FOAM

Density (weight of cured latex foam of unit dimensions)  
Hardness (Indentation hardness – special indenter for latex foam products)  
Compression Modulus (stress-strain behaviour)  
Indentation set under constant load  
Resistance to dynamic fatigue  
Tensile strength & Elongation at break  
Compression Set (Residual Strain)  
(Details of Test Procedure available in ASTM.)

### LATEX TREATED COIR FIBRE PRODUCTS

The coconut coir / fibers (or other large diameter fibers) are bonded together at their points of contact by a droplet of compounded latex. The material has open structure and is resilient with specific gravity range of 0.08 – 0.15.

The products find applications for upholstery, packaging material and manufacture of mattresses & other cushioning materials.

The rubber content varies from 10 % to 40 % depending on the product quality requirements. Higher the rubber content; better is the load carrying capacity & dimensional stability and lower is the permanent set.

The resilience of the final product depends on the quality of coconut fibers used and the diameter to length ratio of the fibers.

### Process of Manufacture

The fibers are picked up by conveyor belts and blended in desired proportion and conveyed to spinning & roping machines to form a tightly twisted rope.

The ropes are exposed to live steam first and then dried and converted into bales and stored in order to 'set' the curl.

Ropes are opened and chopped to give minute coir springs. The curled fibres are then carded and converted to pads of 25 – 50 mm thickness.

The compounded latex is sprayed from both sides to ensure complete impregnation.



The sprayed pads are then dried at 70 – 80 °C in hot air and compressed into a mould to attain desired shape / dimensions.

The mould is heated for 30 – 60 minutes at 100°C in hot air to vulcanize the latex compound. The degree of compression in the mould controls the final product density and the compression modulus.

Over cure of the product s carefully avoided and a positive hot air flow is maintained to ensure quicker drying and uniform curing.

### COMPOUNDING FOR FIBRE LATEX PRODUCTS

The cure system should be a flat cure system to avoid reversion during hot air cure. The cure system should give high state of cure so that compression modulus is high and permanent set is low.

It is essential to include an efficient antioxidant (e.g. TMQ) as the rubber films formed are very thin and require very good heat resistance during hot air cure and the long term usage of the product.

Latex compound should have excellent mechanical stability since spraying techniques are used for coating the fibers.

All compounding ingredients should be carefully dispersed to ensure smooth flow of latex compound through the spray nozzles.

Additional wetting agents should be included in the latex compound to ensure proper wetting of fibers.

Accelerator combination suggested is ZDEC – 1.0 phr along with ZMBT - 1.0 phr and Sulphur 2 – 4 phr depending on the nature of the fibers.

Mineral fillers such as fine particle size clay can be added to improve load bearing capacity of the fiber pad. Water soluble thermosetting resin like melamine formaldehyde type added to improve load bearing capacity.

Maturation of latex compound helps in reduction of accelerator dosages and cure time /temperature. This also reduces residual tack of latex compound, which adversely affects the aging resistance of the rubber component.

### TYPICAL COMPUNDING FORMULATIONS

#### NR LATEX BASED SPRAYING COMPOUND – GENERAL PURPOSE

<u>INGREDIENTS</u>	<u>COIR (PBW)</u>	<u>ANIMAL HAIR (PBW)</u>
60 % NR Latex (LA)	167	167
20 % Sulfated alkyl phenol ethylene oxide condensates solution	4	4
20 % KOH Solution	2	2
50 % Antioxidant TDQ Dispersion	3	3
50 % Zinc oxide Dispersion	10	10
50 % Sulphur Dispersion	5	8
50 % ZDEC Dispersion	2	2
50 % ZMBT Dispersion	3	3
Water	To adjust viscosity (50 – 55 % solids)	

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Cure: 30 min at 105°C hot air

Note: Animal hair fibers contain proteins, which react with sulphur and hence higher sulphur dosage is required. Animal hair fibers are relatively more fire resistant than the coir fibers.

### FLAME RETARDANT SPRAY COMPOUNDS

<u>INGREDIENTS</u>	<u>PBW</u>
58 % Halogenoalkylated NR Latex (15 % trichlorobromomethane)	173
10 % Ammonium fluoride Solution	10
50 % Sulphur Dispersion	8
50 % ZDEC Dispersion	2
50 % ZMBT Dispersion	2
50 % Zinc oxide Dispersion	4
50 % Antioxidant TDQ Dispersion	2
60 % Antimony Trioxide	20
Water	To adjust viscosity

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Cure 20 min at 120°C- Hot Air

*Note* : Ammonium fluoride is activator of vulcanization of the modified latex. Zinc oxide and mineral fillers like Whiting impair flame resistance. Hydrated alumina slurry can be added up to 25 phr on dry rubber basis to improve the fire resistance. Chlorinated Wax up to 5 phr can be added to improve the fire resistance.

