

Natural Rubber Latex

This special on Natural Rubber Latex tries to show the reader some of the particular properties, applications and possibilities of this wonderful material.

Despite opposition due to the, largely unnecessary, allergy problem it is the best choice for a large number of applications. Moreover, Natural Rubber Latex has not only a natural origin, it also takes less energy when produced. A point to ponder in a world in which people are increasingly aware of the need to choose for "green" processes and materials.

From the invention of the vulcanization process products with a very high elasticity, strength and recovery can be made from Natural Rubber Latex. A unique combination that can not be offered by no matter which other natural or synthetic material. Especially products formed directly out of, almost pure, Natural Rubber Latex by dipping possess these properties to a high degree.

Therefore, people use Natural Rubber Latex already during millennia and will stay to do so. The following articles give some "why's" and "how's".

Jaap Havinga



Glove production (see page 10)

Special on NR Latex

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The history of natural rubber has been the subject of many publications because over the last years the centennial of the introduction of the *Hevea Brasiliensis* in the Far East has been celebrated.

The first young *Hevea* seedlings were planted in Sri Lanka, Malaysia and Indonesia as from 1876 and the French started growing this tree in Vietnam in 1897. Now the area under rubber trees, mainly in the Far East, but also in Africa and Middle and South America, covers 8–9 million hectares, with an annual production in 1998 of some $6,600 \times 10^3$ tonnes.

Starting with unselected seedlings, subsequent generative selection resulted in improved clonal planting material. Combined with tapping systems adapted to the generative rubber production capacity of the trees yields increased from less than 500 kg to over 2,500 kg/Ha/year. Thanks to increased use of latex flow stimulating agents even higher yields can be obtained under favourable conditions.

Production of concentrated latex started in the thirties, first bulk deliveries went to the United Kingdom in 1931. Table I gives the development of total NR production and of concentrated latex production and consumption from 1926 to 1998.

Up to 1985 NR latex concentrate production was between 7 and 9% of total NR produced. This share rose to 11.2% between 1986 and 1990 and increased to 12.2% in 1998 (810.000 tons). The sudden increase after 1986 coincides with increased use of protective articles after the outbreak of the AIDS epidemic.

Table II gives an approximate of the percentage consumption of NRL concentrate in different sectors of usage.

Table I
Production/Consumption of Total Natural Rubber and NR Latex Concentrate

	Total NR Production	NR Latex	% Latex
1926	633,000	3,300	–
1933	865,000	15,800	1.8
1940	1,417,000	44,750	9.1
1960	2,145,000	169,750	8.0
1970	2,990,000	256,750	8.6
1980	3,760,000	268,000	7.1
1985	4,350,000	347,000	8.0
1990	5,270,000	590,000	11.2
1995	5,980,000	710,000	11.8
1998	6,600,000	810.000	12.2

Production

The source material for NRL concentrate is freshly tapped field latex. After opening the tapping cut the latex flows out of a system of intercommunicating latex vessels in the soft bark. These vessels are arranged in rings with connections between vessels within a ring but seldom between rings.

Latex is in fact of cytoplasm structure and contains i.e. riboso-

Table II
Approximate Usage of NR Latex Concentrate (1996 in %)

Dipped Goods	52%	gloves, catheters, etc.
	3%	balloons, condoms
Latex Foam	8%	
Latex Thread	10%	
Adhesives and Binders	10%	various types
Binders	10%	binders e.g. for artificial leather and leather board
Carpet backing, Textile	5%	also for embossed foam backings
Miscellaneous	3%	

mes but seldom nuclei. Apart from rubber particles very freshly tapped latex also contains so-called lutoid particles which can be separated by centrifuging at low speed and more or less yellow/ orange coloured Frey-Wyssling particles containing a.o. carotinoïds.

The composition of the fresh latex is rather complex due to its origin and the relative proportions of certain constituents (e.g. proteins and minerals) can show important variations depending on many factors (clone, season, tapping system). The same is true for its rubber content, which is normally between 34 and 38%.

A typical composition is as follows:

Typical Fresh Latex Composition

Total Solids Content	41.5%
Dry Rubber Content	36.0%
Amino Acids and N-Bases	0.30%
Neutral lipids	1.0%
Proteins	1.60%
Phospholipids	0.60%
Inositols-Carbohydrates	1.5%
Salts (mainly K,P and Mg)	0.50%
Water	58.5%

As soon as possible the latex is temporarily preserved with ammonia (the quantity depending on the delay between processing into concentrate and harvesting the crop) in order to prevent bacterial contamination or at least to limit its effects.

The cytoplasm structure of the latex, already altered by physiologic changes due to tapping (trunk contraction and absorption of water from the surrounding cells) is now destroyed and remnants are subsequently eliminated by sedimentation and by centrifugation, together with magnesiumammonium phosphate formed in this ammoniac medium.

Details on the composition and characteristics of latices from clones recommended for planting in Malaysia are given in reference 1.¹



Concentrated latex

The commercial product is nowadays mainly prepared by centrifugation; and there are only two types made on a large scale: *HA (high-ammonia) latex*, preserved with 0.7% ammonia
LA-TZ (low ammonia) latex, preserved with 0.2% ammonia + 0.025% TMTD/ZnO +0.04 - 0.05% lauric acid as ammonium laurate.

In addition are available:

PV latex. The Pre-Vulcanized latex is in wide spread use. Natural latex can be readily vulcanised in the liquid state and the product retains most of the good-processing characteristics of raw-latex concentrate.

Creamed and evaporated Latex. These latices of 65 and 66% DRC respectively are produced each by only one producer in Malaysia.

Zero Protein Cream Latex (new). Contains virtually no extracted proteins.

Typical properties and composition of HA Latex and LA-TZ Latex

The data in Table III has been published in two papers by A.D.T. Gorton and T.D. Pendle entitled 'Processability of LA-TZ (resp. High Ammonia) latices in Relation to their Properties. 2a, 2b In this study 20 samples obtained from European dealers of both types of latex, believed to be representative for bulk material at that time (1983), were tested on:

- parameters as prescribed by the ISO specifications
- viscosity Brookfield LVT at 25°C at 6 and 60 r.p.m.
- stability to ZnO: assessed using the German ZST test and viscosity increase test (ZAAV), in which the ZnO is already present in solution as a $Zn(NH_3)_n^{2+}$ complex.
- and analysed for nitrogen, total and inorganic Phosphorus, Potassium and Magnesium content.

In addition conductimetric titration's were carried out with potassium hydroxide and ammoniated zinc acetate (ZAAV) on latex and serum in order to evaluate the significance of such tests for assessing the concentration of adsorbed anions and ammonium soap on the rubber particles surface.

Chemical Stability

The above study confirmed that for commercial lots there is some direct relationship between the ZST and the mechanical stability test values for LA-TZ latices and that at least for these samples of widely varied origins the ZST gives no more information than the MST test.

For the great variability in ZAAV viscosity no explanation in terms of composition and specification parameters could be found. The assessment of the surface 'soap' was supposed to be too imprecise to permit conclusions on the reasons for the instability found sometimes with the ZAAV viscosity test.

For the HA-Latices the stability when judged by the ZST values was lower than for LA-Latices, but they appear much more stable in the Zinc Acetate viscosity test. This is essentially due to the higher pH of the HA latex as a similar effect is noted when the ammonia content of a LA-TZ latex is increased.

Mechanical Stability

The mechanical stability (MST) is the only property of the standard specifications referring to a fundamental characteristic of colloidal systems-its stability.

Table III
Composition and Properties of Typical Commercial HA and LA-TZ Latices (% by weight)

Item	Latex HA	Total solids film	Latex LA-TZ	Total solids film
Rubber	59.67	97.61	59.61	97.32
Protein, etc.	1.06	1.73	1.03	1.68
Soaps	0.23	0.38	0.38	0.62
Salts	0.40	0.28	0.38	0.38
Ammonia	0.68	-	0.21	-
Water	37.96	-	38.45	-
TCS (%)	61.31	-	61.25	-
DRC (%)	59.67	-	59.61	-
Non rubber solids (%)	1.64	-	1.64	-
PH	10.65	-	10.08	-
Alkalinity (% aqueous phase)	1.76	-	0.54	-
MST(s)	1168	-	1131	-
VFA No.	0.07	-	0.05	-
KOH No.	0.63	-	0.58	-

The rubber particles in the latex are covered with a protective bilayer of phospholipids and proteins. In the ammoniac medium the lipids hydrolyse under formation of higher fatty acids soaps (HFA).

HFA formation during the first 6-8 weeks after ammoniation parallels development of MST, increasing from 100 seconds up to 800 seconds and over.

This process has been studied in some detail for HA latices; in LA Latices like LA-TZ the MST has to be boosted by addition of soap, normally NH_4 -laurate, at about 0.05% on the latex.

In a few clonal latices a.o. from the Clone PR 107, preserved with 0.7% ammonia only this MST increase with time is not observed and there are more clones which require the addition of a small amount of NH_4 -laurate (0.02%) in order to obtain in the HA quality the required MST value of the least 650 seconds. The reason for this abnormal behaviour is obscure.⁴

Also obscure are the reasons for the significant increases in MST after a short heating at 60°C and this phenomenon is at least partially reversible.

It is suggested that this MST increase may be due to a change in the structural configuration of the absorbed protein.

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The Rubber Balls of the Aztecs¹

Martijn Hover

“I don’t get it,” wrote a member of the Spanish court in the 16th century after a visit to the recently conquered areas in Central America. “When they hit the ground, they bounce back in the air with great speed.”

The astonished Spaniard was talking about the rubber balls used by the Aztecs and other Central American nations during a game they played. In this mixture of soccer, volleyball and basketball, two teams of six players attempted to hit the ball through one of the stone rings attached to the wall. In trying to do so, every part of the body could be used except for the hands and feet.

The game, named Chaah, has been around for at least 3,400 years and originally had a ritualistic and religious purpose for the pre-Columbian people of Central America. Remarkably, it developed through the centuries in an increasingly more professional direction, much like the classical Olympic Games and modern-day sports. Every city of significance had a stadium, often with room for thousands of spectators. Rival cities battled out their feuds on the Chaah field and the well-to-do placed large wagers on the outcome of the games. The Aztec capital Tenochtitlán required 16,000 rubber balls from a single province as a tribute.

