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LATEXES by **Bob Dzikowicz**

R.T. Vanderbilt Company, Inc.
30 Winfield Street, P.O. Box 5150, Norwalk, CT 06856-5150
Telephone: (203) 853-1400
Fax: (203) 853-1452, Web Site: www.rtvanderbilt.com

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LATEXES

by **Bob Dzikowicz**

R. T. Vanderbilt Co, Inc.
Norwalk, CT

Author's Notes:

- The terms latex, latex rubber, and rubber latex are used interchangeably in this paper. They refer to tiny (measured in microns and millimicrons) droplets of rubber, called the oil phase, that are suspended in water. The water phase usually also contains water-soluble and -insoluble materials. In order to distinguish them from natural latex, manufacturers of synthetic latexes have identified their products as emulsions, dispersions, liquid dispersions, liquid rubber, etc. However, if they meet the criteria below they will be identified as rubber latexes.
- This paper will not discuss polymers suspended in water that do not possess what is commonly known as rubber-like qualities. Rubbery polymers, upon evaporation of the water, must (a) form films, (b) have the capacity to be stretched to at least twice their original dimension (100% elongation) while maintaining film integrity, and (c) have the capacity (through vulcanization) to return immediately to their approximate original dimension. This paper will therefore not include latexes of polyvinyl chloride, polyurethane, polyvinylidene chloride, vinyl pyridine, polyacrylics and polyvinyl acetates, or thermoplastic materials in general.
- The theories of vulcanization and oxidation have been reviewed in numerous technical papers. They are applicable to rubber deposited from latex as well as dry rubber, and will not be repeated here. Also, the terms crosslinking, vulcanization, and cure may be used interchangeably.

Latex Formulas

Rubber formulations or recipes are written in 100 phr (parts per hundred rubber) dry and wet. Most of the time, the terms *dry* and *wet* are omitted and the assumption is that *dry* parts are referred to, regardless of the concentration of the materials. However, there are instances when description must be explicit to avoid confusion; for instance, when the active concentration (activity) of an ingredient is not known, or is held to be proprietary. It would not be sufficient to instruct, "add 3 parts." Nor would it suffice to say, "add 3 parts wet." The correct instruction would be, "add 3 parts wet to 100 phr dry," or, as in the formula below, "add 3 parts wet to 166.7 parts latex wet." This allows the dialogue between rubber chemists or compounders to be specific.

Table 1: Rubber Latex Formulation (General Category of Ingredients)

| Concentration & Ingredients | Dry | Wet |
|--|------------|------------|
| 60% Latex Polymer | 100 | 166.7 |
| 33% Additional Stabilizer | 1 | 3 |
| 50% Activator Dispersion | 3 | 6 |
| 50% Crosslinker Dispersion | 1.25 | 2.5 |
| 50% Antioxidant Dispersion | 1 | 2 |
| 33% Surface Conditioner | 1 | 3 |
| 10% Thickener | 0.5 | 5 |
| 50% Other Materials | 5 to 50 | 10 to 100 |

A typical dry rubber latex formula does not list *wet* parts, does not identify the ingredient quantities as *dry*, does not include the words *dispersion* or *emulsion*, and *activity* is omitted (as in Table 2). This type of formula is shorthand. The assumption is that all dosages are *dry* parts and activity is immaterial. For instance, many *Activator Dispersions* (as in the formula above) are available in varying concentrations: 40%, 50% and 60% active. The compounder would then calculate the required number of wet parts by dividing 3 (the *dry* parts in the formula) by 0.4, 0.5 or 0.6, depending on the *Activator Dispersion* that was used.

Table 2: Typical Shorthand Latex Formula

| Ingredients | p/hr | Example |
|-----------------------|-------------|--------------------------------|
| Latex Polymer | 100 | NEOPRENE Latex |
| Additional Stabilizer | 1 | DARVAN [®] WAQ |
| Activator/Crosslinker | 3 | Zinc Oxide |
| Crosslinker | 1 | Sulfur |
| Accelerator | 1.25 | SETSIT [®] 104 |
| Antioxidant | 1 | VANOX [®] SPL |
| Surface Conditioner | 1 | DARVAN SMO |
| Thickener | 0.5 | a Polyacrylate |
| Other Materials | 5 to 50 | DIXIE CLAY [®] Filler |

INGREDIENTS

Latex Polymers

The broadest categories of latex polymers are natural rubber latexes and synthetic latexes. Natural rubber latexes include high ammonia latex, low ammonia latex and graft polymer latex.

In the *Hevea Brasiliensis* (rubber) tree, the latex is stabilized by protein. Once it is tapped from the tree, the natural protein is susceptible to attack by bacteria upon exposure to oxygen in the atmosphere. This degradation of the protein and

subsequent coagulation of the latex renders the “field latex” putrid and rancid. The field latex must therefore be preserved and fortified against bacterial attack, which is accomplished by immediately adding ammonia to the latex, since ammonia creates an environment in which the bacteria cannot survive.

Field latex contains approximately 30% rubber, 5% of natural protein, fatty acids and impurities, and 65% water. In this state, it would not be economically efficient for industrial use or for transportation. Centrifuging is the major means by which the solids concentration is increased from 30% to 60% and higher. Creaming, another method of layer separation, is also used, but to a lesser extent.

High ammonia latex is the result of increased stabilization by the addition of further ammonia following concentration of the latex. The additional ammonia raises the pH of the latex to approximately 11 to 12.

Low ammonia latex was developed because manufacturers objected to the noxious ammonia odor in their factories. A popular method to minimize the amount of ammonia in latex is to replace part of it with a combination of zinc oxide and the accelerator tetramethythyuramdisulfide (METHYL TUADS[®] (TMTD)). The pH of this latex is approximately 10 to 11.

