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DEPROTEINIZATION OF NATURAL RUBBER LATEX: RECENT DEVELOPMENTS

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Deproteinised NR latex

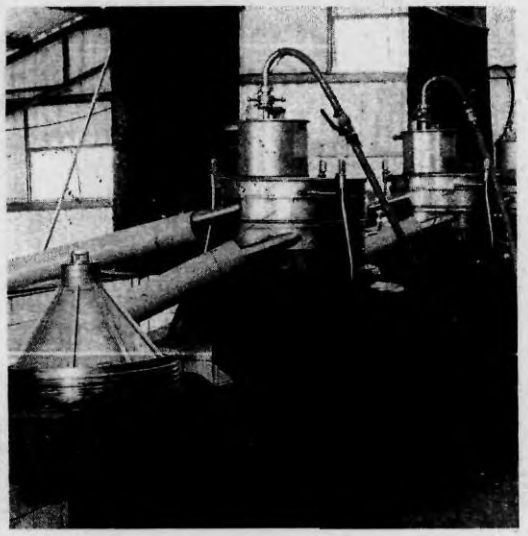
The most abundant non-rubber constituents (excluding water) in fresh latex are proteins, lipids, quebrachitol and inorganic salts. The total protein content of fresh latex is approximately 1-1.5% of which about 25 %

is absorbed on rubber particles. These water soluble proteins are to be eliminated as much as possible to minimize the protein allergic reactions. Centrifugation, enzymatic deprotenization, leaching and chlorination are the most popular methods adopted for deprotenization of Natural rubber latex(NR latex)/products. Extractable protein (EP) in natural rubber latex can be minimized at two stages. First is in the latex stage itself, in which the raw material is treated to reduce the amount of proteins. The second is in the product stage where the latex products are subjected to various treatments such as leaching in water, polymer coating etc. in order to reduce the protein content.

Latex stage deproteinization

Single and double-centrifuged latex

Centrifugation is the most important method adopted for the concentration of field latex. Dilution of the single centrifuged latex followed by re-centrifuging reduces the amount of soluble protein content of the concentrate. Films made from double centrifuged latices have lower EP content compared to the films of single centrifuged latex concentrate. However, the films of double centrifuged latex still require leaching for further reduction of the EP content and the additional cost of production diminished



the acceptance of double centrifuged latex in industry. Re-centrifuging of prevulcanized latex is also found to reduce the EP content when compared to normal prevulcanized latex.

Enzymatic deproteinization

Enzymes are highly specific proteins that catalyze chemical reactions. The antigenic potential of NR latex can be reduced by treating the latex with a proteolytic enzyme to

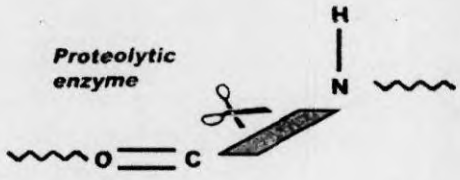


Figure 1. Digestion of proteins with proteolytic enzymes

digest the protein into small pieces (Figure 1). Deproteinization of *Hevea* latex can also be conducted by proteolytic enzymes such as ficin, trysin, protease, bromelan and pepain. Certain drawbacks associated with enzymatic deproteinization are (1) low level of deproteinization (40-50%) under normal conditions (2) selective deproteinization and hence inconsistency in the process and (3) high level of dilution required for latex (3%) which ultimately leads to low PRI.

An enzymatically produced low protein latex concentrate (Loprol) has been developed by RRIM, Malaysia. Though Loprol could meet specifications of examination and surgical gloves, it could not find market due to the high cost of production, requirement for additional centrifugation etc. Other commercially available low protein latices are Laptex (Revertex), Selatex, Startex (Thailand) and Allotex (Indonesia).

Deproteinisation using radiation process

About 25% of the proteins, including the enzyme required for rubber bio-synthesis, are bound to the latex particle surface. During irradiation of natural rubber latex, this particle bound proteins undergo disintegration which later get washed away during centrifuging leading to deproteinized latex. Hence the deproteinized latex can be prepared from NR latex by irradiating the field latex with γ -radiation to a total dose of 20 kGy followed by diluting the latex to

Table 1. Variation of protein content with γ -radiation

Process	Protein content (mg/g)	
	Cream phase	Serum phase
Field latex (after centrifuging)	1.20	11.30
Field latex (after centrifuging & irradiation)	4.40	--
Field latex (after irradiation & centrifuging)	0.60	13.86
Field latex (after irradiation, dilution and centrifuging)	Not detected	14.01

28-30 drc. This diluted latex is then centrifuged which will give concentrated latex almost free of soluble proteins. Table 1 illustrates the variation of soluble protein at each step in the deproteinization process.