However, the native Americans used rubber for other purposes besides the production of sports equipment. It was utilised as incense and lip balm, and also for the production of religious figurines. American scientists have researched how the ancient inhabitants of Central America succeeded in manufacturing an elastic material from latex – the sap of the rubber tree. Western chemists did not master this trick until the nineteenth century.

The method applied by the native Americans is “a fantastic example of technology in an unbelievably early stage,” according to polymer chemist Frank Bates of the University of Minnesota (USA). Furthermore, this technology is still being used, as a team from the Massachusetts Institute of Technology (MIT) in the United States discovered when travelling through Mexico looking for the basic materials used in the manufacture of rubber as identified in old texts. The team observed how local farmers made cuts in the bark of the rubber tree, *Castilla elastica*, collected the latex resin and mixed it with the sap of a climbing plant which wraps itself around the trunk of the tree. The farmers did it exactly as Spanish priests described 400 years ago.

The Americans researched latex and rubber in their laboratories later on, but could not reach any unequivocal conclusions. Rubber is made up of long carbon chains (polymers) which are all linked to one another. Upon closer inspection, latex appeared to be made up of “organic components” which, according to researchers, “probably” prevents the polymers from attaching to one another. Dried latex is brittle and fragile, whereas rubber is pliable and elastic.

The weekly magazine Science reported that researchers are now planning to experiment with various concentrations of the sap of the climbing plant used in rubber production. They want to see if the ancient Maya and Aztecs had the technology to make rubber with all kinds of different characteristics.

¹ Translation from *Brabants Dagblad*, 30 June 1999

Ecological Advantages of NR Latex Production

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The primary production of latex – the cultivation of *Hevea brasiliensis* trees and tapping of latex – has few negative environmental effects. In the wet tropics, crops of trees have a clear ecological advantage over annual crops. The leaf coverage and the root system of trees regulate the microclimate allowing a range of secondary plants to flourish, while the soil is protected against dehydration and the erosive influence of rain. The trees also offer a habitat for a great variety of fauna.

Initially, a damaging consequence of the transformation from tropical rainforests to Hevea plantations is caused by the felling and burning of the primary forest. The soil is exposed to erosion from rainfall and leaching, and the richness of flora and fauna diminishes temporarily. Five to eight years will pass before the young rubber trees are ripe for production. In the interim phase, supplementary measures must be taken to maintain the fertility of the soil and to counteract the effects of erosion. The effects of erosion can be reduced through adequate cultivation measures, such as terracing, construction of small embankments and mud wells, sowing ground covering plants and nitrogen-fixing crops, and placing or allowing shrubs to grow which offer shadow. Farmers often employ combination cultivation in the first years, in which rubber trees are combined with the growing of bananas, pineapples, cassavas and corn. Soil fertility is maintained through the temporary cultivation of nitrogen-fixing crops. As a rule, high-yield Hevea varieties are used, for which fertiliser is of vital importance. Chemical fungicides are regularly applied because these plants are more vulnerable to fungi than average planting stock. This can partially be overcome through cultivation measures such as removing the stumps of old rubber trees, ensuring the presence of a sufficient number of different ground covering plants, and installing drainage provisions in areas with a high groundwater level.

Once in production and dependent on the intensity of tapping, rubber trees continue to supply latex for 20 to 35 years, after which the old trees are dug up and new trees replanted in their place. The Hevea wood is used in the furniture industry as well as in other trades. In many respects, a forest of mature rubber trees is equivalent to a tropical rainforest. An ecosystem of 33-year-old Hevea trees annually produces 450 tonnes of biomass per hectare, compared to 475 to 664 tonnes/hectare in Malaysian rainforests and 295 to 475 tonnes/hectare in Brazilian and Thai rainforests. Given the interest in the warming of the earth’s atmosphere through CO₂ emissions, it is worth mentioning that a rubber plantation is hardly inferior to a primary tropical forest in terms of carbon fixing. Contrary to other agricultural systems, a mature rubber tree forest utilises a closed nutrient cycle. In north-east India, the quality of soils that were depleted as a result of shifting cultivation has improved substantially following the planting of rubber trees.

It can be stated in summary that few or no other crops exist in the wet tropics with the same high ecological qualities of rubber. With the use of adequate cultivation methods, the positive environmental effects will dominate.

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Latex Protein Allergy: Some Questions

Kevin P. Jones¹

There appears to be a marked variance between the assertions made about the incidence of latex protein allergy and the overall incidence of allergic conditions within the general population. Most medical texts consider that as far as can be ascertained the overall incidence of persons susceptible to allergies is about 1% of the population. That is all classes of individual, and all types of allergy. Some materials are known to cause allergies: nickel is one of the commonest. On the other hand, some individuals may be allergic to almost anything, including most fabrics, most foods (nuts are amongst the most potent), and many substances which the vast majority find innocuous. A very small, unfortunate minority is allergic to a wide range of substances: this group is known as atopic individuals. Some substances, notably the venoms produced by insects and plants, whilst unpleasant or occasionally dangerous to most human beings, are especially threatening to some individuals. Thus most people can tolerate a single wasp sting, but a small minority experience life-threatening reactions from such a sting.

It should be noted that about 125 individuals die from eating peanuts in the USA each year¹, that is over the twice the number who die from insect stings. Despite these fatalities, some of whom are relatively high profile such as a young Scottish athlete who died from ingesting some peanuts within a chicken sandwich, few measures appear to be taken to protect such individuals. Some European airlines have banned the distribution of peanuts in flight, however, due to the obvious risks involved. On the other hand some alleged American centres of medical excellence are working towards a total ban on latex gloves. One would hope that these same centres will show equal vigilance towards peanuts and other hazardous food and drugs.

For a time, it appeared that some American medical researchers were attempting to assert that the prevalence of latex protein allergy within the general population is high, but a recent paper by Liss and Sussman² appears to accept that this is not the case and that the overall prevalence of latex sensitization in unexposed groups is "quite low", that is less than 1% are at risk. Thus, Liss and co-workers³, who have asserted that prevalence of latex sensitization in American health care workers is high (in excess of 10% in some groups) accept that this sensitization is at variance with what is normal in the population as a whole.

Latex protein allergy must be set against this background, and it is surprising that a high proportion of the medical literature fails to make this connection. In particular, there seem to be few who are prepared to challenge some of the claims being made for very high levels of allergic responses (one source on the Internet quotes that 18 million Americans are susceptible to latex protein allergy) within specialist populations to a material which was successfully used without any suggestion of danger for much of the twentieth century. Some of the accelerators employed, notably alpha naphthylamines, were subsequently found to be carcinogenic. Apart from a few individuals who reacted to accelerator residues there was little to suggest that latex as such was anything other than a benign material. Perhaps the greatest

evidence of this has been the regular use of latex as an adhesive in a wide variety of applications, including its use by school children. A very recent paper⁴ which reports on experience in a Turkish glove plant appears to reinforce this view. The incidence was 3.2%: five subjects out of a total worker population of 155. This study supports studies into the incidence of allergy amongst Malaysian rubber glove workers⁵, where the incidence rate is around 2%. It should be noted that in both cases the workers would have been liable to experience much higher protein levels than health care workers in the USA.

Nevertheless, American quasi-official documents, such as a recent paper⁶ from NIOSH continue to suggest that: "Allergy to natural rubber latex (NRL) has become a significant health risk among healthcare workers and other persons using latex gloves in the course of their work [NIOSH 1997; Turjanmaa et al. 1996; Watts et al. 1998]. A number of studies indicate that levels of latex sensitization in healthcare workers ranges from 5-12% [Liss and Sussman 1999]. One study indicated that the prevalence of latex sensitivity among 1,351 healthcare workers was 12.1%; and of that same 1,351 workers, 60% reported work-related symptoms [Liss et al. 1997]. Despite the numerous studies performed in this population, little is known about the non-healthcare worker occupations. Occupational asthma and symptoms of latex allergy have been reported in select groups including hairdressers, workers at a latex glove manufacturing plant, and workers at a latex doll manufacturing plant. Prevalence rates up to 11% have been reported in these studies (11% and 9%, respectively, in the latter two studies) [Orfan et al. 1994; Tarlo et al. 1990; van der Walle and Brunsveld 1995). Although the prevalence rate for other non-healthcare worker populations is unknown, these studies indicate that workers exposed to latex gloves or products containing latex may also be at risk for latex allergy."

Not all the references cited above are recorded below, although particular attention will be paid to that³ by Liss et al. 1997 as it quotes some questionable data relating to protein concentrations within gloves. The paper also typifies the elective nature of many of the studies: that is there is a tendency to base such studies upon those who consider themselves to have experienced some form of allergic response to latex gloves. Furthermore, there is sometimes a glib use of statistics: "60% reported work-related symptoms": that is 60% of the 1,351 individuals who had elected to join the study as they considered themselves to be experiencing some form of skin reaction. Such studies lead to extrapolations, such as "more than 18 million Americans sensitized to latex"; the basis for which are also questionable. It is important to note that in general elective behaviour⁷ only 10% of those who consider to be allergic to specific foods are actually allergic when rigorous medical tests are performed. Thus, much of the published literature on latex protein allergy would appear to be at variance with the general literature on allergic responses.

The apparent cause of the latex allergy "epidemic" may be traced to the great increase in the uptake of medical gloves in the United States following the true epidemic of AIDS and the fear



which this induced both in medical staff and their patients. This fear was manifest in all countries, it is particularly acute in the USA where the accidental transmission of such a disease would be extremely expensive given the highly litigious society therein. This market growth for gloves was accompanied by a short term decline in manufacturing standards as entrepreneurs entered the market to meet a sudden increase in demand. There was also a shift in manufacture to natural rubber producing countries: it is possible that the fresher latex used in such countries may contain higher protein concentrations. It is certain that some of the new entrants to the industry were unaware of good factory practice, both at the concentration and dipping phases. Failure to ensure adequate plant cleanliness and water quality for leaching led to gloves being produced with unacceptably high protein concentrations. Sufficient gloves were marketed to cause some potentially allergic (atopic) individuals to acquire an additional allergy. Unfortunately, a few highly susceptible spina bifida patients appear to have died following contact with highly unsatisfactory latex products (enema tips). The industry has reacted to this problem by introducing quality control measures, as typified by the Standard Malaysian Glove. In theory, the number of new cases of latex protein allergy should now decline as the primary cause has been removed from the market.