Graft polymer latex¹ is a copolymer of natural rubber latex (polyisoprene) and polymethylmethacrylate. It is used primarily in the adhesives industry. The polymethylmethacrylate contributes specific adhesion as well as high modulus (immediate strength) to the natural latex.

Due to its superior physical properties, which are unmatched by any synthetic latex, the applications of natural latex are numerous. They include medical devices like condoms, surgeon and examination gloves, lineman gloves, thread used in clothing and undergarments, balloons, molded goods and novelties. However, the recent awareness that the natural protein stabilizer can cause allergic reactions has limited its use. Because of this consideration, natural rubber latex products have been replaced to some degree by synthetic rubber products, especially in unsupported examination gloves.

Synthetic rubber latexes include styrene butadiene rubber (SBR), acrylonitrile butadiene rubber (NBR), polychloroprene rubber (CR), butyl rubber (IIR), and synthetic polyisoprene rubber (IR). There are other specialized synthetic rubber latexes, such as HYPALON[®] latex and EPDM latex, but they will not be discussed because of their limited application.

SBR latex finds its main applications in foam, paper and coatings. While the carboxylated versions of SBR (XSBR) are supplanting conventional SBR latex because of their faster cure rate, the resilience, processing ease and economy of SBR latex keeps it a viable commodity. SBR is very compatible with natural rubber latex, and is frequently blended with it for use in the carpet backing and rug underlay industry. The ratio of rigid styrene to flexible butadiene can be adjusted to alter the physical properties of the latex.

NBR latex was for many years limited to solvent- and grease-resistant applications like paper coatings and non-woven gasketing materials. Due to the allergy concerns mentioned above, carboxylated NBR or XNBR latex is today the most popular synthetic latex alternative for unsupported examination gloves.

Polychloroprene (NEOPRENE) latex is the second most popular synthetic alternative to natural latex for unsupported examination gloves, and is increasingly used in household gloves. Weather balloons and medical breather bags are made from polychloroprene latex because of its good weather and aging resistance. It is also used in many types of coatings and adhesives.

Polyisoprene latex, having been experimental for many years, is gaining popularity in the glove dipping industry.

Butyl latex finds its greatest use in chemical-resistant applications, especially in supported chemical handling gloves and adhesives.

Stabilizers

Ionic stabilization cannot be discussed without an understanding of coagulation. The tiny droplets of rubber (the oil phase) that are suspended in a water medium (water phase) are kept separated by ionic charges in most cases. When the surface of the droplets is negatively charged, for instance, they will never coalesce, because “like charges” repel each other. When the ionic charges are intact and the droplets remain suspended and separated from each other, the latex is stabilized. When the ionic equilibrium is upset and the droplets coalesce or amalgamate, the latex is coagulated. Coagulation is not reversible.

Latexes can be stabilized anionically, as described above, cationically, by positive charges, or even nonionically. Anionic latexes are predominant in the latex industry. When an anionic stabilizer like DARVAN WAQ is dissolved in water, the negatively charged anions are of greater magnitude than the positively charged cations, and surround the rubber droplets so that they repel each other. Cationically stabilized latex would be just the opposite, but is no longer common. Latexes can also be protected physically with nonionic stabilizers that are normally long chain alcohols.² They simply form physical barriers between the droplets of rubber.

There is a fourth type of latex stabilizer called amphoteric.³ Its positive and negative ionic charges are of equal strength. It is an auxiliary rather than a primary stabilizer, reinforcing the charge that already exists on the droplet, whether positive or negative.

It is important to remember that being able to produce coagulation on demand is an essential processing property. Without it, no latex product could be manufactured. The degree of stability in latex must therefore be appropriate to withstand the rigors of mechanical and chemical processing, but not so as to prevent coagulation from taking place at a time and under conditions of the compounder's choosing.

During storage, mixing, and processing, latex stabilization is challenged by both physical and chemical outside forces: time, temperature, phase separation, pH drift, shear in mixing, pumping and coating techniques, addition of incompatible materials like some electrolytes, particles of a substantially different diameter, and dissimilar stabilization systems.

Natural rubber latex is stabilized by natural protein and the soaps formed when the added ammonia combines with the fatty acids in the latex. When the high ammonia content of natural rubber latex is undesirable, low ammonia latex can be substituted, in which part of the ammonia is replaced by an auxiliary stabilizer such as a combination of zinc oxide and tetramethylthiuramdisulfide (METHYL TUADS (TMTD)).

Synthetic latex is primarily stabilized with anionic soaps of the fatty acid and rosin acid type. These are added during the polymerization stage of manufacture to protect the newly formed latex rubber particles against the shear forces of mixing and processing. This is a major characteristic of synthetic latexes versus natural rubber latexes: they are highly stabilized.

In the coatings industry, the migration of water-soluble soaps to the film surface makes it difficult to overcoat or to coat successive layers of synthetic latex. The successive latex films do not “knit” together. The interlayer of stabilizer prevents the latex from becoming an amalgamated unit. The layers of latex film can frequently be peeled away from each other. This same migration of soap also prevents good surface bonding in adhesives.

In the dipped goods industry, it is often necessary to use an excess of external coagulants in order to overcome the effect of the synthetic latex stabilizers and build a suitable film thickness. In so doing, another problem is created, in that leaching times must be extended to remove the water-soluble stabilizer and additional coagulant.

Frequently, additional stabilizers are added to both natural and synthetic latex before compounding. An example is sodium lauryl sulfate. It is added when severe plant processing is anticipated: shear mixing, pumping, fabric impregnation. It is sometimes added when the holding or dipping tanks are large and the latex compound will remain in them for a long time, or to latex that will be prevulcanized, in order to protect against the increased temperature. Usually, the need for additional stabilizers to control the mixing of special ingredients into the latex has to be resolved in the laboratory.