### 3. Latex Extruded Products

#### LATEX THREAD

##### GENERAL PROCESS

Latex threads are produced by Continuous extrusion of compounded latex in to a wet coacervant bath (e.g. 20 – 40 % acetic acid). This is followed by washing with hot water, drying at 60 – 80°C in hot air and vulcanizing at 120 – 130°C in hot air. The vulcanized thread is passed through a bed of talc and wound on to bobbins or drums and post cured at 60°C in hot air for 24 hr.

##### LATEX THREAD: PROCESS STEPS

##### LATEX COMPOUNDING

Latex should be free from non-rubber constituents.

The compounding formulation should have minimum number of additives in solid form.

Dispersions of compounding ingredients should be very finely ground during ball milling.

Dispersions should be free from air bubbles / frothing.

Air entrapment should be nil or minimum during various compounding and processing operations.

Before extrusion, the compound should be passed through a very fine mesh and then allowed to de-aerate by application of partial vacuum.

##### COACERVANT BATH

Acetic acid diluted at 20 % - 40 % range is used as coacervant bath.



When latex threads of relatively larger diameter are produced and when shorter times of immersion in coacervants are used; the concentration of acetic acid is higher.

The outside surface of the thread coacervants first forming a thin-walled rubber film on the surface while the interior latex compound in the thread is still fluid.

The interior latex compound coacervants by the action of acetic acid diffused through the already set layer.

Saline solutions are sometimes preferred for thicker diameter threads as they effect rapid setting of the entire thickness.

When a blend of acetic acid and saline solution is used; the external skin formation on the latex thread is immediate.

This skin acts as semi-permeable membrane and osmosis occurs through this film as a result of which larger quantity of water is lost from the thread, which helps its solidification.

The strength of the coacervant batch is maintained within narrow limits throughout the proces since the same varies considerably due to consumption of acetic acid.

### LATEX THREAD EXTRUSION

The extrusion nozzles are made from boro silicate glass capillary with accurate dimensional control these are then fused into a wider glass delivery tubes.

Several sets of nozzles of different bore sizes are used as per the finished product, diameter requirements.

By varying extrusion conditions, it is possible to use a single nozzle to produce extrudates in a range of diameters.

The extrusion of latex thread takes place under the coacervant batch.

The exact size of diameter of the extrudate depends on nozzle radius ( r-cm ), nozzle length ( l-cm ),  $d_1$  (density of latex compound),  $d_2$  (density of resultant thread), h (pressure in cm of the compound at which the latex is extruded),  $\eta$  (the viscosity of latex compound in centipoises, s (the fractional solids content in the compound and v (the speed in cm/sec at which the thread is delivered from drying and curing belts).

The diameter D (in cm) of the circular cross section of the latex thread delivered from the nozzle is given by following equation.

$$D = 22.15 \times r^2 \times d_1 \times \sqrt{100 h \cdot s / l \cdot d_2 \cdot v \cdot \eta}$$

This equation indicates the factors to be controlled in order to obtain latex thread of given size from a particular size of nozzle.

Feeding the nozzle through a tank, which receives latex from a constant – head device, ensures constant extrusion pressure.

Viscosity of the latex compound has to be carefully controlled for total dimensional control of the product.



### SUBSEQUENT PROCESS OPERATIONS

After the coacervant batch the threads are passed through a hot water bath where water-soluble impurities are leached out. The thread is strong at this stage and is subjected to a 'stretching' process to control the final diameter.

The thread then carried to a hot air chamber for drying and vulcanization. The hot air chamber has a drying zone maintained at approx. 70°C and the vulcanization zone is at about 125 – 130°C. Between the two zones one more zone is maintained at intermediate temperatures between 70°C and 120°C. The total time in the Vulcanizer depends on the diameter of the thread (typically between 5 to 7 minutes). The thread is thoroughly dried before it reaches the vulcanization zone.

The thread is then passed through a bed of talc and is inspected for defects on an inspection table as part of the continuous process. The thread is finally wound on bobbins or drums under slight tension. The bobbins or drums are finally post cured at 60°C in hot air ovens for 24 hr to complete the cure cycle.

Various other quality control tests are then carried out. The compounds have to be designed to with stand degradative forces such as solvent resistance, detergent resistance, superior aging properties, etc. by employing potent non-staining type antioxidants.

### TYPICAL COMPOUNDING FORMULATIONS

#### GENERAL PURPOSE LATEX THREAD

<u>INGREDIENTS</u>	<u>PBW</u>
60 % NR Latex (LA)	167
10 % KOH Solution	3
20 % Potassium Laurate	3
50 % Zinc oxide dispersion	6
50 % Titanium dioxide dispersion	10 – 15
50 % Antioxidant Dispersion	3
50 % Colloidal sulphur dispersion	3.5
50 % ZMBT Dispersion	2.0 – 3.0
50 % ZDBC Dispersion	0.5

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Cure 30 min at 120°C

Note: Drying & Curing in hot air is often combined as described above.