Another factor which has been underplayed is that at about the same time talc, a potentially hazardous material, was replaced by the apparently more benign cornstarch powder as a dusting agent. Cornstarch is a potential allergen⁸ and is relatively similar to wheat flour which is a frequent cause of allergic reactions. Nevertheless, there is a large literature on "latex protein allergy" which fails to recognise that the cornstarch may have a role to play in the problem, especially where it is liable to be inhaled as in the low humidities prevalent in many hospitals in the USA. For a time it would seem that the FDA and other regulatory bodies in the United States were uneasy in condemning a potentially home-produced product, as compared with their response to latex. The FDA now appears to recognise the potential dangers of dusting powders and is regulating their use on gloves made from all polymers. Subsequently, casein (a minor component of some gloves) has been recognized⁹ as being a contributory factor: some individuals are allergic to milk products. The measures proposed (additional labelling) would appear to be unrealistic.

Atopic behaviour has been mentioned. There is a considerable literature on cross reactions between those who have been diagnosed as being "latex sensitive" with their response to other allergens, especially foodstuffs, such as banana and avocado. There is an implicit assumption within such literature that the latex contact has "induced" responses to these other common substances, whereas the response to latex proteins could have followed reactions to bananas, or a vast variety of other common foods. Once again it is noteworthy that the response of regulatory bodies within the USA to the ingestion of peanuts in public places is much less severe than that regarding the use of latex gloves. It should be noted that even in Europe deaths from eating peanuts are relatively widespread (for instance in one year there were six fatalities in the United Kingdom alone)¹⁰, whereas most of the "deaths" associated with the use of latex gloves are far more questionable (the patients may have died from other causes).

Nevertheless, it now appears to be accepted that the prevalence of latex sensitivity amongst healthcare workers in the USA is at

variance with the norm. Thus, either latex protein allergens must be peculiarly severe (to those routinely exposed to them within a medical environment), or the population which opts for health care work must be peculiarly prone to allergic reactions. Furthermore, if the allergen is so severe, then one must consider whether the control of such an allergen is on a par with other comparably dangerous, or significantly more serious allergens, such as peanuts. Peanuts are solely a fairly trivial source of food, whereas latex films form a highly effective barrier against pathogens, including HIV, or the AIDS virus.

Whilst it would be difficult to deny that there has been some increase in the incidence of allergic responses to the proteins within natural rubber latex, it is highly questionable whether this has been sufficient to justify some of the measures being proposed in some supposed centres of medical excellence in the USA. Some such institutions envisage the virtual total elimination of latex gloves without any consideration of the alternative materials being proposed. In many cases the alternatives are poorer, or even utterly ineffectual barriers. Vinyl films are so imperfect¹¹ that there would appear to be little point in donning them. Disposal of them by combustion is banned in many European countries due the risk of the dioxin release. Some of the other favoured materials may contain traces of carcinogens, or are known to cause allergic reactions.

It might appear to be unwise to criticise the literature of a discipline of which one is not a member. Nevertheless, it must be remembered that (1) the implications of such a literature may extend far beyond the boundaries of that discipline, and (2) the medical profession has not been averse to performing tests upon gloves, and publishing the results, with scant regard to whether such tests are legitimate. The medical literature abounds in tests on gloves where the sample sizes are unrealistically small, where no attempt has been made to verify or to apply controls to the samples selected, where no attempt has been made to relate the "studies" to other work, especially that outside the medical literature, and where there is an apparent lack of awareness of the irregularities of the testing processes, some of which were peculiar to the studies. It would not be an exaggeration to state that some papers have been published where the unverified tests for protein concentrations have been performed on open boxes of gloves which were at hand. It is not beyond the bounds of possibility that such boxes may have become "polluted" by other gloves, or even by other materials. Such tests frequently present the data in a form that implies the tests are highly accurate whereas tests for protein concentrations are unreliable¹². For instance, one paper carefully observes with excessive precision that their sample of surgical gloves contained higher levels (324:g/g) of protein than their sample of examination gloves (198:g/g) without observing that this result³ is inherently anomalous: typical surgical gloves have lower protein levels as they are manufactured to higher standards. This paper has been widely cited as it suggests that in excess of 10% of health care workers in their elective study may be susceptible to latex allergy.

In many instances, the literature appears to be setting out to advance a particular position (to assert that many health care professionals are afflicted) rather than to establish the true situation. In part this might reflect a caring attitude for those few co-professionals who have been affected and are seeking some form of redress, but it may also reflect the quest to create



a new industry. Worker compensation is a lucrative business for many within the American legal profession, much of which is financed by successful cases. Within such an environment it would not be difficult to envisage some attempting to present unobjective data to influence such litigation.

Haydn Williams¹³ closed a contribution on the value of latex gloves by noting that: "The casual reader or web surfer on the subject of latex allergy could easily form the impression that there is a crisis of epidemic proportions. This is not so. While in no way denying the very real suffering of some individuals due to allergy, it must be remembered that such individuals are in a small minority. Billions of gloves are used annually in protecting healthcare workers from the very real threat of infection by deadly viruses and antimicrobial resistant micro-organisms. Natural rubber latex, furthermore, is universally agreed to be the best barrier to such organisms. These are essential uses that have very real positive consequences for those at risk of infection. The enormous amount of independent research and international collaboration on understanding the issues involved in latex allergy is bearing fruit. Standards to control allergen levels are and will be developed, and processes are in place to bring about product improvements. Continued efforts in this direction coupled with education of end users will lead to a continued reduction in risk of sensitisation and result in a situation where the vast majority of NR glove users can continue to do so with confidence that they have the best and safest barrier to infection on their hands".

In conclusion, it is difficult to accept that certain sections of the medical profession in the USA and some of the quasi-official regulatory bodies have been fully objective in their approach to what it is agreed has been a genuine problem which the glove manufacturing industry has addressed with considerable vigour. This brief survey covers similar ground to a paper presented at an International Rubber Research and Development Board (IRRDB) Workshop held on Hainan Island, China in October

1999, which it is hoped is about to be published more extensively elsewhere. It is hoped that it may be possible to perform a more rigorous examination of some of the claims being made on the basis of extremely small and elective sample sizes later.

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¹ International Rubber Research and Development Board.

Environmental Issues and Challenges in the European Latex Industry

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In Europe the outlet for Natural Rubber (NR) latex is mainly into a few traditional uses such as molded foam, rubberized hair and adhesives. Only small quantities of NR based gloves and condoms, and some baby teats and toy balloons are still made in Europe. The producers must take care of minimizing residual protein and accelerator levels to minimize the risk of allergy problems. Baby teats must meet the limits set for nitrosamines as described in EU Directive 93/11/EEC. Only Germany has regulated nitrosamines for other consumer goods as described in the BgVV Recommendation XXI (Special Category). Literature describes a number of possibilities for meeting these limits. This paper focuses on the application of the 'nitrosamine safe' zinc dibenzylidithiocarbamate (ZBEC). The potential of ZBEC in post- and pre-vulcanization processes is summarized.

Just like as with NR glove manufacture, production of thin synthetic rubber gloves is concentrated largely at plants in the Far East and US.² There are no dipping plants making thin Synthetic Rubber latex gloves in Europe, industrial gloves are still

made in Europe. The biggest consumers of synthetic latex are producers of carpet backings (XSBR and SBR) and molded foam (SBR). Approximately 60% of high solids SBR are used in the carpet industry, 30% in mattresses and molded foam and 10% in miscellaneous uses (e.g. adhesives and bitumen modification).³ The manufacturers of foamed goods are challenged to handle a variety of environmental issues and challenges o.a. dust, volatile organic compounds, smell, recycling, packaging, zinc and nitrosamines²⁰.

In general, the high standard in processing, production and product quality are safeguarded and further improved, by

- working in accordance to quality management systems like ISO 9000's and MDD (Medical Devices Directive of European Community).

- following the recommendations in ISO 14000 (Environmental Management, for the prevention of pollution), combining with Eco Management and Audit Scheme (EMAS) to cope with new Environmental Rules in the European Union.⁴



Well equipped with these tools, the manufacturers of latex goods are challenged to address – often application specific – environmental issues.

This article will summarize issues associated with the vulcanizing systems used in latex product manufacture, including industrial hygiene (dust, packaging), zinc and nitrosamines. The allergy problems which appears to affect only dipped goods is briefly summarized by reviewing the treatments described in literature that might help minimize residual allergens. References are given on how to access information on food contact regulations and legislation in Europe.

Industrial hygiene

Product forms

Traditionally, rubber chemicals for the preparation of dispersions used in latex product manufacture have been supplied as powders in bags. During unloading, handling and emptying of the bags, a fine dust, which often comprises the working environment is formed. In experiments, a significant reduction in dust formation, together with improvements in general handling and processing are observed when granular form rubber chemicals are used as starter materials.⁵

The development of granules of accelerators used in the latex industry is quite a challenge, since the granules must be rigid enough to withstand transportation but not too difficult to disperse using the standard latex dispersing equipment. Flexsys has commercialized granular forms of ZDEC and DPG and are developing granule forms of ZDBC, ZBEC and ZMBT.

Package wastes

In view of ever increasing emphasis on reducing solid waste disposal, the reduction in packaging waste is a top priority to both producers and consumers. The amount of residual chemical and the total quantity of packaging waste can be significantly reduced upon using rubber chemicals in a granular product form, which enables a nearly complete emptying of the packaging material returnable, flexible, semi bulk containers instead of paper bags.

