3RD TWO-DAY CONFERENCE ON STNTHETIC EMULSIONS NATURAL LATEX AND LATEX BASED PRODUCTS

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TRENDS IN THE INDUSTRY FOR RUBBER LATTICES

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BIOGRAPHICAL NOTE

Dr Prachaya Jumpasut graduated *magna cum laude* from the University of Wisconsin, with a BBA in Economics. He later went to the University of Michigan as a research and teaching fellow, receiving an MA in 1979 and a Doctorate in 1981, specializing in international economics and economic development. He was an assistant professor at the National Institute of Development Administration in Bangkok before joining the International Rubber Study Group (IRSG) in 1982. Since then he has written extensively on a range of topics and has presented many papers at various international conferences. He holds the position of the Head of Economics and Statistics at the IRSG.

Darren Cooper graduated from the University of York in 1996 with an MSc Economics. With an interest in analysis and development economics he took up a position at CRU (Commodities Research Unit) International in London as an analyst focusing on the world steel industry. From here, he moved on to LMC International (formerly known as Landell Mills Commodities), an Oxford based private sector consultancy engaged in economic research of agricultural and industrial sectors, as Economist focusing on the rubber and tyre industries. In 2000, Mr Cooper joined the IRSG in London as Statistician.

Dock No graduated in 1996 from the School of Oriental and African Studies (SOAS) with an MSc in Development Economics. Upon graduation he joined the London based political-economic analysis group, the WMRC before joining the IRSG in 2000. He is the Economist.

ABSTRACT

This paper focuses on broad trends in the natural rubber (NR) and synthetic rubber (SR) lattices industry. Almost twenty years have elapsed since the AIDS epidemic which, in no small part, resulted in a sharp rise in natural rubber latex consumption and prices as world demand for surgical and medical latex gloves expanded strongly. The presentation examines the trends in consumption and production of NR latex at the country, regional and global level. We also look at price trends before and after the AIDS epidemic which occurred during the mid 1980s. The overall position of NR latex with respect to other types and grades of NR is also reviewed. Less is known about synthetic rubber lattices (SR latex). Nevertheless, this presentation provides some key points surrounding these products, including a description of major elastomer types and their uses, issues regarding data availability and broad trends in the industry. One conclusion is that due to the existence of policies aimed at providing value-addition in producing countries, coupled with high transportation costs, consumption of both NR and SR lattices is greatest in countries where processing facilities exist. Malaysia is the largest consumer of NR latex due its large latex goods industry, while Western Europe and North America would appear to account for the largest share of world consumption of SR lattices.

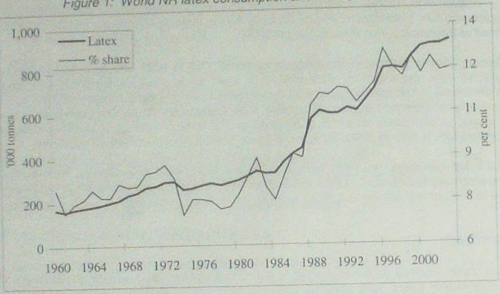
INTRODUCTION

The report is split into two main parts – the first section examines NR latex; the second, focuses on its synthetic counterpart. For NR latex, trends in consumption at the global, regional and country level are examined. This is followed by an assessment of trends in the major latex producing nations. The second part of our presentation provides some important points concerning the industry for SR lattices – an area that is, perhaps, more opaque when compared to coverage of the NR latex sector of the NR industry.

NR LATEX CONSUMPTION

Over the past forty three year the world NR latex consumption had grown at an average 4.2%/year, 1.1% above that of the world NR consumption (Figure 1). The result was NR latex consumption rising from 108,000 tonnes to an estimated 925,000m tonnes over 1960-2003. However, the growth was not smooth, with the modern history of NR latex consumption being neatly divided into two periods; slower growth period over 1960-1983, averaging 3.1%/year and the faster period over 1984-2003, averaging 5.6%/year. In terms of actual tonnage the increase in consumption was 159,000 tonnes for the first period and 597,000 tonnes over the second period. Furthermore, faster rate of growth of NR latex consumption ensured that it also experienced relative growth. From 7–8% share of the total NR consumption in 1960-1984, this had risen to 12.4% by 2003. However, it is noticeable that the relative expansion had come to a halt since the mid-1990s.