#### HEAT RESITANT LATEX THREAD

<u>INGREDIENTS</u>	<u>PBW</u>
60 % NR Latex (LA-T2)	167
10 % KOH Solution	3
20 % Potassium Laurate	3
50 % Antioxidant Dispersion	4
50 % Zinc oxide Dispersion	8
50 % Titanium Dioxide Dispersion	10 – 15
50 % ZMBT Dispersion	3
50 % ZDBC Dispersion	1
50 % DPTT Dispersion	3.0 – 3.5

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Cure 30 min at 120°C

Note: Drying & Curing is often combined as described above.



#### 4. LATEX SPREADING

##### CARPET BACKING

Latex finds applications in two areas of carpet backing. Introduction of small proportions of latex into the glue or starch back-sizing compounds.

Latex compounds are backings for non-woven carpets and integration of cushioning layer with the back of the carpet to eliminate the need for a separate carpet – underlay with a latex foam compound of high modulus.

The function of back sizing compound is to impart rigidity and permanence to the backing. It also improves the anchorage of the piles and eliminates fraying at the cut edges, handling and appearance of the carpet and protects the carpet from dampness, dirt and abrasion. The anti-slip properties are also improved and help in the cost- reduction as looser fabric construction can be used.

The main function of latex binder in a tufted carpet is to anchor the pile yarns into the basic backing fabric for improved dimensional stability, anti-slip properties, increased weight, firmness and improved laying characteristics. Integration of a cushioning layer is done with high modulus latex foam.

##### PROCESS

Most popular method is to use lick-roll application technique for the latex compound. The carpet is placed over a conveyor and after brushing and steaming the carpet back is coated with the latex compound by means of a lick-roller, which rotates in the bath of latex compound. An adjustable doctor blade is used to control the deposit thickness. The backing is then dried and cured by passing through a hot air oven. The latex compound may also be applied by using Spreading technique or by Spraying.

##### TYPICAL CARPET BACKING COMPOUNDS

###### ANCHOR COATS FOR TUFTED CARPET

###### INGREDIENTS

###### GENERAL PURPOSE (PBW)

60 % NR Latex (LA)	167
25 % Surfactant	3
20 % KOH Solution	1.5
50 % Zinc oxide Dispersion	7.5
50 % Sulphur Dispersion	4.0
50 % China Clay Slurry	100
50 % ZDEC Dispersion	2
50 % ZMBT Dispersion	2
50 % Antioxidant Dispersion	2
10 % Thickener Solution	10

Drying time 20 min at 130°C in hot air for 5 mm thickness.

**FOAMED CARPET BACKING**

<u>INGREDIENTS</u>	<u>PBW</u>
60 % NR Latex (LA-TZ)	167
20 % Potassium Oleate	5
20 % Surfactant	3
50 % China Clay Slurry	50
50 % Blowing Agent Dispersion	10
50 % Zinc oxide Dispersion	6
50 % Sulphur Dispersion	4
50 % ZDEC Dispersion	2
50 % ZMBT Dispersion	2
50 % Antioxidant Dispersion	2
20 % Ammonium Acetate	5
10 % Thickener	10

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Drying time 20 min at 130°C in hot air for 5 mm thickness

**FLAME RETARDANT FOAM BACKINGS**

<u>INGREDIENTS</u>	<u>PBW</u>
60 % NR Latex (LA)	167
20 % Potassium Oleate	20
50 % Antioxidant Dispersion	2
50 % Sulphur Dispersion	5
50 % ZDEC Dispersion	2
50 % ZMBT Dispersion	2
50 % Chlorinated Wax	10
50 % Aluminium hydroxide Dispersion	50
50 % China Clay Dispersion	50
5 % Thickener Solution (Polyacrylate)	As required
50 % Zinc oxide Dispersion	5
20 % Ammonium acetate solution	12.5
50 % Tetra bromo bisphenol A	15
Water	Required for 67 % total solids

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Drying time 20 min at 130°C in hot air for 5 mm thickness.

**5. LATEX CASTINGS**

The latex castings (or moldings) involve the formation of solid (or hollow) objects from latex compound by gelation inside the mould cavity.

The articles are a sharp impression of the inside mould design and surface finish .

The production processes depend on the type of mould used which influences gelation mechanism to be selected to suit the way in which the mould is used.

### Plaster of Paris Moulds (Calcium Sulphate Dihydrate)

The latex is gelled due to absorption of water by the porous mould surface and also the calcium ions tend to diffuse into the latex which lowers the latex stability. Thus, a gradual deposition of latex compound takes place on the mould surface from inside. The mould surface gets slightly eroded and sharp edges are lost.