Reduction of Zinc

Zinc is an essential trace metal for most animals. However, a lot of aquatic organisms are sensitive to high concentrations. Authorities have not yet given definite directives but have asked the rubber industry to limit the use of zinc oxide.⁴

Of course the use of zinc bearing ingredients do not create an environmental problem if their release into the environment is prevented. The potential sources of zinc in latex formulations for foamed carpet backings and foamed goods are

- the cure activator ZnO, commonly used at 2–5 phr level.
- the accelerators, ZDEC or ZBEC in synergistic combination with (Z)MBT (and DPG) at 1-2 phr level.

Over the past years we have performed application research to evaluate the potential of low-zinc or zinc-free formulations in latex foam formulations. Effort was put into testing the effect of

- decreasing/eliminating ZnO
- alternative metal oxides
- zinc free vulcanizing systems.

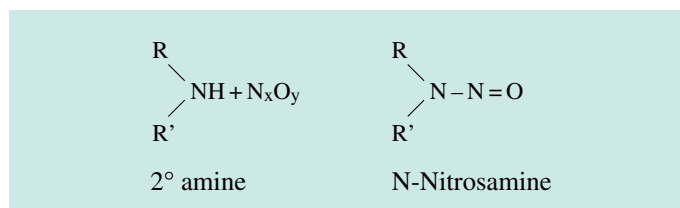
Summarizing:

- Cure rate is not significantly affected upon lowering the dosage of ZnO from 6 to 0 phr. This is in accordance with literature.⁶

- As the ZnO content of formulation is reduced the state of vulcanization decreases. Upon eliminating ZnO, reversion is observed upon over curing. This results in a reduction of the modulus and aging resistance. This reduction in aging resistance can be explained from the fact that ZnO is influencing the relative distribution of mono-, di- and polysulfidic sulfur crosslinks.⁷ The benefits of using higher performance anti-oxidants like to restore the resistance to aging might be worthwhile to evaluate.
- Elimination of ZnO from AAG gelled foam formulations is not feasible since it plays an essential role in the process.
- In vulcanization of solid SBR rubber applications MgO was found to be an effective cure activator.⁷ Indeed, the cure characteristics were adequate for latex, but MgO did not provide a controllable sharp gelation.⁸ The latter is most likely due to its destabilizing properties in highly alkaline latices.⁹
- Using the zinc-free and ‘nitrosamine-safe’ accelerator TBzTD, a minimum amount of ZnO is required for rapid vulcanization to a reasonable state of cure.

Nitrosamine

Put simply, nitrosamines are formed by nitrosating secondary amino compounds.



The use of accelerators derived from secondary amines will lead to N-nitrosamine generation.

Literature^{13, 14, 15} supports the idea that the carcinogenicity does not originate from the nitrosamines themselves, but their metabolites from enzymatic hydroxylation in organisms (in animal tests). Whether the N-nitrosamines of the related secondary amines are carcinogenic is believed to be determined by the character of the alkyl groups R and R'.¹⁶

Indeed, studies on the carcinogenicity of nitrosamines of secondary amines showed that not all are carcinogenic in animals under the described conditions.¹³

The ‘TRGS552: N-Nitrosamines’¹⁷ identifies hazardous N-nitrosamines. It also and lists some nitrosamines that are regarded as being safe according to current knowledge. Among others, N-nitroso-dibenzylamine is regarded as a safe nitrosamine.

The confidence in ZBEC is shown by its inclusion in the German BgVV Recommendation XXII¹⁸ under Category 1 (food contact covering uses) and Special Category (e.g. teats, soothers and toy balloons) at maximum dosage 0.5 phr.¹²

Baby teats and soothers must meet the limits set for nitrosamines and nitrosatables as described in EU Directive 93/11/EEC.¹⁹

No country other than Germany has regulated:

- Nitrosamines for other consumer goods. The BgVV included nitrosamines and nitrosatables limits to cover all products in the ‘Special Category’. This means that these products for sale in Germany must comply with these regulations. Specific details are given in the BgVV Recommendation XXI
- Airborne presence of specific nitrosamines. This regulation affects production and warehousing. The ‘TRGS552: N-nitrosamines’ list should be consulted for details of concerned

nitrosamines. Many other countries in Europe have Occupational Exposure Limits for nitrosamines.

Practice

It appears that the accelerators, including zinc dibenzyl-, diisobutyl- and diisononyl-dithiocarbamates can be used to meet the EU limits.¹¹ A formulation for transparent teats, based on the 'safe' ZBEC can be obtained from literature.²⁰

To avoid the risk of exposure of workers and customers to potentially carcinogenic N-nitrosamines, the producers of tufted foam carpet backings associated in the GUT (Gemeinschaft Umweltfreundliche Teppich) have been using the 'safe' ZBEC instead of ZDEC for a few years now.²¹

Zinc dibenzylthiocarbamate

Over the past years application research has been performed to evaluate the potential of ZBEC for pre- and post vulcanization processes.²²

- *Post-vulcanization.* Replacement of ZDEC by ZBEC on equal weight basis leads to a reduction of the cure rate and modulus. ZBEC can be activated using either DPG or thiozoles, the latter being most effective.
- *Pre-vulcanization.* On its own (0.5 phr) ZBEC is not very active in prevulcanization at 65°C. The potential of ZBEC is most effectively utilized upon 0.05 phr of MBT and/or 0.2 parts of ZnO.

Allergies

The allergy problems appear to affect only dipped goods.²³

Type I allergy is caused by exposure to water soluble rubber latex protein. The characteristics are immediate and include urticaria and possible anaphylaxis. This issue is extensively reviewed and discussed elsewhere by experts in this field. Further discussion is beyond the scope of this paper.

The Type IV allergy is a (delayed) contact allergy, which can occur with chemical allergens such as some accelerators and other vulcanizing ingredients. The characteristic symptoms are reddened skin, eczema and blisters, recovery after stopping exposure. The risk of Type IV allergic reactions due to residual accelerator levels in the finished product must of course be kept to a minimum. According to literature this can be achieved by

- using accelerators in combinations and at minimal initial level, combined with an adequate final vulcanization (and halogenization for gloves).^{23, 24}
- extended leaching time and temperature (e.g. 85°C) prior to vulcanization (and halogenization of gloves).²⁴

Lowering the accelerator content can reduce the product's aging resistance.²⁴

Food contact regulations and European standardization

In general, food contact regulations for rubber articles are most often referenced by either German BgVV Recommendation XXI¹⁸ or American CFR21 FDA 177.2600.²⁵ Of course one should consult the latest publications for detailed information. Latex goods must meet the specific requirement of the countries in which they are sold. Reference should always be made to the particular health regulations in force.

The CEN (European Committee for standardization) consists of a 'system' to carry out formal processes shared between national members and associates. Members are obliged to implement the European Standards (EN's) by giving them the status of a national

standard. More detailed information can be found at www.cenorm.be which is part of the www.europe.eu.int internet site.

Abbreviations

AAG	ammonium acetate gelation
BgVV	Bundesinstitut für gesundheitlichen Verbrauch und Veterinärmedizin
DPG	N,N'-diphenylguanidine
EU	European Union
FDA	Food and Drugs Administration
MBT	2-mercaptobenzthiazole
TBzTD	tetra-benzyl-thiuramdisulfide
TRGS	Technical Rules for dangerous substances
ZBEC	zinc-dibenzyl-dithiocarbamate
ZDEC	zinc-diethyl-dithiocarbamate
ZMBT	zinc-2-mercaptobenzthiazol

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Natural Rubber Latex Technology

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Dipping

Production of condoms and gloves

Introduction

Condoms and gloves are produced in very large numbers on highly automated production lines. This industry relies almost exclusively on natural rubber latex since its ability to form smooth, continuous films on drying is outstanding and its vulcanizates have high strength and elasticity.

In the dipping process a suitably shaped former is immersed in a latex mix for an appropriate time and carefully withdrawn to produce a uniform layer of latex on it. The latex deposit is then dried and vulcanised before the rubber product is removed from the former.

Latices concentrated by centrifugation to 60% dry rubber content are most commonly used. High-ammonia (HA) centrifuged concentrate and low-ammonia concentrate preserved with zinc oxide and tetramethylthiuramdisulfide (LA-TZ) are particularly recommended.

Sulphur is used as the primary vulcanising agent with zinc oxide as activator and one or more ultra-fast accelerators.

Latex storage

Natural rubber latex concentrate is delivered to the consuming factory either in bulk, i.e. 9,000-14,000 liter (2,000-3,000 gallon)

Origine of the name

The word condom is probably derived from Latin 'condus' meaning receptacle. Another explanation is that the gut condom was invented by the English army doctor Colonel Quondam around 1645 and that the word is a corruption of his name. It is not known who invented condoms, but it is known that they were in use. There is evidence of this in the writings of Marquis de Sade, Casanova and James Boswell. The latter, a Scottish lawyer and writer, protected himself against sexually transmitted diseases by using a linen condom. During a visit to an Amsterdam brothel in 1764, he drank with a prostitute, but the encounter went no further as he had left his 'armour' behind. When visiting a brothel in Marseilles, Casanova tried so-called 'English raincoats', and spoke of reaching great heights.

tanker loads, or in 200 kg (45 gallon) drums. In both cases it is important to ensure that the latex is stored properly prior to use. Latex storage tanks may be made from mild steel, stainless steel or reinforced plastics. Cylindrical tanks are normally used for latex storage. These are preferably mounted with the longest axis vertical, although horizontal tanks may also be used. Natural latex has the tendency to cream. When left undisturbed the rubber particles move upwards and tend to concentrate at the surface. Therefore the latex must be stirred by means of large diameter rotor blades at relative low speeds. The duration and frequency of stirring depends on temperature. The required storage tank capacity is clearly dependent on the consumption, but each tank should be at least large enough to take one full tanker delivery. Storage tanks must be regularly cleaned and disinfected. All pipelines and fittings to the tank should be free from copper or copper-containing alloys. Pipelines also should be cleaned and disinfected regularly.

Preparation and mixing of compounding ingredients

To ensure uniform mixing of compounding ingredients, and to avoid subsequent settling out, water-soluble ingredients are added to latex as aqueous solutions and water-insoluble ingredients are added as aqueous dispersions or emulsions. De-ionised or soft water should be used.