Sulfated methyl oleate (DARVAN SMO) is a special stabilizer. It not only reinforces the ionic charges protecting the droplets of rubber in the latex, but has come to be recognized for its more specialized purpose use as a film conditioner.

Crosslinkers

Vulcanization creates a “memory” in a rubber polymer. After the stress or strain of distortion or stretching is removed, the polymer returns to its original shape. This is what distinguishes a rubber from a thermoplastic. It is accomplished by connecting the molecular chains of the polymer to each other.

Crosslinkers are the chemicals that connect these molecular chains. Since the chains are linked, a force is required to pull them apart. The strength of this force is a measure of the efficiency and number of connectors or crosslinks. The force required to stretch a crosslinked polymer to a specified elongation is called a modulus. The force required to completely separate a crosslinked polymer is called the tensile strength.

Sulfur is the primary crosslinker for most natural and synthetic rubbers. In polychloroprene (NEOPRENE), however, sulfur is the secondary crosslinker. Zinc chloride (zinc from zinc oxide and chlorine from the polymer) constitutes the primary crosslinker.

There are other crosslinking or vulcanizing systems. Carboxylated polymers are crosslinked with metal oxides.⁴ In peroxide curing⁵, free radicals are formed on the carbon chains by the excitation of decomposing peroxides. The free radicals formed connect with each other to create carbon to carbon crosslinks.

Activators

Sulfur alone will vulcanize (cure or crosslink) rubber latexes. However, at elevated temperatures, the process will theoretically take days, during which time oxidation would destroy the polymer before sufficient crosslinking could take place. Zinc oxide activates the crosslinking action of the sulfur. A sulfur/zinc oxide cure of a rubber latex can take place in a matter of hours at elevated temperatures, subject to the degrading effects of oxidation.

Accelerators

Accelerators have made latex a viable industry, and have made latex products readily available worldwide by reducing their cure time to minutes. Most accelerators for sulfur cures are nitrogen-bearing. They fall into classes called dithiocarbamates (BUTYL ZIMATE[®], SETSIT 9), thiurams (METHYL TUADS (TMTD), SULFADS[®] (DPTT)), sulfenamides (MORFAX[®]), and thiazoles (CAPTAX[®] (MBT), ZETAX[®]). The xanthates (PROPYL ZITHATE[®]) are an exception because they do not contain nitrogen. Guanidines (VANAX[®] DPG and VANAX DOTG) and thioureas (THIATE[®] U and THIATE EF) accelerate the zinc chloride crosslinking of polychloroprenes. Accelerators for metal oxide crosslinking in a carboxylic polymer are not necessary unless a dual system of metal oxide and sulfur vulcanization is required for optimum properties.

The combination of crosslinkers, activators and accelerators not only determines the rate of cure, as mentioned, but the state of cure. It is the responsibility of the latex chemist to optimize the desired physical properties of the finished article by manipulating the levels of the crosslinker, the activator, and the accelerator. In the case of natural rubber latex, vulcanization can take place in the colloidal state; rapid cures may therefore not always be desirable.

Antioxidants

Oxygen attacks and degrades latex rubber films in the same manner that it degrades dry rubber products. The process by which antioxidants deter oxidation is explained elsewhere in this book.

Of the two major types of antioxidants used for latex, the phenolic types (VANOX L) are found in most applications. While their performance is not as efficient as the amine types (AGERITE® STALITE® S), their minimal staining and discoloration are preferred for gloves, condoms, balloons, thread, foam and carpet backing. Amine antioxidants are limited to products where staining and discoloration are of no consequence, such as some adhesives and saturants for paper, and non-woven coatings that will be manufactured into gasketing products.

Antioxidant Synergists

The major difference in oxidation between latex films and dry rubber products occurs during the vulcanization cycle. Most dry rubber products are cured in closed molds which excludes air and, therefore, oxygen. Vulcanization and the subsequent development of physical properties are allowed to proceed uninhibited, without the interference of oxidation.

Most latex products are cured in circulating hot air ovens. From the very moment that the latex film dries and the water evaporates, it is open to attack by oxygen. During the cure cycle, vulcanization (crosslinking) can be inhibited by oxidation. At the same time that physical properties are being generated, oxygen attack is destroying them. Therefore, a good antioxidant synergist is required to minimize oxidation and permit crosslinking to build physical properties quickly and efficiently. 2-mercaptotoluimidazole (VANOX MTI), and its zinc salt (VANOX ZMTI), are effective antioxidant synergists for that purpose. They should always be used with an antioxidant.

Film Surface Conditioners

A common latex film defect, especially with synthetic latexes, occurs upon drying. The evaporation of water causes the film to shrink, which creates striations, valleys and "mud cracks" in the surface of the film. The exact cause of this phenomenon is unknown. A surface conditioner like sulfated methyl oleate (DARVAN SMO) can relieve the internal stress of the drying film to reduce shrinkage, thereby eliminating or decreasing these defects.

Thickeners

The viscosity of natural rubber latex is not easily modified, and the addition of compounding ingredients and decreases in pH makes it difficult to keep the viscosity under control. Except for SBR, synthetic latexes almost always require a thickening agent to facilitate dipping and coating operations. Viscosity plays a key role in building film thickness and suspending dispersed compound ingredients.

There are two general types of thickeners: polymeric and mineral. Water-soluble polymeric, whether synthetics like polyacrylates and polyvinyl alcohols or natural gums like cellulose and alginates, thicken latex by virtue of their very long molecular chains. Mineral thickeners like bentonite and smectite are very hygroscopic and swell in the presence of water to many times their original particle size.