### Metal Alloy Moulds

Light alloys based on aluminum and magnesium are used as mould making materials. Heat sensitive latex compounds are used for these moulds.

The buildup of deposit depends on the temperature of the mould, its heat capacity and the heat sensitivity of the latex compound.

The plaster of Paris moulds are generally used for products with lower production volumes as these have limited life and the metal alloy moulds are used when longer production runs are expected.

### MODE OF MOULD USAGE

#### SLUSH MOULDING

The mould is completely filled with latex compound and after the desired thickness build up is achieved; the fluid latex compound is poured out leaving behind the mould with hollow deposit. Small amount of latex compound is left to gel and plug the pouring hole to ensure complete continuity of the article.

#### ROTATIONAL MOULDING

Just sufficient latex compound is poured in the mould and the mould is rotated about several axes simultaneously to ensure latex flow in all directions. The latex gels to produce hollow articles in which no holes are required. This method gives uniform deposits and the thickness of the deposit depends on the quantity of latex compound added. However, the method requires metallic alloy moulds and a special mould rotating device.

#### PLASTER OF PARIS MOULDS

Plaster of Paris is mixed with water to a smooth cream. The cream is cast in the former and allowed to dry and set. The porosity and hardness of the plaster mould depends on the ratio of plaster and water used for casting the mould. Typical Plaster of Paris: Water ratio recommended is 1.5: 1.0 but some times more water is used for perfecting the mould finish. Small amounts of calcium hydroxide retard the setting of plaster, which may be desired for better mould finish.

Generally two-piece moulds are prepared and the plaster slurry is poured down on to the surface of the former. Plaster of Paris expands on setting hence the surface must be lubricated for better separation from the former. The mould is assembled and filled with latex compound and allowed to stand for predetermined time to deposit desired thickness. Excess latex is poured out and a plug is inserted in the pour hold.

The mould is inverted so that excess latex remains in the region of pour hole. The latex deposit is dried and vulcanized at room temperature (since Pre-vulcanized latex has been used for the latex compound).

The moulds are never heated over 100°C, as they may explode. The time required for drying at room temperature could be 2 – 3 days whereas at 100°C it may take few hours.



A controlled degree of flocculation by addition of 5 % solution of aluminum alum at 25 pbw helps the water to drain away from the deposits more rapidly and discourages blocking of mould spores.

A dry desiccated mould should be used for each operation. About 25 to 30 castings are obtained from each mould after which the mold has to be discarded.

Generally only Prevulcanized latex is used for castings since it eliminates the curing stage. Filler loadings determine the hardness and flexibility of the products. Whiting at 30 pbw is used for semi-rigid products whereas about 250 pbw may be used for display models.

#### TYPICAL COMPOUNDING FORMULATIONS FOR CAST LATEX PRODUCTS: PLASTER MOULD

<u>Ingredients</u>	<u>PBW</u>
60 % NR Latex	167
20 % KOH Solution	2
20 % Polyethylene oxide condensate	0.2
50 % Sulphur dispersion	2
50 % ZDEC dispersion	1
50 % Zinc oxide dispersion	2
50 % Styrenated Phenol Emulsion	2
60 % China Clay Slurry	50 – 250
2.5 % Aluminium Sulphate	30 – 40

Cure : 30 min at 100°C

#### CASTING WITH METAL MOULDS

##### MOULDS

Die-cast aluminum moulds or stainless steel moulds are generally used. The mould material should be free from impurities such as copper, manganese, cobalt, etc. since such impurities cause product discoloration and promote accelerated aging of the product. The mould thickness will control deposit thickness of the heat-sensitive latex compound, which is normally used for the production of the article. Uniform mould thickness will produce article of uniform thickness and thus, where higher or lower thickness of the final product is desired; the mould thickness is adjusted accordingly.

Allowance of 10 – 15 % shrinkage of the final product is considered during mould design.

##### MOULDING PROCESS

The moulds are thoroughly cleaned and lubricated with a solution of paraffin wax and stearic acid in an organic solvent.

After solvent evaporation the mould is heated to desired temperature e.g. 85 – 90°C in hot air or hot water bath.

The mould cavity is then completely filled with latex compound and allowed to stand for a predetermined time e.g. 2 – 3 minutes to build up the desired deposit thickness. The excess latex compound is then poured out and the pour hole is plugged. The mould is then inverted to allow the residual latex to run down over pour hole region.



The mould and the deposits are then allowed to stand for 10 – 15 minutes to complete the setting of the rubber deposit and the excess latex is blended with the latex compound stock when it has reached room temperature.

The rubber deposits are then removed from the mould; dried at 45 – 50°C, washed in cold water and finally cured in hot air for 30 minutes at 100°C.