Sulphur, zinc oxide, accelerators and solid antioxidant dispersions are prepared in a ball mill or attritor, or a similar grinding device, using dispersing agents. Various ceramic balls are needed to reduce the particle size of the ingredients to the required fine sizes for compounding. The inside of the ball mill is mostly made from steatite, a very hard material.

Water-insoluble liquid compounding ingredients are emulsified with suitable emulsifying agents using a high-speed stirrer or homogenizer. It is essential that the particle size of the dispersed material is less than 5 microns. Coarse particles can make processing difficult by settling in the dipping tanks, and may also cause defects in the products.

Latex mixing is needed after adding the dispersions to the latex. The colloidal stability of the latex must be maintained during and after the addition of ingredients and subsequently handling. The ingredients are added to the latex under slowly stirring in order to become a base compound, with the exception of the colour pigment dispersion. To achieve an even distribution through the mix each dispersion should be stirred slowly into the latex for about 5-10 minutes (It is also possible to become pre-dispersed vulcanisation pastes). The viscosity of the compound can be adjusted with distilled water. The compound is gently stirred for about 2 hours.



Maturation

The order in which ingredients are added to the latex can be important in maintaining mix stability.

After mixing, the vulcanizable latex mix is matured, i.e. stored, before use. Typical storage times of 12-16 hours at a temperature of 25–30°C normally is sufficient to ensure adequate dispersion of the compounding ingredients. Besides, maturation allows time for any air bubbles in the mix to rise to the surface.

The mix should be gently stirred during maturation to prevent creaming and skin formation. After maturation the mix is cooled, if necessary, to 16-20°C and strained through an 80-100 mesh nylon or stainless steel gauze. The sieved mix is then fed, avoiding air entrapment, into the dipping tanks.

Dipping

A chain moves continuously around the top and bottom level of the dipping machine. Turning movable formers are connected to both sides of the chain. The formers can turn and also move up and downwards on the chain. The power transmission chain, as opposed to the conveyor chain common in dipping lines, gives smooth movement of the formers. The speed of the chain with the formers can be electronically adjusted. The formers pass several stations and at the end of the cycle stripping can be done manually or automatically.

After being stripped, the formers are lowered into a weak acid solution, conveyed through and then withdrawn. The acid dissolves any deposits remaining on the formers. After acid treatment, the formers are lowered into circulating hot water to wash away the acid and remove any loosened deposits remaining. The formers are dried then in an oven, which is maintained at a constant temperature by re-circulating hot air.

For the production of condoms a straight dipping process is used: After the hot water cleaning and drying the formers go straight into the latex dip.

For the production of gloves a coagulant dipping process is used: After the hot water cleaning and drying, the formers are lowered into the coagulant. Next the coagulant is heated to dry. The dry formers are slowly immersed in the latex mix, left for an appropriate dwell time, then slowly withdrawn. Immediately prior to commencement of the withdrawal the formers are dipped for a further short distance to give a very thin deposit, which is rolled into the bead later on. On withdrawal from the mix, the formers are quickly rotated to even the deposit at the end. The thin layer on the formers can be dried and vulcanised, or a greater deposit thickness can be obtained by partially drying the first layer (at about 60-80°C), and re-immersing the formers in the latex. The first layer must not be too dry or the two layers will not be completely integrated. This process can be repeated a number of times to give the required film thickness.

The thickness of the rubber layer obtained from one straight dip depends on the total solids content and viscosity of the latex mix, but is usually around 0.05 mm. Coagulant dipping gives a rubber layer with a thickness of about 0.5 mm.

Drying and vulcanising

Drying and vulcanising are two quite different processes but, in practical terms, the distinction between them is unnecessary as both processes take place at the same time, although at different rates. The dipped products are usually dried and vulcanised in hot-air ovens. The deposit on the formers is often partly dried at a relatively low temperature, e.g. 80-90°C, before the final drying stage.

After the first drying stage the formers are successively lowered into tanks of hot water (leaching) and after that the formers are immersed in water containing a suitable de-tacking agent. There is an increase of allergic reactions from the latex gloves. In order to make the risk of allergy as little as possible leaching can be done a second time. A special washing machine has been developed. After this washing the gloves has to be dried on the inside and outside.

Final drying and vulcanisation is normally carried out at temperatures of 110-120°C in a cure oven. The oven is divided into four zones, each having its own fan, heat exchanger and adjustable temperature control for requisite temperature graduation of heating conditions as the formers progress through the oven. After curing the products (condoms, gloves) are cooled down by jets or cold air and a pneumatic blow-down system loosens the product sufficiently to strip off the products with ease. A dipping line can produce about 2,500 up to 12,000 products per hour.

Beading

Condoms and gloves as well as toy balloons, are produced with a rolled bead or rim at the open end. The bead is made by rolling down the topmost portion of the deposit on the former. The rolling may be performed mechanically by means of rotating brushes. The rolling is carried out when the deposit is substantially dry but not fully vulcanised; the natural tack of the rubber holds the bead in position during the completion of vulcanisation.

Stripping

The final operation on the production line is cooling down and stripping, i.e. removal of the products from the formers. This is carried out by automatic stripping systems, dry (with compressed air) or wet (with water jets). When a wet stripping process is used the products need re-drying. Finally, to reduce friction the condoms are lubricated with silicone oil.

Quality control

For quality assurance the products (for example, surgical gloves) will be inspected by lot when they are stripped. They will be classified by size, weight and batch number, and random samples will be taken from each lot. The gloves will be inflated, and a visual inspection performed for major/minor defects and cosmetic faults. A surgical glove is packed in a paper bag, left and right hand glove. This is done by an inner-wrapping machine. This bag with the pair of surgical gloves is put on a conveyor belt to the outer wrapping machine. After packing the complete set is sterilised.

Formers

Condoms and gloves are frequently produced on hollow glass formers which, since they have relatively little mass, are rapidly heated and cooled and thus facilitate high-speed production.

Production of special medical products

In contrast to the production of condoms and gloves, special medical products are produced on a much smaller and only semi-automated scale. Often special, product-related machinery is used.

Thin-walled articles are produced by straight dipping, as described above. For the production of thick-walled products (balloons, ultrasound transducer covers, catheters) coagulant dipping or heat-sensitive dipping processes are used. Latex tubes are produced



in lengths of 10 metres, which requires a very special dipping line.

To minimise the risks of latex-allergy an intensively washing of all the products for medical applications is very important. In this aspect producers of medical articles are working on alternative materials to meet the upcoming demand for non-latex products. For sure there is no synthetic material with comparable characteristics to latex. The last production steps are the packing conform medical requirements in clean rooms and the sterilisation.

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Foaming

B. van Baarle LPRI⁴

In foaming processes ambient air is introduced into the latex by whipping or beating. The first machines used to create latex foam were simple, unadapted standard type cake mixers. Later on, more advanced latex foam machines were introduced. However, the essentials of the foaming process are still the same. It is of interest to consider briefly the mechanism how such whipping processes produce foam. It is necessary that the wire whip should travel through the latex sufficiently fast to create a void behind it. This void fills with air, and a large bubble is trapped as the latex flows in over the top. Subsequent rotations of the whip comminute this bubble so that it is reduced to a very large number of little bubbles. These air cells can be exceedingly even in size, although their walls are thin. This process of comminuting large bubbles to form small ones is continued until the desired expansion has been achieved. The last turn of the whip incorporates a few larger bubbles, which usually work their way to the surface, and discharges them. Between these last large bubbles and the very fine bubbles also immediate bubbles are formed.

Dunlop foam process

The first stage of the batchwise process is the compounding of the latex with stabilizers, foam promoters and the remainder of the formulation ingredients, with the exception of foam stabilizers, zinc oxide and the delayed action gelling agent. After a period of maturing at warm room temperature, the compounded latex is rapidly foamed with the whip rotating at a high speed. As whipping proceeds, the volume of the foam produced increases at first and then passes through a maximum. The presence of this maximum is associated with the exhaustion of the foam and latex stabilizers, and with loss of ammonia. Foaming is slower and the maximum foam volume is usually lower if zinc oxide is present at this stage. The viscosity of the latex compound can also have a marked influence the rate of foam formation.

When the desired degree of expansion has been achieved, the whipping rate is reduced while the foam is refined. During the refining, all large bubbles should be eliminated, and the cell size of the resultant foam should become more uniform. At this point the foam stabilizer may be added. At the end of the refining, the zinc oxide and a delayed-action agent are added, either se-

parately in that order, or together. When the zinc oxide and sodium silicofluoride have been added, the foam must be rapidly transferred to the warmed mould. In a well-balanced latex foam formulation, the foam will require about 5 minutes to set, and this must be regarded as the upper limit to the time which is available for transferring the sensitized foam from the bowl to the mould. The moulds are closed and then left to stand for a period of 10 minutes or more to allow gelation to be completed. In the next stage the moulds are placed in a (continuous) oven or in hot water for vulcanization to take place. After curing, the moulds are cooled somewhat and then stripped. After cleaning the moulds are ready for service again.

Continuous foaming processes were also developed. Dunlop patented the first continuous foaming process. Compounded latex and air were metered into the base of a long vertical chamber and beaten to foam. The foam flowed continuously from the chamber down a chute into a second chamber, also provided with a beater, where the zinc oxide and gelling agent dispersions were metered in as the foam passed down to an aperture in the base. It takes only a few seconds to mix and to pass the two stages. The materials to be mixed are proportioned in a continuous stream through the head, and in consequence every region of the mixture is processed to the same extent. In this case the materials being mixed are latex and air, and the result is fine-celled foam of uniform texture.

It is claimed that natural rubber latex foams of specific gravity as low as 0.06 can be produced with this mixing head. The foam density is varied and controlled by means of the ratio of air to the latex which is fed to the machine. The throughput of latex is controlled by means of a latex pump and an air regulator.

Typical specifications for natural rubber latex concentrates are available. The initial ammonia content must be higher for the batchwise processes than when foaming is continuous. This is because a certain amount of ammonia is lost during the stage of prolonged beating and exposure to the atmosphere.