Miscellaneous Ingredients

Fillers

The tensile strength of a thin latex film is rarely increased by adding fillers like clays, talcs and calcium carbonates. In use, latex articles will be stretched (elongated or extended), often to four or five times their original dimensions (400% to 500% elongation). Film integrity is therefore a very important feature of dipped goods like balloons, condoms, and gloves. Upon stretching, poorly dispersed fillers can be seen with the naked eye. They promote pinholes and interrupt the continuous nature of the latex film.

Latex products that will not be stretched to any significant degree, however, can be highly filled. Carpet backings can be filled with 50 to 200 phr calcium carbonate. Trowel-type cements like tile, wallboard and construction adhesives can frequently be loaded with similar amounts of DIXIE CLAY and NYTAL[®] talcs. Textile coatings can be filled because the substrate will determine the very small degree of elongation. In these applications, the main uses of fillers are to detackify surfaces and increase viscosity, as in caulks; they also reduce compound cost.

Carbon blacks are primarily used for pigmentation of the latex.

Resins

The major disadvantage of working with resins is their preparation. Since they are primarily oil-based, they must either be dissolved in hydrocarbon solvents or melted to achieve a pourable viscosity so that they can be emulsified (see the section on Dispersions and Emulsions). Hydrocarbon solvents or VOCs (volatile organic hydrocarbons) are not environmentally friendly, and there are significant safety risks when working with melted resins at elevated temperatures. Further, only resins with melting points below 100°C, the boiling point of water, can be considered. It is best to purchase the resins already emulsified or dispersed with a minimum of solvents, or no solvent at all.

Latexes can be compounded with resin emulsions to increase the tack of an adhesive. Rosin esters are popular tackifiers. Substantial amounts (20 to 50 phr) must be added, however, to achieve the benefit. At low levels, the tackifying effect will be masked by the combination of emulsifiers and stabilizers in the latex system.

Modifying resins like phenolics, terpenes and hydrocarbons⁶ (VANTACK[®]) can be used in latex adhesives for specific adhesion to substrates like textiles and plywood in order to create laminates or to improve cohesive strength.

Resorcinol formaldehyde resins are prepared in water systems. When mixed with some synthetic latexes, they provide excellent adhesion to cotton, rayon,

and blends of cotton with nylon or polyester textiles. Resorcinol formaldehyde latex (RFL) is a technology career in itself.⁷ (See the section on Textile and Non-Woven Saturants.)

Fire Retardants

Some materials, when added to a latex compound, impart a degree of fire resistance to the dried film. These fire retarding compounds can be used to treat textile and upholstery products, rendering them, in turn, fire retardant. Polychloroprene is the latex of choice because the polymer contains approximately 35% of chlorine by weight. Hydrated alumina, chlorinated paraffin, antimony trioxide, phosphates and other halogen containing chemicals are fire retardant additives for latex. Mineral fillers, mentioned above, can be considered fire retardants, but they do so simply by diluting the amount of flammable polymer.

Plasticizers and Waxes

The major consideration when a plasticizer is used is its compatibility with the polymer. Plasticizers are not popular additives for latex because they tend to migrate to the surface of a drying film even when they are compatible. Plasticizers can soften a latex film, significantly decreasing physical properties.

Waxes are sometimes used in small amounts to decrease tack and increase ozone resistance in static applications. The emulsification of a wax poses the same problems as that of a resin. Wax emulsions are usually of very low solids content.

UV Reflectors and Absorbers

Ultraviolet light tends to discolor latex film. Opacifiers like carbon black and titanium dioxide are UV absorbers and reflectors, respectively, and are usually the best protection. When neither of these can be used, chemicals that absorb UV light can be considered. Those that are available for this purpose vary in effectiveness. Each must be evaluated for the specific compound and application intended; there is no across-the-board recommendation.

In addition to its function as an antioxidant synergist, zinc 2-mercaptotoluimidazole (VANOX ZMTI), has significantly improved the resistance to discoloration of latex films when exposed to UV light.⁸ It is not known whether it functions as a UV reflector or absorber.

Antiozonants

Waxes (VANWAX[®]) can protect latex films in static conditions, as mentioned above, but most applications for latex articles are dynamic, requiring them to be flexed. This makes them more susceptible to ozone attack. The most effective antiozonants are the p-phenylenediamines (VANOX 6PPD), which, unfortunately, severely discolor latex film, and therefore are not a popular compounding ingredient.

DISPERSIONS AND EMULSIONS

Generally, neither dry powders nor water-insoluble liquids like oils can be added to latex without disrupting the colloidal balance. Both must be processed

into a form that will be miscible with the latex, as a dispersion and an emulsion, respectively. The commonality is to reduce the size of the particles or droplets and to protect them so that they:

1. will be compatible with the latex colloidal system,
2. can be dispersed uniformly throughout the latex, and
3. will not agglomerate or coalesce.

Dispersions

A dispersion is prepared by grinding the powder in a ball mill or attritor, with water, a dispersing agent, and a suspending agent (thickener or viscosity modifier). The use of pH modifiers and wetting agents is optional. It is the use of these materials in combination at different levels that distinguishes an experienced latex chemist from a novice. A typical 50% active accelerator dispersion recipe is shown in Table 3.

Table 3: Typical Accelerator Dispersion

| Ingredient | Parts | Example |
|----------------------|--------------|------------------------|
| Water | 47.6 | ----- |
| pH Modifier | 0.1 | Sodium Hydroxide |
| Dispersing Agent | 2.0 | DARVAN 1 |
| Accelerator (Powder) | 50.0 | BUTYL ZIMATE |
| Suspending Agent | 0.3 | VAN GEL [®] B |
| Total | 100.0 | |

A wetting agent can be used to reduce the surface tension of the water to allow the solid particles to wet out.