### TYPICAL HEAT SENSITIVE COMPOUNDING FORMULATIONS

#### FOR METAL CAST

#### MOULDED PRODUCTS (SOFT, FLEXIBLE MOULDINGS)

<u>Ingredients</u>	<u>PBW</u>	
	<u>A</u>	<u>B</u>
60 % NR Latex (HA)	167	-
60 % NR Latex (LA)	-	167
20 % Polyethylene oxide condensate	0.5	-
50 % Sulphur	4	4
50 % ZDEC Dispersion	2	2
50 % Zinc oxide dispersion	6	3
50 % Antioxidant dispersion	4	4
50 % China Clay Slurry	40	40
20 % Ammonium acetate	7.5	-
15 % Poly vinyl methyl ether	-	20

Cure: 30 min at 100°C

Note : The moulds to be heated to 90-100°C. Gel time approx. 2- 5 min depending on product thickness desired.

#### AFTER TREATMENT OF CAST LATEX PRODUCTS

The seam marks are removed by buffing.

Flash is removed by trimming followed by buffing or by cryogenic flash removal process.

The articles are washed thoroughly by water to remove all water-soluble salts and dried.

If a lacquer is to be applied on the product, the same should produce a film which is more flexible than the product (e.g. room temperature vulcanizable rubber lacquers are used for soft products whereas cellulose nitrate lacquers may be used for hard and rigid moldings).

Lacquers based on polychloroprene rubber or chlorosulfonated polyethylene (Hypalon) offer excellent weathering and ozone resistance to the products.



## 6. Misc Latex Products

### BATTERY SEPARATORS

Battery separators are micro porous ebonite products manufactured using acid resistance ebonite compounds based on latex.

Heat sensitive latex compound is prepared and filled in the moulds. The moulds are heated to gel the compound.

The wet gel is vulcanized in an autoclave under water for 4 hr at 160°C. The cured product is treated with hydrochloric acid to decompose sulfides. It is then washed and dried.

### TYPICAL COMPOUNDING FORMULATION

<u>Ingredients</u>	<u>PBW</u>
60 % NR Latex HA	167
20 % Polyethylene oxide condensate	0.5
50 % Sulphur dispersion	70 – 80
50 % Zinc oxide dispersion	8
50 % ZDEC Dispersion	2
50 % ZMBT Dispersion	2
20 % Ammonium acetate solution	10 – 25
20 % Ammonium polymethacrylate	5 – 10

### LATEX ADHESIVES

Latex adhesives are widely used for paper, leather, textile, metals, glass, ceramic tiles, etc.

Latex adhesives based on synthetic rubbers are used as bonding agents for synthetic fibers such as rayon, nylon, etc. in the manufacture of rubber products such as tyres, beltings, etc.

Latex adhesives offer several advantages over solvent based adhesives such as low cost, non flammability, absence of toxic solvents, possibilities of a wide range of solids contents and viscosities, possibility of depositing higher molecular weight polymers of superior aging resistance and better polymer penetration and wetting properties.

The disadvantages of latex adhesives are their susceptibility to freezing, tendency to shrink the textiles, tendency to wrinkle paper, lower water resistance, poor electrical properties, possible contamination and corrosion by metals, lower rate of drying, lower bond strength because of restricted inter-particle coalescence and the presence of surface active chemicals.

Latex adhesives are particularly suitable for application to porous surfaces which are easily wetted by water. Latex films once formed and dried cannot be removed by water or dilute alkali and nor can be refreshed or reactivated.

Even the brush or roller used for the application purpose is difficult to clean. (Generally, the brush or roller, which has to be used for adhesive application, is first rinsed with dilute alkali or in detergent solution before use and is thoroughly washed with the same solution immediately after use.

The adhesion bond is generally a 'mechanical' bond.

## LATEX ADHESIVES: COMPOUNDING

### POLYMER

Choice of polymer depends on the nature of the surfaces to be bonded and the service conditions of the product.

Cost and easy availability

Porosity and polarity of the surface and absence of electro static effects. (Polarity of the latex and surface to be bonded should match)

Copolymer lattices are more effective adhesives than homo-polymer lattices.

Polymers should have good heat and ozone resistance and moderate resistance to solvents.

Non-polymer constituents (other than water) to be considered for their possible effects on the surface/material to be bonded (e.g. ammonia content /alkali content in latex can corrode aluminum foils).

### ADHESION PROMOTORS

Aqueous solutions or dispersions of resins like casein, resorcinol formaldehyde can act as adhesion promoters. Polymer latex as hydrocarbon portion promotes adhesion with rubber phase and the resorcinol formaldehyde resin portion promotes adhesion with more polar textile material like rayon / nylon.

### TACKIFIERS

Tackifiers are used to improve surface tack life and to develop initial strength (quick grab strength) required for holding the surfaces of the adherence together so that the main bond strength develops over a period.