Talalay foam process

The modern Talalay process is briefly described by Madge. A mechanically-foamed latex is expanded by application of vacuum, and is then fixed by a freeze-gel technique.

The latex is placed in aluminum moulds which are specially designed to allow the circulation of heat-transfer fluids through their bodies, and which are equipped with cord paper gaskets in order to make the cavity permeable to gases but not to latex. The foam is then quickly cooled to a temperature below the freezing point of water. As a result, the viscosity of the foam continuum increased, drainage and collapsing tendencies are arrested, and a limited amount of cells interconnection occurred. It is interesting to note that this preliminary foam fixation take place without any appreciable change of pH. Allowing carbon dioxide completes fixation to permeate through the foam, when a very positive gelation occurs as the pH falls. The mould is then warmed and heated by the circulation of suitable fluids (poly-ethyleneglycol), in order first to thaw and then to vulcanize the foam.

A compound of relative high ammonia content is employed, and one of the functions of the carbon dioxide is to increase the solubility of the zinc oxide through the formation of ammonium



ions and through the fall in pH. Gelation occurs by interaction between complex zinc ions and fatty acid like stabilizers. Compounded latex is converted, without prior maturation, into fairly heavy density foam. A carefully metered amount of this pre-foam is transferred into the mould, and a partial vacuum is applied after mould closure. Expansion of the foam takes place, after which the foam is frozen and gelled with carbon dioxide. It is then thawed and vulcanized by means of fluids, which are circulated through the body of the mould.

The advances of the Talalay process as compared with the Dunlop process are that the foam density, and hence compression modulus, may be readily varied by adjusting the amount of pre-foam placed in the mould. Furthermore, the process itself is more readily to automation; on the other hand capital expenditure is higher.

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Spraying

J. van der Hout⁵

When talking about rubber most people can mention a range of products. When talking about latex, almost everyone think of wall-paint, only a few people will think of dipped- or foam products. And there is only a single individual who is aware of latex as a binder for (natural) fibres.

From the earliest days of mankind one looked for a soft place to sit or to sleep on and during ages a bundle of hay or fur counts as a comfortable solution. In more recent times people started experimenting the use of NR latex as a binder for fibres like cocos and animal hair. By twisting the fibre and then fixating the curl by steaming an excellent volume and resilience was obtained but after a short period these properties were lost.

This problem was solved in the early sixties when a company in England (Curled hair) introduced a process where the curled fibres were dipped in latex and then vulcanized. Now it was possible to produce filling materials with excellent properties and a high durability. Moreover, due to the structure of the material and the adhesive properties of the latex it became possible to manufacture all kind of shapes and products like packing materials, car seats, filters, mattresses etc.

Natural latex offers the ideal properties for such products. Due to the low viscosity of the liquid, the latex is able to spray on the fibres. The little droplets partly cover the fibre but mainly slide over the fibre surface until they hit a point where fibres cross. Due to the low surface tension the droplets cover both crossing fibres, thus creating a strong and flexible bond while drying. The sheet then formed is strong enough to handle. The form is not fixed yet; the dried latex shows a high degree of tackiness. A property that is very important in the further process of giving the product its final shapes. Normally there are two principles used:

1 One or more layers of sheet are pressed in a plywood press. Heated steel plates, up to 120°C, compress the sheet to a certain thickness. The heat removes the remaining moisture from

the latex and starts vulcanization. The residence time in the press is for capacity reasons as short as possible. The product is taken from the press as soon as the thickness is fixed (does not blow or collapse) and the product can be safely brought to the vulcanisor. Because the press heats the sheet from the outside inwards, the outside of the sheet reaches a higher degree of vulcanization than the inside of the sheet. For this reason the accelerator of the system in the latex compound is rather slow in order to prevent over-cure of the surface. In more modern systems the plywood press is replaced by a system where passing hot air through the sheet does the heating. The open structure of the rubberized fibre is an excellent heat exchanger. The drying and heating process is then much faster and more uniform.

2 For more complicated forms moulds are being used. Unfortunately it is not possible (yet) to inject fibre and latex into a mould. Therefore moulded products are manufactured from building up a form by compressing pre-cut sheets into a mould. Also here the tackiness of the latex is very important. When pushed into the mould the latex holds the fibre in the desired shape. Normally a special compound is used that gives a higher degree of tackiness. The pre-cut pieces are sprayed with it and dried to create maximum tackiness. By hand the sheets are then placed in the mould. The mould is closed and heated until the form is fixed.

In both forming processes only a part of the vulcanization step is carried out. The sheet or moulded products are placed into an autoclave to vulcanize the products completely. This process takes 20–60 minutes depending on the formulation. In most cases hot air is used, but due to the low density of the products, open steam vulcanizing gives the best results.

For a short period these products were very popular and used on a large scale because alternatives were not available. Then synthetic foam appeared on the market and took over because it was cheaper and easier to process. Nowadays the market has become much smaller. But still there is an ongoing interest for these products, because their unsurpassed ability to control humidity and temperature in a seat and mattress.

Besides that, it is a product of 100% natural materials. This aspect is becoming more and more important. And because being based on natural materials is not a guarantee for being free from harmful components, this aspect is also a new challenge for compounders. Their formulation has to meet all the new requirements: nitrosamine free, carbon-disulphide free, anti-allergic etc.

There is still a lot to learn and to improve on this old product. A challenge for us to continue the production of rubberized cocos.

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Sheeting

R. Scott⁶

The successful high quality production of latex sheet is the result of an investigation, which started over 30 years ago. Today, sheet is produced on a continuous basis providing widths up to 4 meters and thicknesses from 0.2 to 3.0 mm with a tolerance of $\pm 10\%$. To meet market demands the products are available in a wide range of colors and blended with synthetic latex rubbers. There are less than five companies worldwide practicing continuous manufacture of sheet and giving good profit margins, but no doubt future-manufacturing costs will rise to accommodate compliance with international standards and regulations to ensure maximum product reliability and product safety.

Industrial products are vacuum blankets, release membranes, special effects for film and television. Typical medical products are as dental dams, surgical straps and operating theatre needs. Other products are exerciser bands for leisure and clothing (fashion and fetish).

The use of pre-vulcanized natural rubber latex compounds form the major part of the production, plus the use of post-vulcanized natural rubber latex and some synthetic rubber latex compound. Compounding is on conventional lines with materials added as aqueous-dispersed preparation. The essential process parameters being viscosity, temperature, and heat sensitivity and an air free condition.

Modified viscosities may be entertained for special needs and for this, it may be necessary to use vacuum for air removal, but surface tension control will also be used. Nominal viscosities come from a Technical Specified Compound of $55\% \pm 5$ solid content. Compound prior to use is filtered and when at the specification temperature, it can be gravity fed or delivered from a pressure vessel. The feed rate being determined by a mix of parameters to produce a sheet specification. The method of delivery is similar to that used for foam in carpet production, via a traversing hose line into a holding trough. Different aperture troughs can be put into place for different film thicknesses, this possibly preferred for quality control purposes to use an adjustable aperture system.

The parameters of many processes rely all often on each other, and here is no exception e.g. machine running speed (1 meter/minute), compound gelling rate, compound delivery rate, over drying rate and so on, in all a quite complex program for the technical and production staff, but once optimized it is reliable. Proprietary brands of pre-vulcanized natural rubber latex compounds can be adequately monitored for quality by a chemical stability test (Dunlop) and the sheet compound by a gel bomb test.

The carrying belt may be either stainless steel or a textile, impregnated and coated with a suitable polymer. A good choice is necessary so that water ingress from the latex compound is at a minimum, not forgetting that the compounds are of alkaline nature. The natural latex compound also will deposit protein traces etc, which can adversely affect the sheet quality being deposited. These deposits have to be removed periodically and result in down time, and this problem may be prevented by selecting a polymer with high surface tension nature, so, that

the protein travels preferentially with the deposited layer of compound or sheet.

The gelation can be carried out in an oven by infra-red heating prior to the main drying program where the deposited layer travels into an oven with steady increasing temperature with the length. This practice starts with a slow dry so as not to over dry the surface too quickly which can prevent moisture by skinning. A major consideration with moisture removal is the efficient way in which it is taken away to allow the oven temperature to function correctly and is assisted by the strategic positioning of extractions. The attention to ambient temperatures and draughts is also essential to ensure the manufacture of good quality sheet and consistently.

After following adequate drying and prior to roll up of sheet an (anti-tack) agent will be needed to apply a de-tack to one surface. The selection of an agent takes account of sheet, which may be fabricated, using adhesives, and therefore non-silicone systems could be used. Until recent times simple dry powders held in a trough at a suitable point in the process line were acceptable, which also satisfied machine design costs, when considering wet slurry application.

However, future legislation possibly concerned with allergies and in particular with the powder adsorbed protein issue, may see the use of de-tack systems more like those used in dry rubber industry and certainly with regard to good housekeeping and personnel health and safety. Currently excess powder is removed for the above, and controls to minimize the application anyway come from powder conditioning, ultrasonic and the simple use of a soft rotary brush extractor at the sheet surface.

Evolving within the glove industry, legislation is endeavoring to ensure that latex products present, the minimal risk to users, and one of the requirements is to leach the latex product. This practice for the latex sheet manufacturer will present a significant issue with respect to existing plant, the likely event being that additional units will be installed off line, and at a cost! This situation does not stop there, for it may well be necessary in the not too distant future that employees will have to be screened for their reaction to protein etc. as a safeguard against litigation.

Extrusion

B. van Baarle LPRI⁴

There are two main natural latex extrusion processes, latex thread extrusion to manufacture small diameter thread, and tube extrusion to produce a kind of hose from which for example inner tubes for sporting bicycles are manufactured. In the first case a coagulant dipping extrusion process is used, in the other case compounded heat sensitive natural rubber latex may be used.

