

Introduction to latex and the rubber Industry

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SUMMARY : The natural rubber latex (NRL) protein allergy issue has created one of the biggest market drivers for improved and new products in the glove industry. Manufacturers have responded by funding research into the area of understanding how their processes and products may have been involved in the cause and propagation of the allergy. Efforts were focused on how to reduce the NRL proteins during the manufacturing process. Reliable and relevant test methods for the protein allergen content are still being sought to help assist manufacturers in the monitoring of their products.

KEY-WORDS : Latex Gloves – Natural Rubber Latex Allergies – Glove Manufacturing,

The natural rubber latex (NRL) protein allergy issue became part of our everyday lives when the FDA issued a "Medical Alert on Latex Allergy" in March of 1991. In March of 1992 the American College of Allergy and Immunology circulated a draft on interim recommendations to health professionals and organizations regarding Latex Allergy Precautions. The next major event to heighten the awareness of the issue occurred when the FDA held the first "International Conference on Latex Allergy" in Baltimore, Maryland, USA.

The natural rubber industry was suddenly faced with a problem about which there was little or no information as to how the problem arose and what part their processes and/or products played in the causation or propagation of the allergy. Since these early days a great deal of highly productive research, some sponsored by industry, has taken place. This research has assisted in the understanding of the NRL protein allergy but even with the many breakthroughs that have been achieved many key questions still remain unans-

wered. Some of these questions are: What is the threshold of sensitization?; What is the sensitization mechanism?; What is the significance of cross-reactivity?; What is a safe level of protein?

Natural rubber latex is obtained from the controlled wounding of the *Hevea Brasiliensis* tree. The milky white fluid consists of approximately:

- 34 % rubber *cis* - 1, 4 - polyisoprene
- 2 - 3 % proteins
- 0.1 - 0.5 % sterol glycosides
- 1.5 - 3.5 % resins
- 0.5 - 1.0 % ash
- 1.0 - 2.0 % sugars
- 55 - 65 % water.

Field latex is concentrated to approximately 60 % rubber by a process called centrifugation. In this process, an ammonia preserved blended field latex is fed into a centrifuge bowl rotating at a speed of about 7000 rpm which exerts an ave-

rage centrifugal force of 8000 G on the latex particles causing the latex to separate into two fractions: a rubber rich less dense concentrate and a dense skim. The concentrate can either be preserved with only ammonia or a mixture of ammonia, zinc oxide and tetramethylthiuram disulphide (TMTD). The preserved concentrated latex is the raw material which is used for the manufacture of a examination and surgical gloves.

The first part of the manufacturing process involves the compounding of the latex with the vulcanizing chemicals. The main function of the vulcanizing agents is to form sulphur crosslinks between the cis -1, 4 -polyisoprene molecules of the rubber. These crosslinks improve the mechanical strength and barrier effectiveness of the rubber. The main vulcanizing agent is normally sulphur but using sulphur alone is not efficient and other chemicals such as accelerators and activators are added to improve the efficiency of cure. In order to protect the rubber from oxidative degradation caused by ozone, antioxidants or antiozonants are added as well during compounding.

Typical accelerators used in the manufacture of latex gloves are:

- **Thiurams.**

- dipentamethylene thiuram tetrasulphide
- tetramethyl thiuram disulphide

- **Dithiocarbamates**

- zinc dimethyldithio carbamate
- zinc diethyldithio carbamate
- zinc dibutyldithio carbamate
- zinc pentamethylene dithiocarbamate

- **Thiazoles**

- 2 - mercaptobenzothiazole
- zinc, 2-mercaptopbenzothiazole
- N-cyclohexyl-2-benzothiazyl sulphenamide

- **Xanthates**

- sodium isopropyl xanthate.

This is by no means an exhaustive list as there are still a large variety of accelerators to choose from not mentioned in the above list. One further step can be carried-out during compounding and this is the prevulcanization step. Compounded latex can either be used directly on the dipping lines or it can be pre-heated to a pre-determined level of vulcanization or cure. This heat treatment is referred to as pre-vulcanization.

Once the latex is compounded it is ready to be used on the dipping lines. A schematic representation of the dipping process is shown in figure 1.

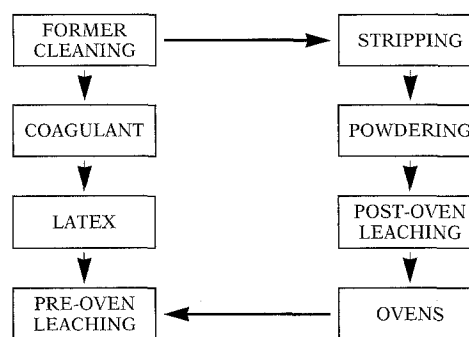


Fig. 1

Most manufacturers use porcelain formers which are designed to the producers preference. All gloves made from these formers must meet the dimensional requirements of the standard so as to ensure uniformity of fit. The first stage of the dipping process involves the cleaning of the formers with either acidic or alkaline or strongly oxidizing solutions. These solutions can either be used separately or in combination. The aim is to achieve as clean a surface as possible so that a uniformly thin continuous film can be deposited on the surface.