Tackifiers such as phenol formaldehyde resins, rosin esters, hydrogenated resin, terpene-phenol resins, and polyisobutylene are commonly used. Polyisobutylene and terpene phenol resins are used as tackifiers in pressure sensitive adhesions (e.g. self sticking labels, masking tapes). The tackifiers resins are used at 5 – 75 % by weight of adhesive films. At lower dosages the tackifiers improve tack and help in the retention of the flexibility of the bond. However, some times dosages higher than 50 phr are also used for further tack improvement and cost reduction with a compromise on reduced bond strength and reduced aging and solvent resistance.

Cooked/uncooked starches are widely used in paper adhesives. Starch is regarded as modifier of latex adhesive and cheap extender. Uncooked starches are used for the manufacture of heat sensitive adhesives to absorb water on application to heated surface and the adhesive develops 'quick grab' properties.

Small proportion of latex adhesive added into starch adhesive used for paper application make the starch bond flexible.

### PLASTICIZERS

Polymeric plasticizers in latex adhesives improve the low temperature flexibility of the bonds and impart tack.



Solvents such as benzene, toluene are some times added to improve the film forming ability of the adhesives. Plasticizers can be added up to 20 phr without any significant effect on the bond strength of the adhesive. Excessive usage of plasticizers can cause bloom, migration or weakening of the bond. Suitable plasticizers include mineral oil for general purpose polymers and ester plasticizers for CR, NR, PVA copolymer.

### CURATIVES

The decision to use curatives depends on whether vulcanization will offer any advantages such as increased bond strength or flexibility at low / high temperature, improved aging and water resistance or it may damage the adherents. Appropriate dosages of cross linking agents like Sulfur, Accelerators along with Zinc oxide, etc. can be used to vulcanize the latex film.

### FILLERS

Mineral fillers are added in latex adhesives to reduce the overall cost, to increase the stiffness and total solids content, to increase the solvent resistance, to modify the flow properties of the adhesives, to prevent undesirable tack, etc. Generally, filler loading is not over 20 – 25 parts by in some cases these may be over 100 parts.

### THICKENERS

Thickeners like methylcellulose, polyvinyl acetates, bentonite clays with quaternary ammonium salts are added to increase the adhesive viscosity when desired (e.g. application to vertical surfaces, latex paints, etc). The inclusion of thickener also suppresses the tendency of the serum to filter out of latex when the adhesive is to be applied on a porous surface. Use of thickener can affect water resistance and impart anti-colloidal properties to the adhesive.

### OTHER ADDITIVES

Antioxidants are included to retard the aging effects of adhesive bond. Surface active agents improve the latex stability. Anti-forming agents ensure smooth and even application of the latex adhesive film. Fungicides, corrosion inhibitors, flame retardant, colorants, deodorants are added in latex adhesives when required. Some of these may affect the bond strength hence due care must be taken to avoid excess dosage or eliminate these when not required.

All care must be taken while selecting the compounding ingredients for incorporation in the latex adhesive for a particular end application (e.g. food packaging applications).

LATEX ADHESIVES: TYPICAL COMPOUNDING FORMULATIONS.PAPER ADHESIVES (NR LATEX)

Ingredients	Parts by weight (Wet)		
	(1)	(2)	(3)
60 % NR Latex (HA)	167	167	167
15 % Ammonium Caseinate Solution	100	-	100
50 % Zinc oxide dispersion	4	4	4
50 % Sulphur dispersion	4	4	4
50 % ZDBC Dispersion	2	2	2
25 % Antioxidant dispersion	4	4	4
10 % Sodium Naphthalene formaldehyde sulphonate solution	5	-	-
15 % Starch solution	-	667	-
50 % China clay dispersion	-	-	100
Total Solids Content, %	42.5	24.3	44.9
Vulcanization at 100°C : 30 MIN			

PAPER ADHESIVES: (POLYVINYL ACETATE)

Ingredients	Parts by weight	
	(1)	(2)
55 % Polyvinyl acetate – unplasticized	182	182
Dibutyl phthalate	12	20
5 % methyl cellulose solution	10	-
5 % sodium carboxymethyl cellulose	-	20
67 % Whiting Slurry	-	45
67 % China clay slurry	-	45
10 % Sodium oleyl-p anisidine sulphnate solution	5	10
Total Solids, %	54.1	56.6
Filler Volume, %	0	17.8

Note: Dibutyl phthalate is added to PVA Latex drop by drop with stirring. This is followed by incorporation of the remaining ingredients.