While ball mill grinding and attritor grinding are different operations, the principle is the same: a solid particle is trapped between 'stones' that collide, crushing the particle and reducing its size. With continual grinding, all the ingredients become homogeneous and can be added to the latex.

Emulsions

An emulsion is prepared by reducing oil droplets to microscopic size in a medium that will be water-miscible. In other words, the oil becomes part of a soap. It is usually made by blending a water phase and an oil phase under high shear. A typical 50% emulsion recipe is shown in Table 4:

Table 4: Typical Emulsion Formulation

| Ingredient | Parts | Example |
|-------------------|--------------|---------------------|
| Part A | | |
| *Water | 41.7 | ----- |
| *Alkali | 0.3 | Sodium Hydroxide |
| 12% Thickener | 5.0 | Sodium Polyacrylate |
| Part B | | |

| | | |
|-------------|------|--------------------|
| Antioxidant | 50.0 | AGERITE SUPERLITE® |
| *Fatty Acid | 3.0 | Oleic Acid |
| Total | | 100.0 |

The ingredients prefixed with an asterisk (*) above are the basic materials that make up a soap. Alternate formulations can be prepared by using synthetic emulsifying agents like sodium alkyl sulfate (DARVAN WAQ), which was previously identified as a stabilizer. As a soap, it performs a dual function. The synthetic emulsifying agent greatly simplifies the process. One need only dissolve the soap in water, add the oil, and then pass the mixture through a homogenizer.

APPLICATIONS

Dipping

The largest application by far for latex is the dipped goods industry. This is the process by which:

1. a latex compound is made to coagulate on a former or dipping mold,
2. the latex compound is dried and vulcanized on the former, and
3. the finished product is stripped from the former.

Unsupported gloves and balloons are made by the coagulant dip process. The former, usually ceramic, is dipped into a first bath filled with an electrolytic solution. This solution (usually calcium nitrate or calcium chloride), upon drying, leaves a uniform coating on the former. The coating is totally incompatible with the latex. Therefore, when the former is dipped into a second bath of the latex compound the coating destroys the latex stability in its immediate area. When the former is removed from the bath it is coated with a gelled film of latex compound. A third bath filled with warm water acts as a leaching tank. In it all water-soluble materials like coagulants, stabilizers, dispersing and wetting agents, pH modifiers and water-soluble thickeners are removed and carried away from the gelled film on the former. Then the former proceeds to a circulating hot air oven where the film is dried and vulcanized. There is some residual tack to the latex product. Dusting and/or chlorination operations are designed to remove the residual tack of the polymer and allow for the easy donning of gloves. They can be performed on line (before the product is stripped from the former) or as a post-treatment. Their use also permits the packaging of many gloves in the same box without them sticking to each other.

A similar process is involved in heat-sensitized dipping. The difference is that a heat-sensitizing chemical is compounded into the latex. The former, usually aluminum instead of ceramic, is heated or warmed. When the warm former is immersed in the latex compound, the heat sensitizer is activated to coagulate the latex on the former. This eliminates the need for an external coagulant and the coagulant dip bath.

Thin-walled latex products like condoms and membranes are dipped and processed without the use of any coagulants. This is called straight dipping.

Supported gloves like chemical handling and industrial gloves are manufactured without the use of coagulants, but the former is covered with a fabric called a liner (the support for the coating). The assembly is dipped in the latex compound and dried and cured in an oven. The gloves are rarely leached to remove water soluble materials.

Controlling these processes with regard to compound stability, viscosity, coating weight pick-up, line speed, and drying and curing times are essential skills for manufacturers, and matters beyond the present discussion. Nevertheless, the reader can appreciate the importance of technique in dipping operations.

Extrusion

Latex extrusion is the method by which expandable thread for garments and for some medical tubing is produced. The manufacture of thread is the second largest application for natural rubber latex. The latex compound is continuously pumped through an orifice directly into a mild acid bath that immediately gels the latex. This gelled or coagulated latex is drawn through the bath and into a drying and curing oven prior to being washed and wound onto a spool. The principle is straightforward, but in practice the operation must be well-designed and monitored closely. The nature of the small diameter thread demands it.

Virtually all thread is produced from natural rubber latex because of its very high wet gel strength and ease of coagulation. Acetic acid is normally used in the bath because of its relatively low cost and effectiveness. The acid bath can be easily disposed of after neutralization with mild alkali, and is therefore environmentally friendly.

Textile and Paper Coatings

Latex coatings are generally metered onto continuous webs of textiles by knife-over-roll (KOR) techniques. The web is then drawn into an oven for drying and/or curing. Upon exiting the oven it is collected onto a wind-up roll.

Paper webs are normally coated by a transfer process. Rather than applying the coating directly to the paper, a transfer roll is partly immersed in the latex compound. As it turns in the opposite direction of the moving web, it transfers the coating onto the paper. Instead of passing through an oven to dry, the paper web is passed over rotating heated cylinders, called drying cans, that evaporate the water.

Tapes of all kinds are manufactured by both of the above methods when the latex coating is an adhesive. Rolls with narrow width, sometimes less than one inch wide, are slit from a web that can be sixty inches wide.

Textile and Non-Woven Saturants

Continuous webs are drawn through a bath of latex compound. The excess is then removed by either squeeze rolls or offset knives (dull, not sharp). Specific latex compounds can impart fuel resistance, fire resistance, waterproofing, etc. to non-wovens. Gasketing materials are manufactured in this way.

Textiles can be impregnated with resorcinol formaldehyde latex (RFL) adhesives. These saturated fabrics are subsequently coated or calendered with films of rubber. Upon high temperature molding, the RFL activates, providing tenacious adhesion between rubber and fabric. Automotive and conveyor belts are made by this process.

Foam

Polyurethane foam has supplanted latex foam in many areas due to its lower cost and ease of processing. However, high quality latex mattresses, pillows and foamed carpet backings are still manufactured.