Latex thread extrusion

For thread production, both high- or low-ammonia types of natural latex are used. Standard thread formulations may be varied to a certain extent to meet factory requirements. A typical thread plant consists of a header tank wherein the latex is stored



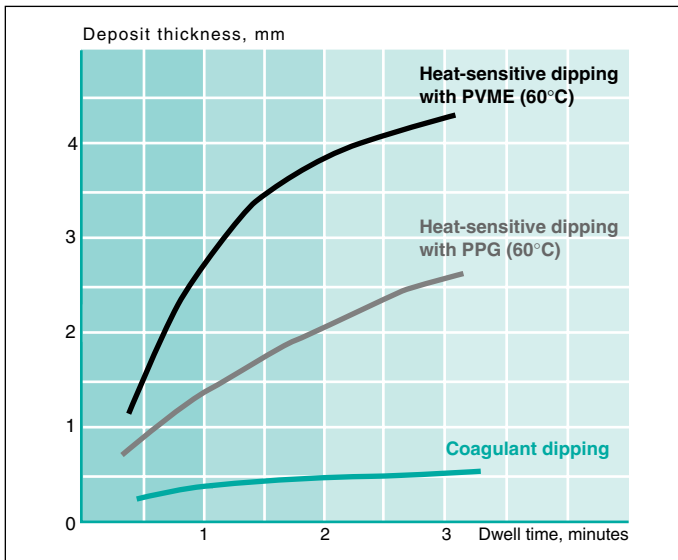


Figure 1. Deposit thickness obtained with coagulant and heat-sensitive dipping.

and flows through a pressure regulator to the manifold. From the manifold the latex passes through a capillary (spinneret) placed under an angle of 45° and gels (under liquid level) in contact with the acetic acid in the coagulation bath (also other mixtures or solutions of salts are possible). The gelled filaments are pulled along and pass through a washing bath into drying and vulcanization ovens, starting drying at 90°C up to vulcanization at 140°C at the end of the oven.

Latex tube extrusion

Heat sensitive latex is prepared by incorporating a heat-sensitizing agent in the compounded or pre-vulcanized latex. As heat sensitizing agent a polypropylene glycol (PPG) solution or polyvinyl

methyl ether (PVME) is used. These agents are more effective than coagulant dipping, this means that the wall thickness can be much larger than straight or coagulant dipping (figure 1). The heat-sensitive process is thus excellent for producing thick latex thread or tubes by means of extrusion. Depending on the used heat-sensitive agents wall thicknesses up to 4 mm are possible within seconds. PVME is more active than PPG. The choice of agent depends on the used temperature; standard temperatures are 50–70°C.

A heat-sensitive natural latex compound flows from a constant level device to the extruder. The extruder-head is made of concentric polished glass tubes fitted with a cold water jacket at the top and a hot water jacket below. When the latex compound enters the heated zone around the hot jacket, it gels in the annulus between the concentric tubes and is slowly extruded from the bottom of the apparatus. The cold jacket is maintained at about 20°C and the hot jacket is normally at 50–70°C depending on the cross-section of the tubing that is required. The tubing in the form of a wet-gel is passed through a water bath for leaching and is dried and vulcanized in a hot air oven.

The described methods are used to manufacture extruded products for different applications. The thread is used in the clothing industry, like elastic braiding and foundation garments. The tubes are mostly used in sport inner bicycle tires.

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Natural Rubber for Medical Devices

D. Ingles¹

Introduction

The use of natural rubber in medical devices dates back to the middle of the last century when, shortly after the discovery of the vulcanisation process. The unique characteristics of natural rubber namely, flexibility, resilience, high mechanical properties en extendibility, has meant that their use is still attractive. However, over recent years the dramatic changes that have occurred within the medical device industry, have led to the introduction of a diverse range other elastomers with desirable characteristics.

Key properties

The Medical Devices Directive (June 1998) states that devices may only be placed on the market and used if all the necessary steps have been taken to ensure that they do not compromise the health and safety of the users and patients. Therefore, to qualify as a suitable material for biomedical applications, elastomers must be shown to exhibit the following key properties: Biocompatibility, Sterilisability, Processibility, Cost.

Biocompatibility

Probably the most important characteristic is the biocompatibility of the device.

All materials must meet certain medical requirements before they can be used in a medical device. These requirements are far above and beyond those required for non-medical applications and are dependent upon the nature and duration of the end use of the product. Before a brief description of some of the tests that a potential biomaterial must undergo, it is worth remembering that medical product testing must take place on the device in its finished form. This means that account must be taken of the fact that materials that may pass such tests before processing, may well fail afterwards. For this reason, approvals given by manufacturers can only serve as an indication.

Biological Testing

The level of testing required for a particular application is dependent upon the type and duration of contact of the device in use; for example, a long-term implant will require more in-depth testing than a sticking plaster. The rules for this procedure are outlined in ISO 10993, as are all the test methods.



Chemical testing

It is obviously important to assess the identity and levels of any substances that may leach out of the material during use. To this end there are various extraction studies and regulatory requirements outlined in the US and European Pharmacopoeia, which prescribe, limits for species such as Heavy Metals, Residual Monomers, Cyanide etc.

Natural rubber is often formulated with numerous (chemical) additives, for example, activators, vulcanisation ingredients and fillers. The potential for these substances to leach out of the final product either renders them unsuitable for medical applications or means that the product/material has to undergo a washing process to reduce the levels. An example of this is that certain rubber formulations are used as positive controls since their extractions are known to fail cytotoxicity tests.

Physical testing

It is important to assess the suitability of the material in terms of its long-term performance under physiological conditions. Most types of devices are covered by nationally or internationally generated, product specific, standards, which can be used for this purpose.

Sterilisability

The majority of products supplied into the medical market are supplied sterile and so the materials from which they are made must be able to withstand the rigours of the various sterilisation processes.

The table outlines the most commonly used sterilisation techniques and their effects on natural rubber (latex).

Most commonly used sterilisation techniques and their effects on natural rubber (latex)

steam sterilisation	not so good
ethylene oxide	good
radiation	good
gas plasma	under development

At this time, ethylene oxide gas is the process most commonly used by device manufacturers, however, it is soon to be overtaken by radiation methods, for economic, safety and simplicity reasons. In hospitals, the steam autoclave is still used to enable re-use of products designed for that purpose.

An appreciation of the effects of the sterilisation process upon the device and its materials must be considered early on in the design process as well as confirming the situation by post-sterilisation testing.

Processibility

The ease of processing is a major consideration for manufacturers of medical devices when specifying a material for use in a medical device. Natural rubber is generally brought in from outside vendors due to the requirement for special vulcanising equipment and processes.

Cost

Until recently, the attitude of medical device manufacturers has been 'safety at any cost', consequently, the emphasis has been on risk reduction rather than cost reduction. In addition, the

regulatory controls are so stringent that, once the design of a device has been finalised, any changes due to attempted cost reduction have been discouraged. However, recently the emphasis has changed and more attention is being paid to the materials and processes in order to achieve the ideal balance of performance, safety and economy.

Natural Rubber

For many years natural rubber has accounted for the bulk of all elastomers used in medical devices. The excellent elasticity, flexibility and resistance against splitting make it the material of choice for several applications however, the blood compatibility of natural rubber is poor compared with other elastomers (work has been done on improving the haemocompatibility of natural rubber by grafting various species onto it, however, this tends to increase the cost of the items).

Unfilled natural rubber has a high resistance to the action of aqueous biological media; however, a particular problem associated with the material is latex protein allergy. All parties including manufacturers, regulators, and users have taken various measures. Manufacturers have been actively improving their production processes to reduce the levels of protein in the finished articles (mainly gloves and condoms), primarily by a process of washing.

Natural rubber device applications

membranes
diaphragms
blood pressure cuff coils
seals
covers
tubes

The Regulatory Bodies of Europe and USA disagree on the severity of the problem and therefore the nature of the response. It is the MDA's (section of the Dept of Health) opinion that rubber items such as gloves that have been used in the UK have been of sufficiently high quality so as not to cause a problem. This is endorsed by the fact that there have been no recorded incidents of latex protein allergy.

The FDA in America, on the other hand, takes a much more serious view due to the fact that up to 5% of exposed people are reportedly sensitised to latex.

Whatever the reason, the FDA have declared that all medical products that contain any natural rubber should be so labelled with a consequence that latex-containing goods are readily identified and can be excluded from tenders.

Summary

Natural rubber continue to play an extremely important role in the manufacture of medical devices and additional components, however, the move towards consistency, safety and economy is driving designers to be more resourceful in the ways in which these materials are used.

In addition, the stringent regulatory environment and the potential for litigation is making it increasingly difficult for suppliers to enter what is still an extremely profitable market.

¹ RAPRA Technology Ltd., Shawbury, UK.



Natural Rubber in the New Millennium

Dr H.P. Smit¹

The world rubber economy depends heavily on the world economy. Natural rubber accounts for nearly 40% of the total elastomer consumption worldwide. However, the natural rubber industry is facing a double problem: over-supply in the short and medium term, and possible shortage in the future. This article will give some new aspects.

Economic growth

Projections will be provided for world economic growth. Future growth rates are based on relative simple models, as described by Burger and Smit (1997), where necessary adjusted to accommodate additional information. The key role is the aggregate for the world economy. Growth rates for the past and the future are given in figure 1. Shown are the old projections and the new outlook, incorporating what now is seen as the effect of the Asian crisis. The differences are partly caused by the crisis and are partly due to just incorporating new information. The years 1996 and 1997 turned out to be slightly better than originally predicted, but 1998 and 1999 are expected to be worse. The future peaks are anticipated to be roughly at the same level, but the troughs are not expected to be as deep as originally expected.

World production was in 1999 6,600 thousand tonnes. The projections for the near future are for production to go up but not with the same increase as has been seen in the last few years (figure 2). But this depends on the effects that the changes in the East Asian exchange rates have on the local economies. By itself, the currency depreciation in the major Asian producing countries leads to substantially lower world market prices in US\$. But lower prices trigger more demand, and a new equilibrium can be reached.

An early indication of possible future shortages or surpluses can be obtained comparing trends in total rubber consumption and normal production of natural rubber. The two sets of growth rates, total rubber consumption on the one hand and normal production of natural rubber on the other hand are shown together in figure 3. It is clear that in the near future growth in normal production is close to growth in total rubber consumption but it is a bit lower. Not before 2003 can a more tight market be distinguished. This is expressed in terms of projections of prices, NR consumption and NR shares.