SELF-SEAL ENVELOPE ADHESIVE

Ingredients	Parts by weight
60 % NR Latex (LA-TZ)	167
10 % KOH Solution	2
50 % ZDEC dispersion	1

ADHESIVES FOR METAL, CERAMICS, GLASS

Ingredients	Parts by weight	
	(1)	(2)
50 % Polychloroprene latex	200	200
15 % ammonium caseinate solution	133	133
30 % Zinc oxide dispersion	30	30
50 % Sulphur dispersion	-	4
33 % Thiocarbonyl dispersion	-	6
25 % Antioxidant 2246 dispersion	8	8
10 % Sodium silicate solution	2.5	2.5
Potassium dichromate (dry)	1	1
Total Solids, %	36.9	37.0

Note: Formulation (1) is non-vulcanizable and suitable for bonding paper to aluminum.  
Formulation (2) is vulcanizable and is suitable for aluminum to aluminum with High bond strength.

QUICK GRAB ADHESIVES

Ingredients	Parts by weight
60 % NR Latex (LA-TZ)	167
Toluene	3 – 5
50 % ZDC dispersion	2
Note: Stability is improved by adding thickener or by diluting with water.	

PREVULCANIZED LATEX FORMULATIONSPV- LATEX GENERAL PURPOSE

Ingredients	Parts by weight	
	Low Modulus	High Modulus
60 % NR Latex (HA/LA-TZ)	167	167
20 % Potassium Laurate solution	1.3	1.3
10 % Potassium hydroxide solution	2.5	2.5
50 % Sulphur dispersion	0.4	4
50 % ZDEC dispersion	0.4	2
50 % Zinc oxide dispersion	0.4	0.4

PV- LATEX HEAT RESISTANT

Ingredients	Parts by weight
60 % NR Latex (HA / LA-TZ)	167
10 % Casein Solution	5
25 % Non ionic surfactant	2
10 % Potassium hydroxide solution	3
50 % ZDBC dispersion	2
50 % Zinc oxide dispersion	2
30 % TETD dispersion	10
10 % Thiourea dispersion	10

## PV- LATEX FOR TRANSPARENT PRODUCTS

Ingredients	Parts by weight
60 % NR Latex (HA/LA-TZ)	167
20 % Potassium Laurate	1.3
10 % Potassium hydroxide	2.5
50 % Sulphur	2
50 % ZDBC	1

PRE-VULCANIZATION: 60°C – 4 hr.

### LATEX QUALITY CONTROL TEST PROCEDURES

#### TOTAL SOLIDS CONTENT

Weigh  $2.5 \pm 0.5$  gm NR Latex sample to nearest 1 mg in a tared weighing dish with the lid. Add 1 ml. Distilled water and distribute the latex over approx.  $32 \text{ cm}^2$  area. With the dish uncovered, dry the specimen in vented air oven for 16 hr at  $70 \pm 2^\circ\text{C}$  or 2 hr at  $100 \pm 2^\circ\text{C}$ . Replace the cover and cool in a dessicator to room temperature. Repeat drying and weighing until the mass is constant to 1 mg

Calculation :

$$\text{Total Solids, \%} = [(C - A) / (B-A)] \times 100$$

A = mass of weighing dish, gm, B = mass of dish plus original sample, C = mass of dish + dried sample

#### 2 DRY RUBBER CONTENT

Weigh approx 10 gm latex sample to nearest 1 mg into a porcelain evaporating dish (100 mm dia / 50 mm depth). Add distilled water to adjust solids content to approx 25 %. Add 80 ml of dilute (2 %) acetic acid with constant stirring over a period of 5 minutes to completely coagulate the latex.

Place the dish on a steam bath and leave undisturbed for 30 min (a clear serum should result. If not, repeat above procedure exactly as stated with excess quantity of dilute acetic acid).

Pickup coagulated latex particles with the main body of the coagulum, wash in running water and pass between rolls.

Repeat above procedure five times to reduce the sheet of coagulated rubber to 2 mm thickness.

Dry at  $70 \pm 2^\circ\text{C}$  in vented air oven. (If oxidation occurs, dry the sheet at  $55 \pm 2^\circ\text{C}$  or add an antioxidant to the latex before coagulation). Cool in a desecrator to room temperature and weigh. Repeat the drying and cooling until the mass is constant to 1 mg or less.

Calculation:

$$\text{Dry Rubber Content (DRC) \%} = (\text{Mass of dry coagulum} / \text{mass of sample}) \times 100$$

#### TOTAL ALKALINITY

Take approx 5 gm latex sample in a 10 ml glass weighing bottle having ground glass cap and weigh to nearest 1 mg. Pour in to a beaker containing approx 300 ml distilled water, re-stopper quickly to prevent losses of ammonia and reweigh. (The sample mass is equal to the difference between the two weighing). Insert electrodes of a calibrated glass electrode pH meter into the liquid and note the pH. Slowly and while stirring constantly, add 0.1 mol. Dilute HCl until a pH of 6.0 is reached (addition of 0.1 mol.HCl



should be in 1 ml increments and pH reading to be taken after 10 seconds of each addition. As the pH of 6.0 is approached, smaller increments should be added). Alternately, add 6 drops of 0.1 % solution of methyl red indicator into the sample and the solution is titrated against 0.1 mol HCl until the indicator turns pink against white background of slightly coagulated latex.