Once the former is clean it is coated with a coagulant. The coagulant usually is a mixture of calcium nitrate, calcium carbonate and a wetting agent. The calcium nitrate is the actual coagulating agent; in fact; any soluble divalent cation can be used to coagulate the latex. The calcium carbonate is used as a parting agent. This prevents the rubber from adhering to the former surface. The wetting agent ensures that the former is evenly coated. The coagulant is usually air dried prior to dipping into the latex. The strength of the coagulant will also play a part in determining the thickness of the glove.

The coagulant coated porcelain former is then dipped into the compounded latex. The coagulant strength and the "soak" time in the latex will determine the thickness of the glove. When the correct thickness has been reached the former is withdrawn from the latex and is the newly formed glove is ready for leaching.

The pre-oven leach which is usually heated to between 45 to 80°C assists in the removal of residual calcium nitrate and to some extent the extractable proteins. The leach water must be well circulated and replenished on a continuous basis for it to be effective.

After the leaching process the formers are passed into ovens to vulcanize or cure the gloves. Ovens can be zoned so that the gloves are exposed to a gradient of temperature or a single zone

Table I

Year	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996
No. of license issues	5	6	45	272	61	11	13	13	6	8	9	5

oven can be used. The vulcanization process normally takes anywhere between 10 - 20 minutes at temperature between 120 - 140°C. If the compounded latex was precured, then shorter times and lower temperatures can be used. Sufficient temperature and time must be allowed for the vulcanization process to impart the required physical properties to the glove.

When the gloves emerge from the ovens they can be leached prior to powdering. The post-oven leaching is usually done at temperatures above 80°C and is most effective in removing extractable proteins. The leached gloves are then dipped into a modified corn starch slurry, which provides the lubricating powder for donning. The gloves are then stripped from the formers and the cycle begins again.

This gives you a brief overview of how a powdered glove is made. Of course many manufacturers have their own design of machine and have their own preferences for formulations used, times of dipping and temperatures so that not all gloves are the same.

At this point a historical perspective on how the number of manufacturers has changed over the years should be of interest. The number of companies producing NRL gloves in Malaysia has changed dramatically over the past few years. The table (Table I) lists the number of licenses granted by the Malaysian Industrial Development Association (MIDA) to compare the production of latex gloves between 1985 to 1996.

The peak was reached in 1988 where 272 licenses were granted. Of the total 454 licenses granted between 1985 to 1996 only 108 are currently involved in the manufacture of gloves in Malaysia. The interesting implication is that the manufacturers who supplied gloves that may have helped to create a problem may no longer be in existence.

During the last 5 to 6 years the market has moved dramatically in that there has been a shift away from powdered gloves to powder-free. Also we have seen synthetic gloves become increasingly important.

Powder-free gloves are usually manufactured by the washing of the gloves in chlorine water. The chlorine reacts with the surface rubber, rendering the glove surface non-tacky. Chlorination of the

glove produces a surface which allows the glove to be donned without the aid of powder. The chlorination process due to its washing action and the denaturing effect on proteins usually produces gloves which have low protein allergen content. This has been the main reason for the market preferring to use powder-free gloves. Consequently manufacturers are currently installing more and more capacity to produce powder-free gloves to meet the market demand.

Manufacturers are always working under the rules set by the Regulatory Authorities. The NRL protein allergy has caused much controversy in the regulatory world as to what we need to measure, how we need to measure it and at what levels do we control? As we know, there are more than 250 different proteins in NRL and only approximately 60 of these are involved in the observed allergic reactions. Consequently, is a total protein measurement valid or should we only be looking at allergic proteins?

To-date the only recognized test method is the modified-Lowry test for the determination of extractable proteins from gloves. This is a total protein measurement and unfortunately suffers from many interferences from accelerators, antioxidants or other chemicals containing nitrogen.

These interferences can cause a great deal of variation in the results obtained for gloves. Within our own laboratories we have experienced variations in results for the same product when using the modified Lowry test. In order to check how reliable our results were, we sent out series of samples to other registered laboratories. Table II details the outcome of the analysis.

Table II

Sample	Laboratory	1	2	3	4	Range
A1		240	125	336	403	36-451
A2		270	36	342	451	
B1		98	271	120	181	93-271
B2		100	93	122	135	
C1		147	54	123	124	54-147
C2		122	70	126	106	

Value are in µg/g.

Samples A1 and A2 are equivalent as are B1 and B2 and C1 and C2. Samples A1 and A2 are of a different formula to C1 and C2 but have been dipped and processed in the same manner. This shows the impact of formulation. The range shown for samples A1 and A2 is far larger than that shown for samples C1 and C2. Samples B1 and B2 represent an alternative form of processing. The ranges obtained from the results of the four test laboratories are unacceptable, and will eventually cause a great deal of confusion in the market place. For example, if you were presented with a glove which had a values of 36 µg/g and another with a value of 451 µg/g, which would you choose? Obviously the preference would be to take the lower value gloves but both gloves are

identical. Regulatory bodies are trying to establish acceptable levels of proteins, so that the industry will be regulated to produce gloves with low levels of extractable proteins. Although this is a commendable approach the industry needs to have a reliable and dependable test method.

Manufacturers have recognized the need to produce low NRL protein gloves and surveys such as those conducted by the National Agency for Medicines in Finland and the Mayo Clinic in the USA have shown that the number of low NRL protein gloves is increasing. In general, manufacturers are responding to the need for low NRL protein gloves but assistance is still required in the area of test methods and safe level determinations.