In reality in most cases production and consumption react to prices which then are determined at such level that in broad terms supply equals demand. The analysis for supply of natural rubber is based on the assumption that the tapping intensity depends on prices. Tapping intensity is formulated as the ratio of actual production to normal production. While total consumption of rubber is supposed not to be influenced by relative prices, the share of natural rubber is indeed affected by relative prices. Developments in the end-use composition of rubber consumption are included in a recently developed complete new model.

In the past, world shares have increased from a trough of less than 30% in the late 1970's to a peak of over 40% in the early 1990's. A major reason for the increase of the share on a world scale is the geographical composition of world consumption.

The increase is explained by two major factors in this area: the shift of consumption growth to natural rubber producing countries with a relative high share (e.g. India and Malaysia) and the reduction by over 80% in the former Soviet Union, which applied a share of natural rubber of less than 10% in the late 1980's.

Price formation

Singapore natural rubber prices (TSR20) in US\$ terms are expected to recover in 2000, reaching twice the current levels in 2001 (figure 4). The rise is likely to continue significantly in 2003. The prices are likely to increase steadily to levels close to US\$ 2.00 during the remainder of the following decade. After the recession around 2010 prices increase to around US\$ 2.50. The US\$ price projections are lower than earlier projections (figure 5). The new S\$ exchange rate induced the higher S\$ prices, which remain lower but later on exceed the earlier

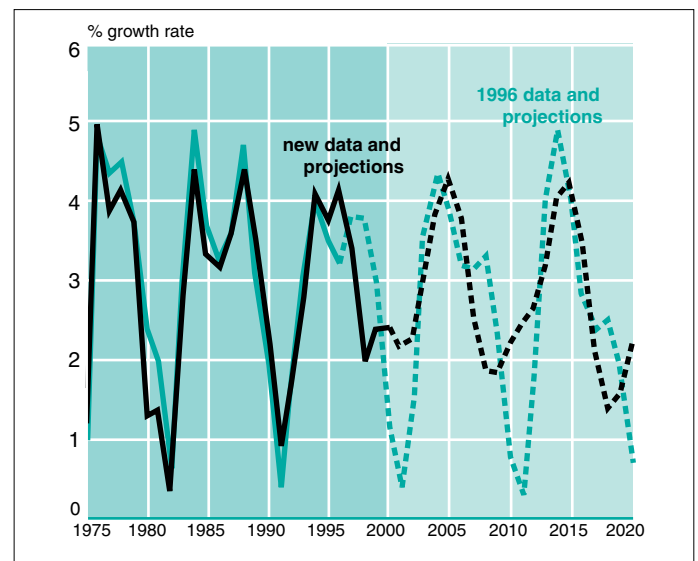


Figure 1. World growth in GDP

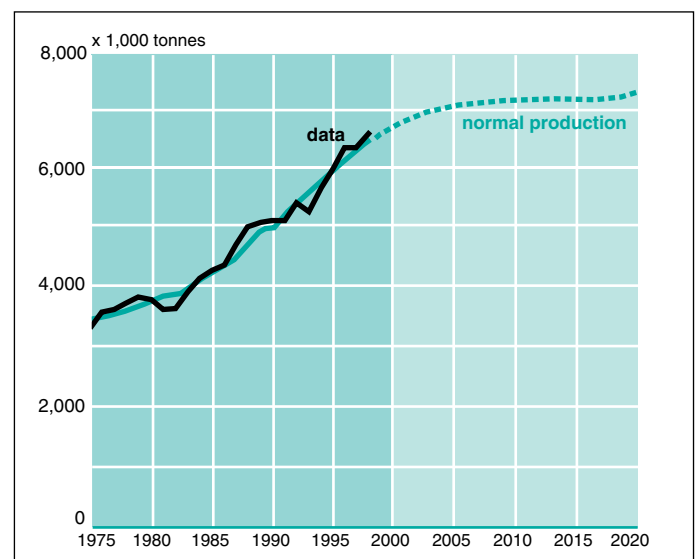


Figure 2. World natural rubber production

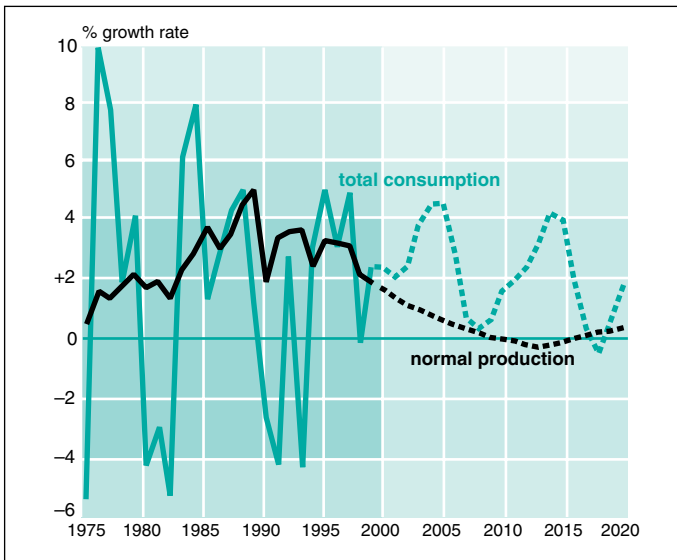


Figure 3. Growth rates

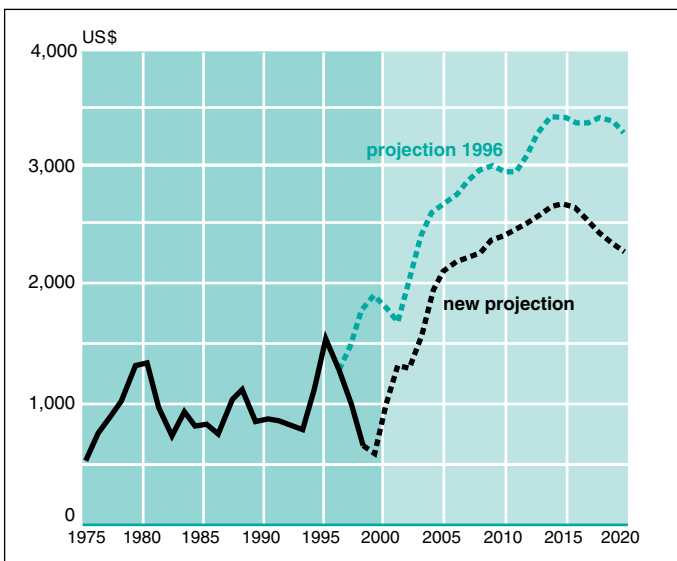


Figure 4. Natural rubber prices (TSR, Singapore) in US\$

projections. A comparison between the natural rubber shares in consumption as they were projected in 1996 and the current analysis is shown in figure 6. Because of lower prices the share is slightly higher during most of the period. Obviously, the improved model also leads to somewhat different projections.

Conclusion

A shortage of natural rubber is still likely to come forward, although the current crisis allows a few more years to cope with it. Prices are still likely to reach the levels up to S\$ 4.50,

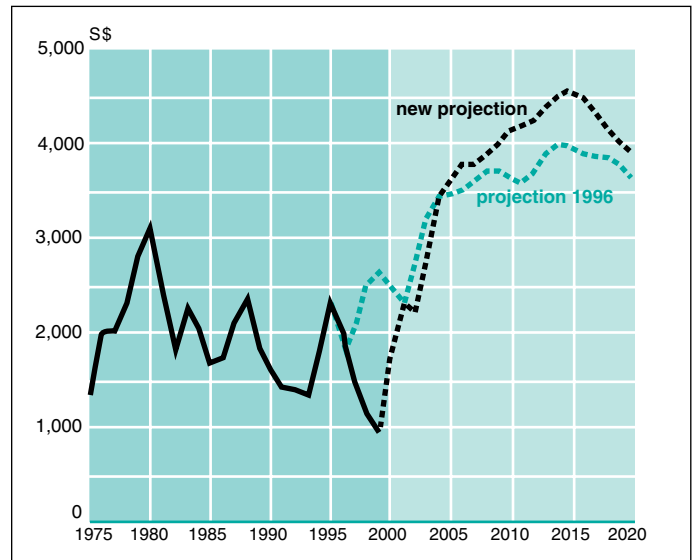


Figure 5. Natural rubber prices (TSR, Singapore) in S\$

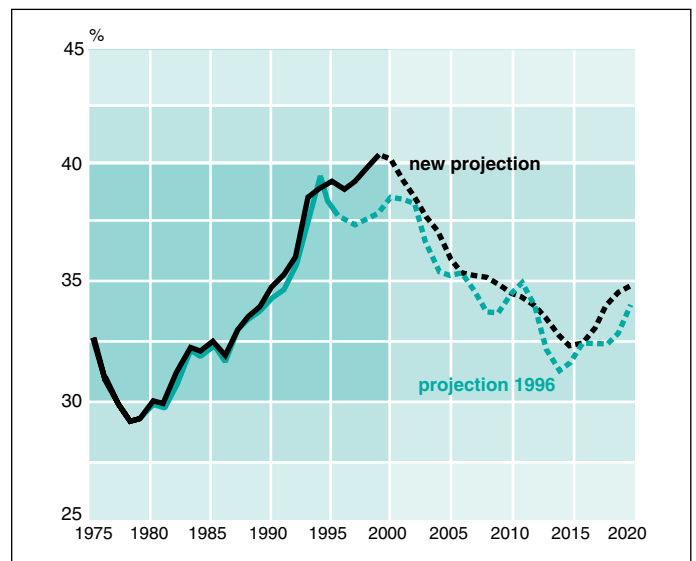


Figure 6. Share CN/CR

although the US\$ prices will be lower than expected before the crisis. All this will lead to a decline in the share of natural rubber from the current 40% levels to levels of around 35%. Additional calculations show that, if there were enough natural rubber available and prices were adequate this would lead to a rather stable level of the share at around 40%.

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