Figure 1: World NR latex consumption and share, 1960 –2003



Tragically, the divide, and the main driver of the faster rate of growth of the latter period was and still is due to the AIDS scare and the consequent heightened awareness for the need for protection. This is reflected in the rapid rise of demand for medical and surgical gloves, in particular, since the mid-1980s. Using imports as a proxy for demand it can be seen that annual US & EU consumption of surgical gloves had increased from 3.8bn pieces in 1989 to 37.5bn pieces by 2002 (Figure 2).[1] This is a ten fold increase in just fourteen years. However, this is not to imply that gloves were the sole source behind the rising NR latex consumption over the past twenty years, but to highlight the leading role it had and is still playing in the rubber world. The product base of NR latex is wide and varied, ranging from industrial to household.

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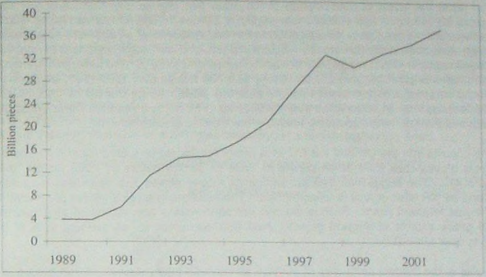
[1] They are the two largest markets for surgical gloves and account for the global demand and it has been assumed tha imports of surgical gloves are all NR latex based, although there are known production capacities for non-NR latex glove around the world. The trade figures of gloves are not split along rubber types.

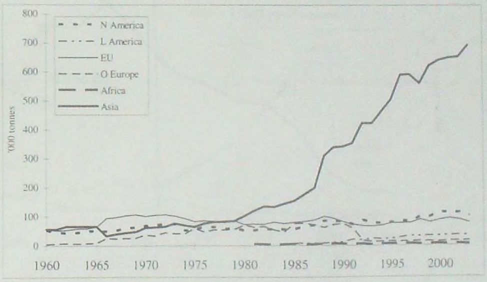
Figure 2: US & EU imports of surgical gloves, 1989-2002[2]



SOURCES OF GROWTH

The main source of growth is Asia (Figure 3). Over 1984-2003, the average growth rate for the region had been 9.2%/year, increasing its annual consumption from 144,000 tonnes to 692,000 tonnes. The average growth rate for Asia is 5% above that of the world rate for the same period. The underlying cause for the rise in demand for NR latex had already been given, but how or why was Asia in the near-sole position to take benefit from it? The explanation lies with their comparative advantage in the latex based manufacturing, especially in the labour intensive areas of dipped goods. Moreover, Asia also had absolute advantage in material and transportation costs as NR latex is produced in the area. Responding to the increase in demand for rubber gloves from the medical field from the middle of 1980s, global and indigenous companies' set-up new facilities and increased their existing capacity in the region.

Figure 3: Regional NR latex consumption, 1960 –2003



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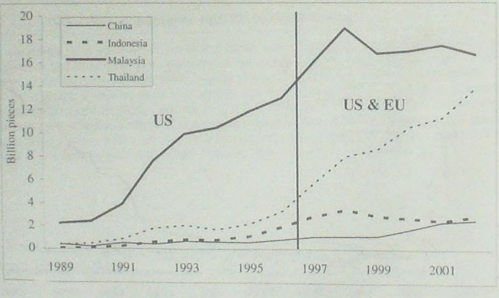
[2] The data for the US imports have been extracted from the United States International Trade Commission (USITC) online information centre – http://www.usitc.gov. In the course of obtaining the data some discrepancies have been noted. There is the possibility that misclassification may have occurred since the beginning of 2002 to the present. There is the possibility that the codes 401511 and 401519, the latter a six digit reference number for all rubber gloves other than surgical gloves, have been mixed up. This study assumes a mistake in the recording of data may have occurred and, hence we use what we perceived to be "correct" data. If not we find that the imports fall dramatically.

As of 2003 the levels of consumption of the other five regions are: North America 101,000 tonnes, Latin America 33,000 tonnes, EU 78,000 tonnes, Other Europe 14,000 tonnes and Africa 4,000 tonnes. However, as a large part of the rise in Asia's consumption is a reflection of an absolute increase in global demand the current level of consumption of other regions did not, in most cases, represent a reduction. As compared to 1984, all regions, with the exception of Other Europe and the EU, have seen an increase. Other Europe saw its NRL consumption fall from 20,000 tonnes to 9,700 tonnes over 1989-1991, which has subsequently been hovering at around 12,000 tonnes for the past ten years. As for the EU its level had marginally fallen by 3,000 tonnes, from 81,000 tonnes over 1983-2003. The fall in demand in Other Europe was as result of the collapse of their domestic economy following the demise of Communism.