Product stage deproteinization

Leaching Process

Leaching is an essential process in the production of almost all latex products. Leaching removes the excess coagulants, water soluble non-rubber materials such as proteins and residual compounding ingredients from products. This imparts good physical properties and better film clarity to the products. Leaching can be done either to the wet-gel in the online or to the dry-film in the off-line process.

In the production of latex examination gloves, wet-gel leaching often carried out for a period of several minutes, usually 1-10 minutes in a continuous chain dipping line. It was found that a slurry dip immediately after drying gives much more effective reduction of extractable protein content in latex gloves. In some cases a combination of wet-gel leaching and dry-film leaching is desirable for removing the EP. Surface coating of finished products, either by dipping or by spraying is another technique used for reducing the EP content.

Polymer coating

Migration of protein can be limited by coating NR latex gloves with a synthetic polymeric barrier which also provides easy donning in the absence of powder. The coating materials normally employed for medical gloves are hydrogel, acrylic, silicone polymer, polyurethane or polymer blends. Polymer coating therefore, is a suitable alternative to chlorination for the production of powder free latex examination gloves of low extractable protein content (Figure 2).

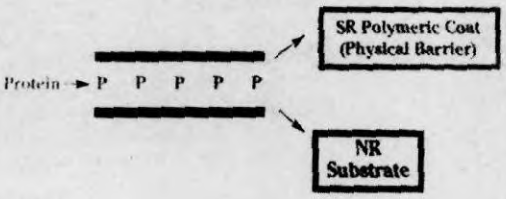


Figure 2. Polymer coating of NR films

Chlorination

Chlorination, which is used to reduce surface friction and tack, markedly decreases EP. Online chlorination of NR latex products is performed by immersing the products for 2-3 minutes with 0.3% of chlorine solution. After chlorination, the articles should be washed in a 2% aqueous ammonia solution. They are then washed in water and dried.

Reactions of chlorine with NR products results significant reduction in the level of extractable latex proteins due to the additional washings carried out during and after chlorination and the conversion of some latex proteins to insoluble forms due to chlorination.

NRL Gloves + Chlorine ----- Chlorinated Gloves

Table 2. Reduction in protein level with different processes*

Method	Amount (%)
Extractable protein in fresh field latex	100
After enzyme treatment	2
Centrifuged latex	13
Double centrifuged latex	8
Compounded latex (by solubilization)	8
In-process leaching	10
Vulcanization	15
Off-line leaching	4
Chlorination	0.3
Radiation processing	Non detectable

*Data from Ansell Int, relative levels

surface of the latex particle and subsequently substituting the protein molecules and displacing them (Figure 3). After displacement, the protein becomes mobile and easier to dispose of.

Assessment of protein content

The most commonly used methods for the measurement of extractable protein (EP) content are modified Lowery method, notably the RRIM modified lowery, which is adopted as MS 1392: 1998, the ASTM D5712-95 and 99 and EN 455-3:1999. The reductions in protein content by different processes are listed in Table 2.

Responding to the concern of consumers, ASTM has recommended upper powder limits for examination and surgical gloves (Table 3.)

Table 3. ASTM recommended powder limits

NR Gloves	Powder limits		ASTM standards
	Powder-free	Powdered	
Surgical	2 mg/glove	15 mg/dm3	D 3577-00
Examination	2 mg/glove	10 mg/dm3	D 3578-01a

Fumed silica

The addition of fumed silica to NR latex compounds will results in the production of NR gloves with lower extractable protein. The silica is postulated to attach itself to the

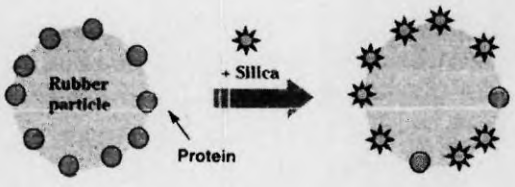


Figure 3. Replacement of rubber bound proteins by silica

Consumers are now given a variety of NR latex medical gloves with minimal health risk to choose from. They are namely: powder free gloves- chlorinated and /or polymer coated ;

low powder/ low protein gloves; gloves lubricated by alternative powder that almost do not bind proteins.

SUMMARY

The latex protein allergy problem has led to intensified research effort since early 1990s for the development of deprotenized natural rubber latex with reduced amount of allergens and low allergic potential. Several versions of low protein latices have been developed through suitable treatment of field latex, latex concentrate and prevulcanized latex that involve either mechanical or chemical means.

The mechanical route involves essentially multiple centrifugation of a diluted latex, whereas the chemical approach involves the use of suitable proteolytic enzyme or surfactants (no-enzymatic), followed by suitable purification process such as centrifugation or radiation followed by centrifugation.

A recent benchmarking exercise of both the experimental commercial low protein latices has shown wide variations in nitrogen contents, protein contents of raw latex cast films and vulcanized latex dipped films. For vulcanized latex dipped films, a combination of wet-gel and post-cure leach or chlorination would be necessary to ensure films with low allergens.

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