Mattresses and pillows can be manufactured by mechanically frothing the latex compound and filling a mold cavity. The latex compound is then gelled and the cell structure stabilized (see below). Vulcanization is accomplished with steam, after which the foam article is extracted and washed. This is the Dunlop process. In the Talalay process the latex compound is expanded into foam by the catalytic decomposition of hydrogen peroxide and/or by pulling a vacuum on the closed mold. It is quickly frozen in place by rapidly lowering the temperature, and gelled by introducing carbon dioxide into the closed mold. Combinations of these two methods are sometimes employed.

Spread foams are commonly used on carpet backing. The latex compound is mechanically frothed and metered onto the carpet that moves as a web under a coating knife. Gelling agents and stabilizers are employed to hold the cell structure of the foam in place until vulcanization is complete. The process is continuous. Sodium silicofluoride is a common gelling agent; potassium oleate is a common cell structure stabilizer. Both are also used in the Dunlop process.

There are of course variations in the above techniques and the details of each process, such as the amount of gelling agent and stabilizer used, and the precise timing of coagulation. These refinements are generally trade secrets.

Paper

The manufacture of paper is the most notable example of latex used as a binder for other materials. Wood pulp, rags and various fibers are shredded and mixed with latex in an operation called "beater addition". When the latex and pulp are sufficiently homogeneous, the latex is coagulated, usually with alum. The mass is pressed and squeezed by mill rolls into a continuous sheet. This sheet, carried on a web, is further compressed, drained and dried until it passes through rolls with decreasing nip space that provide the desired thickness.

Adhesives

Like dry rubber or solvent adhesives, latex adhesives can be engineered with resins and modifiers. Some latexes are especially suited to adhesives. For instance, natural rubber has inherent tack and is used with few other modifiers (antioxidants are essential, however) for envelope sealing. Polychloroprene (AQUASTIK®) latex can be designed for pressure destabilization known as "quick break". Simply applying pressure coagulates the latex. Quick break adhesives

are used in the packaging and construction industries. Coatings of rubber can be adhered to textiles by the use of resorcinol formaldehyde latex (see above).

Molding

Toys and novelties are made by a process that resembles the mirror image of dipping. Instead of dipping the mold or former into the latex, the latex is poured into the mold and then removed, leaving a thin latex film on the inside of the mold. When it dries and the mold is opened, a toy or novelty is extracted which conforms to the inside of the mold.

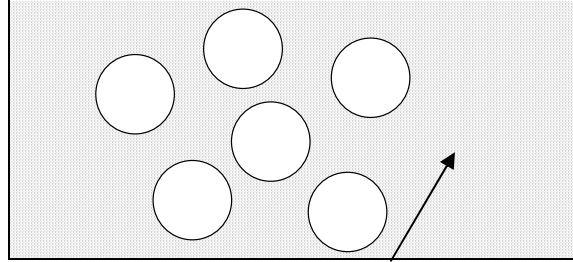
PREVULCANIZATION, MATURATION AND PRECURE

Natural rubber latex can be crosslinked in the colloidal state. This process is called prevulcanization. When the water is removed from the prevulcanized film or finished article, a degree of crosslinking has already occurred. The film should not be fully vulcanized; however, the crosslinking that has occurred enables the manufacturer to decrease the time required for an optimum cure in the circulating hot air oven. An additional benefit is that less time at elevated temperatures means less opportunity for oxidation degradation.

Prevulcanization is accomplished by introducing the dispersed ingredients of the cure system into the latex and elevating the temperature for a period of time. Through the use of ultra accelerators like the dithiocarbamates, the temperatures and the holding periods have been reduced. This advance in latex technology does not come without the introduction of a new consideration, an increase in the maturation rate.

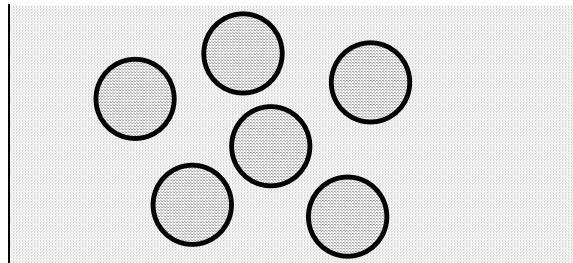
Maturation is the slower but continuous crosslinking that takes place at room temperature with ultra accelerators. When crosslinking proceeds too rapidly during maturation, the compound will be difficult to process, the viscosity will increase, and the resultant dried films will have poor physical properties. This advanced and undesirable state of crosslinking in colloidal suspension is termed precure.

Professor C. C. Ho (Department of Chemistry, University of Malaya) has proposed⁹ a mechanism that best explains the relationship between prevulcanization, maturation and precure, and their effect on film formation. A detailed examination of the mechanism is beyond the scope of this chapter, but the illustrations in Figures 1 - 4 depict how the "shells" of latex particles in colloidal suspension are crosslinked in sequence.



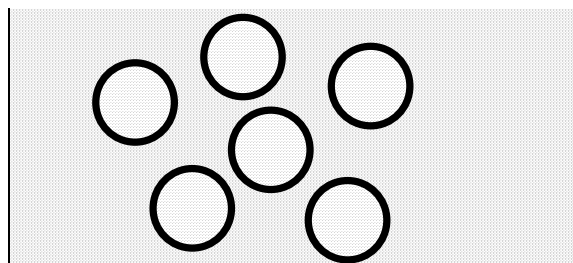
Particles dispersed in aqueous phase are separate, uncrosslinked, and homogeneous throughout.

Figure 1: Latex Particles in Colloidal Suspension



Dispersed particles, still separate but lightly crosslinked.