Using imports into the US and the EU as a proxy for the region's production it can be seen that outputs of surgical gloves rose from 3.1bn pieces in 1989 to 35.8bn pieces by 2002 for the four countries in Asia (Figure 4)[3]. The suggestion that production of rubber gloves had been and is underpinning the rise in demand for NR latex in Asia is reflected here. The increase in surgical gloves production is just below twelve fold in just fourteen years. Such is the concentration Asia is now estimated as accounting for over 75% of world gross exports of surgical gloves. Asia had accounted for an average 92% of the US and the EU imports over 1989-2003.

Malaysia is the biggest producers of surgical gloves with total output of 16.7bn pieces in 2002. The simple reason for this is that international companies relocated and indigenous companies started up in Malaysia to take advantage of its then status as the largest producer of natural rubber. Since then Malaysia had lost that status to Thailand, who is gaining quickly on the gloves front also. Back in 1989 the ratio of Malaysia-Thailand production was 5.9:1, which has been reduced down to 1.2:1 by 2002. These translate into an increase in annual production from 0.37bn pieces in 1989 to 13.79bn pieces by 2002 for Thailand. Behind these two market leaders are China and Indonesia with total production of 8.38bn pieces in 2002, with the former country holding a margin advantage. However, the Chinese output has been increasing robustly since the late 1990s, while the Indonesian production had been falling, which has reduced a substantial output gap that had existed between the two countries. Under the current trend, it is possible that China would over take Indonesia in the next couple of years.

Figure 4: Sources of US & EU surgical gloves imports, 1989-2002



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[3] Production of surgical gloves do not equal imports to the US and EU, but they account for a high percentage.

CHANGES IN REGIONAL CONSUMPTION

The exceptional growth in Asia has had a profound impact upon relative distribution of consumption levels, which are shown in Figures 5 & 6. From a comparatively strong position of holding 44% share in 1984 Asia's share of world NR latex consumption had risen to 75% by 2003. The area which had borne the burnt of this was Europe in the form of Other Europe and the EU that combined to lose 27% of the market share over 1984-2003. From accounting for 37% of the world consumption of NR latex the share had fallen to mere 10% by 2003 for the combined Europe. North America had emerged relatively unscathed losing only 6% share, falling from 17% down to 11%. However, Latin America had managed to increase both absolute and relative consumption level over 1984-2003. The region's market share had risen from 0% to 4%. This may be a reflection of the region's status as a NR latex producer, in a similar fashion to Asia.

Figure 5: Regional distribution of NR latex consumption, 2003

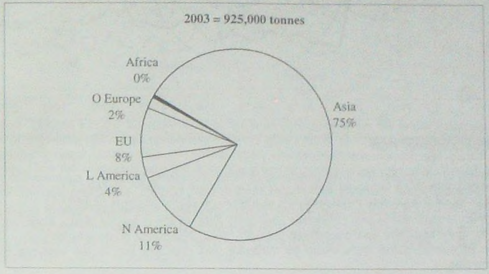
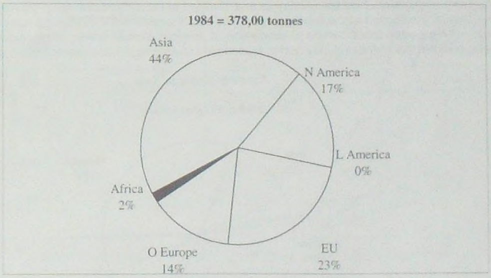
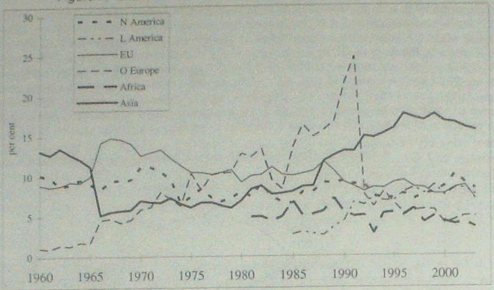


Figure 6: Regional distribution of NR latex consumption, 2003



One further point of change to be noted is the increasing importance of NR latex consumption in overall consumption of NR in Asia (Figure 7). From 7.8% in 1984 this had risen to 17.4% by 1999, which was the peak level of share, but has subsequently fallen to 15.5% by 2003. What is also clear is the near collapse of share of consumption in Other Europe over 1991-1992, when it fell from 24.7% down to 7.6%. In fact, the share of latex consumption continued to decline, falling to a mere 4.8% by 2003.