Calculation:

Total alkalinity, as  $\text{NH}_3$ , % =  $1.7 \times M \times n$  / W

M = mole of the standard HCl  
 n = volume of standard HCl in ml  
 W = original mass of the latex in gm.

If total alkalinity is desired based on water phase,

Calculation:

Total Alkalinity, as % of water =  $(1.7 \times M \times n) / W (1 - \text{TS}/100)$

Where, TS = % total solids content.

### COAGULUM CONTENT

*Apparatus* : 180 micron (80 mesh) sieve cut into the seat of a pipe union having inside diameter of 40 mm (approx)

Weigh 200 gm well stirred latex sample and dilute with equal amount of 5 % alkali soap solution (Potassium Oleate soap solution). Filter the mixture through the 180 micron screen and wash the coagulum retained on the screen with 5 % alkali soap solution. Finally, wash with distilled water to free from soap solution.

Remove the screen from the union and dry at  $100 \pm 2^\circ\text{C}$  for 30 minutes. Cool in desiccators and weigh. Repeat until the loss in mass between two successive weighing is less than 1 mg.

*Calculation*

Coagulum content, % =  $(m_1/m_0) \times 100$

$M_0$  = mass of test sample, gm.  
 $m_1$  = mass of coagulum, gm.

### pH

Use pH meter dependant on electronic measurements, and a glass electro calomel assembly for pH measurements between 8 – 14.

Calibrate the pH meter.

Take a convenient volume of latex sample in a beaker and adjust the temperature to  $23 \pm 1^\circ\text{C}$  by mildly agitating the sample beaker in a water bath at suitable temperature. Determine the pH and record the pH and temperature of the test.

KOH NUMBER

Apparatus : pH meter with electrometric measurements and a glass electrode Calomel assembly for pH determination (Range 8 – 14)

Reagents :5 % acid free formaldehyde solution (Dilute analytical grade formaldehyde to 5 % with distilled water and neutralize with 0.1 ml KOH using phenolphthalein indicator to faint pink color) 0.5 ml carbonate free KOH solution (Refer ASTM D-1076 for preparation).

Weigh accurately a sample of latex containing approx. 50 gm. Of solids in to a 400 ml beaker. Adjust the ammonia content to 0.5 % on the water basis by addition of 5 % formaldehyde (1 ml = 0.0189 gm NH<sub>3</sub>) while stirring.

Calculate the amount of formaldehyde solution for this adjustment as follows :

Formaldehyde solution (5 %) ml =  $W (100 - TS) (\% \text{ NH}_3 \text{ on water phase} - 0.50) / 189$   
 W = gm of wet latex sample, TS = % of total solids

Add water to dilute the latex to 30 % solids. Place the beaker containing latex near the pH meter and insert the titration electrodes. Determine the pH and record the results Add slowly 5 ml of 0.5 mol KOH solution while stirring and record the pH after 10 seconds after each addition. The end point of the titration is the point of inflection of the curve of pH vale Vs volume of KOH in ml. At this point, the slope of the curve (first differential) reaches a maximum and the second differential is zero.

Example: Following data is example of point of inflection determination (Readings are in the area approaching the inflection).

KOH Solution, cm <sup>3</sup>	pH	First difference $\delta \text{ pH} / \delta \text{ cm}^3$	Second difference $\delta (\delta \text{ pH} / \delta \text{ cm}^3)$
13.0	10.47	-	-
13.5	-	0.18	-
14.0	10.65	-	0.03
14.5	-	0.21	-
15.0	10.86	-	0.07
15.5	-	0.28	-
16.0	11.14	-	-0.04
16.5	-	0.24	-
17.0	11.38	-	-0.09
17.5	-	0.15	-
18.0	11.53	-	-

By the slope of the line from + 0.07 to -0.04 the intercept with zero gives a ratio of 7/11 of the distance between 15.0 & 16.0 cm<sup>3</sup> of KOH. The point of inflection is  $15.7/11 = 15.64$ .

Calculate KOH number (gm of KOH required to neutralise the acids present in 100 gm. Of solids in latex) as follows :

$$\text{KOH No.} = (\text{cm}^3 \text{ KOH} \times M \times 561) / (\text{TS} \times \text{mass of the sample})$$

TS = % of total solids, M = mole standard of KOH solution

OTHER TESTS

Density (Density Bottle)

Mechanical Stability (using high speed stirrers – 14000 rpm)

Viscosity (Brookfield Viscometers)

Sludge Content (centrifuge operating at  $12000 \text{ m} / \text{s}^2$ ).

Volatile Fatty acids

Boric acid content

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