Figure 2: Particles with Pre-vulcanization

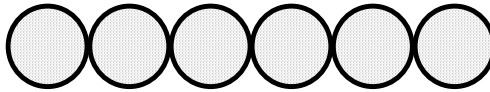


Particles with crosslinked surface and very slightly crosslinked interior.

Figure 3: Particles with Precure



Upon drying, precured particles agglomerate and form only a weak film because the thick particle skin interferes with homogeneous vulcanization.



Prevulcanized particles agglomerate and form a good film with homogeneous crosslinking.

Figure 4: Film Formation Contrasts

While the use of prevulcanization is very desirable for more efficient latex processing, a careful balance must be struck in the maturation process in order to secure the advantages of prevulcanization without the high risk of continuing into precure, with its negative effect on final film properties.

CURRENT LATEX ISSUES

Allergic Reactions

Medical devices such as surgeon and examination gloves, condoms, and tubing are under close scrutiny by the US Food and Drug Administration (FDA). A very small number of individuals are allergic to the innate protein in natural rubber latex. Cases of individuals going into anaphylactic shock due to contact with natural rubber medical devices have been reported. This rare reaction is a Type I allergy and is very severe. A more common allergic reaction, affecting a small percentage of the population, is Type IV allergy where the major symptom is skin irritation. It has been found that individuals not inherently allergic to the protein can develop a Type IV allergy over time by chronic contact with natural rubber latex products.

Synthetic latex medical gloves that contain no protein have to some degree replaced natural rubber latex gloves. This would seem a logical alternative but it is not an ideal solution. No synthetic latex, to date, can provide the superior barrier protection that is afforded by natural latex due to its outstanding physical properties. Also, protein is not the only source of allergies. Common compounding ingredients of natural and synthetic latexes, especially accelerators, can also cause Type IV allergic reactions.

New Technology

The above concerns have sparked a variety of new technologies, including:

*Protein Reduction*¹⁰

Natural rubber “field” latex contains approximately 30% rubber. The non-rubber portion is mostly water, with a small percentage (less than 5%) of protein,

fatty acid and impurities. Double and triple centrifuging, and modified creaming techniques, significantly reduce the protein content, but a method to remove 100% of the protein has yet to be found. If this were possible, however, the latex would be less stable.

*Enzyme Treatment*¹¹

Certain enzymes, when added to colloidal natural rubber latex, have the ability to chemically digest the proteins, reducing them to smaller units and rendering them unable to cause allergic reactions. This enzyme treatment of natural rubber latex is in use today, but not universally.

*Finished Product Treatments*¹²

Immersion of natural rubber medical devices into various chemical salt solutions has been shown to significantly reduce the protein content of the processed article. This leaching process is called protein extraction.

*Coating*¹³

A coating on the inside and/or the outside of a natural rubber medical glove provides a barrier through which, in theory, the protein cannot pass. This would protect both the wearer and patient.

*Guayule*¹⁴

Guayule (pronounced why-you'-lee) is a latex that is naturally produced by the *Parthenium Argentatum* shrub native to the southwest United States and Mexico. The US Department of Agriculture is sponsoring research on the cultivation of the shrub, the harvest of the latex and its processing into useful products. The protein in guayule is different than that of *Hevea Brasiliensis*, and is believed to cause no allergic effects in humans. While the inherent physical properties of guayule do not approach those of natural rubber latex, work is continuing to improve them through compounding and vulcanization techniques.

*Peroxide Vulcanization*¹⁵

Molded dry rubber products can be peroxide (VAROX[®])-cured because oxygen is excluded from the vulcanization process. Curing of latex products, however, is normally accomplished in a circulating hot air oven. The oxygen atmosphere prevents free radical, carbon to carbon crosslinking. Recently, a process for the peroxide curing of both natural and synthetic latexes in an oxygen-free environment has been developed. With this proprietary process¹⁶, Type IV allergies due to sulfur- and nitrogen-bearing chemicals are eliminated. It has also been claimed that the allergenic protein content of natural rubber latex products is significantly reduced.

* * * * *

This article is a revised version of Chapter 7, as originally published in "Fundamentals of Rubber Technology", copyright 2003 by Technical Consulting Services, in association with the Rubber Division, American Chemical Society. R.J. Delvecchio, Editor.

R.T. Vanderbilt trademarks have been substituted for generic chemical names where appropriate. A glossary of latex terms has been added for reference to help assimilate the new technologist to latex terminology.

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¹³ United States Patent, 5,780,112, Pugh and Culp (July 14, 1998)

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Latex Glossary

Activity – The amount of functional material in a latex, dispersion or emulsion expressed as a percent of the total composition. Activity differs from “solids concentration” in that surfactants and auxiliary chemicals are not included.

Attritor – A mill designed for the wet grinding of powders to prepare dispersions. Grinding reduces the particles of the powders to a very small and uniform size (see Grinding Media, Stones).

Ball Mill – Sometimes called a pebble mill, a ball mill performs the same function as an attritor but in a different manner (see Grinding Media, Stones). Technically, the ball mill is the machine that rotates the ball mill jar.

Beater Addition – A process for making paper.

Centrifuging – A mechanical process for concentrating 30% field latex to 60% and higher. The operation relies on the difference in specific gravity between water (1.0) and the rubber polymer (0.91).

Chlorination – A treatment for latex articles to remove residual tack and reduce surface friction. This treatment facilitates the donning of latex gloves.

Coagulant – A chemical that is incompatible with the stabilization system of the latex. It destroys the ionic charges that surround the rubber particles and allows them to gel into a continuous film.

Coagulant Dipping – A manufacturing operation that employs a coagulant to deposit a rubber coating on a mold or former. Most latex gloves are manufactured in this manner.