Figure 7: Share of NR latex in total NR consumption, 1960–2003

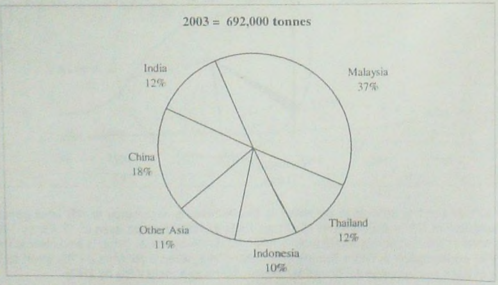


ASIAN CONSUMPTION

Malaysia is the largest NR latex consumer in Asia, accounting for 37% of consumption in 2003 (Figure 8 & 9). Behind are four countries with shares ranging from 10-18%, with China leading this group with a 18% share. Most of the current standings are result of significant changes undertaken in a relatively short space of time. In 1989 the largest consumer was Other Asia, which is mainly Japan, Korea and Taiwan with 32% share, while Malaysia was placed second with 25%. Thailand's share was only 5%. All this implies that most of relative gains were made by Malaysia and Thailand and at the expense of the more mature economies.

It is noticeable that Indonesia had failed to gain market share over 1989-2003, falling from 14% down to 10%. Languishing far behind both Malaysia and Thailand in production of surgical gloves, the loss in market share may be a reflection of the relative importance of this sector to the overall NR latex consumption of the country. With earlier noted decline in production of surgical gloves, unless other sectors are developed it may be possible that Indonesia may further lose market shares of NR latex consumption within Asia.

Figure 8: Share of Asia



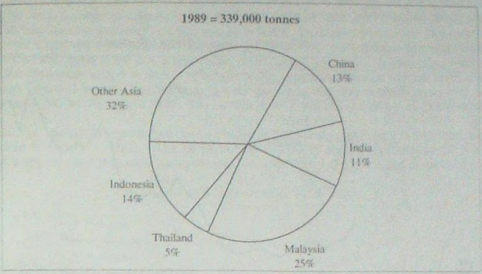
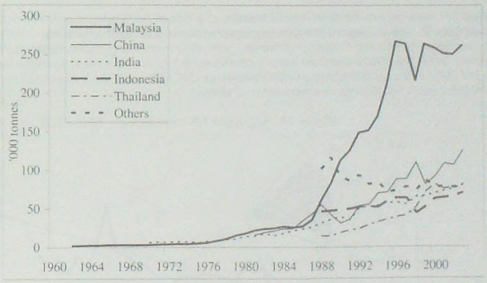


Figure 9: Share of Asia

The process of changes and the absolute level of NR latex consumption for the major Asian countries and their shares of their total NR consumption are shown Figures 10 & 11. Malaysia became the dominant country following a sharp upturn over 1987-1988 when consumption was raised was 35,300 tonnes to 61,100 tonnes. Over the next eight year the level of consumption rose every year without much interruption and it peaked at 267,500 tonne in 1996, but at the end of 2003 its level had been estimated down at 262,500 tonnes although it represents a sharp climb up relative to the past three years. On the opposite end of fortune was Other Europe, which over 1989-2003 saw its consumption drop from 101,000 tonnes down to 16,500 tonnes, although the lowest point was reached on 1955 at 71,000 tonnes. The estimated level of consumption for the four other countries in 2003 are 125,000 tonnes, 81,200 tonnes, 70,000 tonnes and 80,000 tonnes for China, India, Indonesia and Thailand.

Figure 10: Consumption of NR latex[4]



Over the past twenty years not only had the absolute level of NR latex consumption risen in Asia, but it had also increased the level importance to the local rubber industry. For Malaysia the share of NR latex in total NR consumption had risen from 20% back in 1976 to 43% by 1987, the take-off year, and peaking at 81% in 1997. However, the share had fallen marginally since and at the end of 2003 it is estimated at 73.5%. For Thailand the share had peaked at 32% in 1999, although it is now estimated at 27.5%. However, the level of share of the total NR consumption is low for China and India at 8.6% and 11.4%, respectively in 2003,

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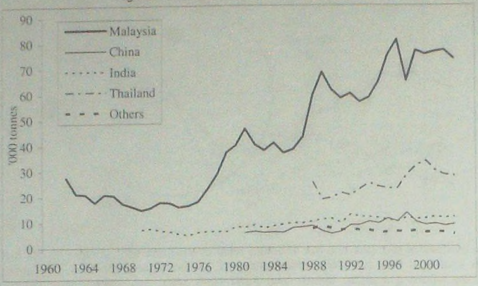
[4] The Indonesia consumption has been derived assuming 45% share of total domestic consumption of NR.

although the absolute level of NR latex consumption is on par with of Thailand. Moreover, the share in the two countries had never reached more than 13%.