Colloid – An intermediate state between a true solution and a suspension. Latex contains both suspended rubber particles and surfactants and other water-soluble chemicals.

Concentration – The amount of active and non-active ingredients in a latex, dispersion or emulsion, expressed as a percent of the total composition. It differs from “activity” in that all auxiliary and modifying materials, and impurities, are included.

Creaming – A chemical process for concentrating 30% field latex to 60% and higher. Like centrifuging, it depends on the difference in specific gravity between water (1.0) and the rubber polymer (0.91). Creaming agents are added to vessels containing field latex to hasten phase separation.

Dipping – The general term for the manufacture of latex articles by immersing formers in compounded latex. When the formers are withdrawn, they are covered with a continuous film of latex.

Dispersing Agent – A chemical that is used to keep solid particles in a dispersion from agglomerating or joining with other particles to form a cluster. They are usually electrolytes that separate the individual particles with like charges.

Dispersion – Solid particles suspended in water. A dispersion is the required medium for adding water-insoluble powders to latex.

Dry Parts – The amount of active ingredient in a dispersion, emulsion or solution that is added to 100 active parts of a latex.

Dunlop Process – A process for making latex foam articles.

Emulsifying Agent – A soap or an essential ingredient of a soap that is used to separate the droplets of an oil phase medium in water. A necessary ingredient for making an emulsion.

Emulsion – Droplets of oil, rubber and other water-immiscible materials suspended in water.

Enzyme Treatment – A process for treating natural rubber latex in order to reduce the allergenic effects of the protein.

Extrusion – A process for making latex thread.

Field Latex – Natural rubber latex as it is collected from the rubber tree.

Former – Sometimes called a “mold” or an “external mold”, a former is a shaped device used in the dipping process. A wet-gelled film of compound covers its surface after it has been immersed in latex.

Gel – Latex that has been uniformly coagulated, coalesced or destabilized while still in the colloidal state.

Gelling Agent – A chemical that uniformly destabilizes latex during the manufacture of useful articles.

Graft Latex – A term associated with a blend of natural rubber latex and polymethylmethacrylate.

Grinding Media – The flint stones or ceramic spheroids and ellipsoids used in attritors and ball mills for wet grinding. When they are agitated, solid particles caught between them are reduced in size.

Guayule – Latex harvested from the *Parthenium Argentatum* plant which is native to the southwest United States and Mexico. It is a potential alternative to *Hevea Brasiliensis* latex.

HA Latex – High ammonia latex.

Heat-Sensitized Dipping – A process for manufacturing latex articles by which gelled rubber films cover formers that have been preheated.

LA Latex – Low ammonia latex.

Latex – Tiny droplets of rubber polymer suspended in a water medium.

Leaching – A manufacturing process for removing surfactants and coagulants from rubber articles by immersing the gelled or dry (post leaching) films in a warm water bath.

Maturation – The slow colloidal crosslinking of a latex compound at room temperature.

Mold – A shaped device in the configuration of the finished article, upon whose surface a film of latex compound collects. The mold can be internal or external depending on which surface, inner or outer, the film is deposited (see Former).

Mud cracks – The valleys or striations in a latex film that are caused when the water is evaporated and the film shrinks.

Pebble Mill – See Ball Mill.

Phase Separation – The separation of a latex or an emulsion into distinct layers: one is comprised of water and water-soluble materials while the other predominantly consists of oil, rubber and water-immiscible materials.

Pinholes – Small holes in a latex film. Sometimes the films need to be stretched in order to observe the pinholes.

Precure – 1. The colloidal crosslinking in a latex compound that takes place during maturation. It is frequently measured by the chloroform test. 2. The random, undesirable and uncontrolled crosslinking that takes place in a latex compound at room temperature. It is evidenced by a rapid increase in viscosity.

Prevulcanization – A manufacturing process to initiate desirable, homogeneous and controlled colloidal crosslinking of a latex compound.

Protein – Nature’s latex stabilizer.

Quick Break – The rapid coagulation of latex under pressure. A term frequently used for the relative development of tack in a latex adhesive.

Stabilizer – 1. A chemical, natural or synthetic, used to preserve the integrity of a latex by preventing it from coagulating. 2. In the manufacture of latex foam, it is the chemical or agent that prevents the gel structure from collapsing prior to the evaporation of the water.

Stones – A colloquialism for “grinding media” resulting from the original use of flint stones in pebble mills (see Grinding Media).

Straight Dipping – A manufacturing process for latex articles that does not use coagulants or heat sensitizers. Sometimes called Dip and Dry. Thin-walled condoms are manufactured by this method.

Surfactant – A class of chemicals added to a latex, dispersion or emulsion to modify the water medium, the suspended particles or the interface between the two. Within this general classification are stabilizers, dispersing agents, wetting agents, foam and surface tension modifiers, thickening and suspending agents, soaps and emulsifiers.

Suspending Agent – Sometimes called “thickener”. A material, natural or synthetic, that increases the viscosity of the latex, dispersion or emulsion. The small solid or liquid particles are thereby suspended in the water medium.

Synergist – A material that does not perform a function by itself but improves the performance of the primary material. An antioxidant synergist is the best example. While not an antioxidant, the synergist improves its performance.

Talalay Process – A manufacturing process for latex foam.

Thickener – See Suspending Agent.

Viscosity – A measured resistance to flow. In simple terms it is a description of pourable liquids: molasses is a high viscosity material and water is a low viscosity material.

Wet Parts – Regardless of the activity or concentration, it is the total amount of a dispersion, emulsion or solution added to 100 active parts of latex.

Wetting agent – Sometimes called a “detergent”. A chemical that reduces the surface tension of water. In dispersions, it allows for the rapid incorporation of powders into water. In adhesives and coating compounds it is a rheology modifier and allows increased flow over or absorption into a substrate.

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