Figure 11: Share of total NR consumption



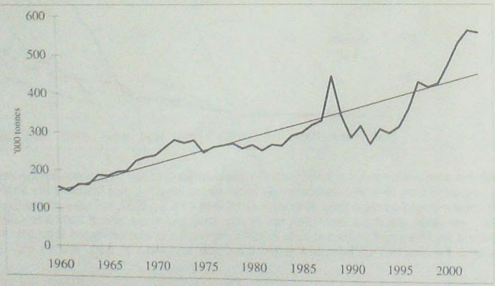
TRADE AND PRODUCTION

Data on NR latex production is not freely available for all producing countries and, as such, output trends in certain countries can be gleaned from trade data. In some countries, a large portion of output serves expor markets, although as clearly demonstrated earlier, many producing countries, such as Malaysia and Thailand, are consuming increasing quantities of the raw material.

EXPORTS

World NR latex exports have increased steadily at a rate of 3.5%/annum over 1960–2003 (Figure 12). The lower growth rate in exports relative to consumption is due to the fact that a large portion of latex is consumed in producing nations. However, coinciding with rising demand export rose sharply from the second half of the 1980s and then again from the early 1990s. As a result absolute level of export had rise to 559,000 tonnes by 2003 from 268,000 tonnes in 1980, although the latest level is a drop of 4,000 tonnes over 2002 when 563,000 tonnes were shipped abroad.

Figure 12: Aggregate NR latex exports, 1960–2003

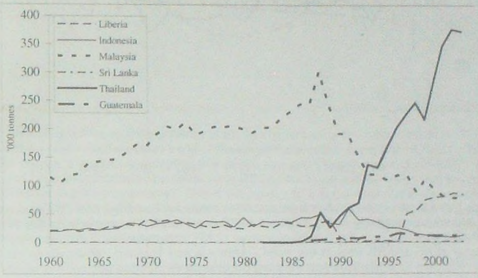


SOURCES OF EXPORTS

There are three main sources of exports of NR latex; Liberia, Malaysia and Thailand (Figure 13). These three countries had together exported 534,000 tonnes in 2003. Traditionally Malaysia had been the leading exporter, but this position had been lost to Thailand since 1993. This is a reflection of overall increase in NR production in Thailand, while at the same time reduction in overall production in Malaysia. Furthermore, the reduction in the Malaysian export is also a reflection of the country's increase in local consumption of NR latex. Although Liberia is one the leading exporters this accolade had only recently been won, with exports reaching above 50,000 tonnes only in 1997. The current level of output in Liberia is 83,000 tonnes.

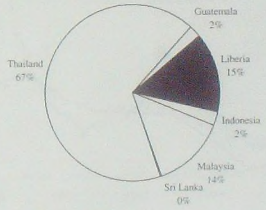
It is noticeable that Thailand's exports have been clipped in 2003 down just over 9,000 tonnes, which explain the overall drop in exports in 2003. The factor behind the fall in exports appears to be the rising local consumption, and possibly due to latex being diverted into production of other types of rubber.

Figure 13: NR latex exports, 1960–2003



As of 2003 Thailand accounts for 67% of world NR latex exports, while Liberia and Malaysia has shares of 15% and 14%, respectively.

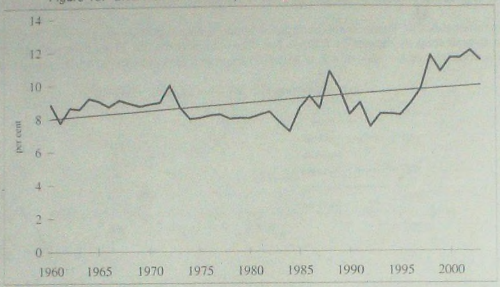
Figure 14: Distribution of NR latex exports, 2003



IMPORTS

It has been stated earlier that exports of NR latex have risen robustly since the middle of 1980s, which implies that imports must also have increased over the same period. This could be seen in Figure 15. Fluctuating around 8–9% over 1960-1984 it rose to 11% by 1987 below falling and rising again to peak at 12% in 2002. At it can be seen the share has fallen slightly in 2003 to 11.4%.

Figure 15: Share of NR latex imports in total NR imports, 1960–2003



Given that a large portion of latex is consumed in producing countries, how do we account for the substantial rise in exports, especially in the 1990s to the present day? The explanation lies with trade between two producing countries, one the largest consumer of NR latex in the world and other the largest producer and exporter of NR and NR latex in the world – Malaysia and Thailand. While we do not have at our disposal data regarding Thai NR latex exports from an officially recognised source, it is widely understood that the majority of all material moving from Thailand to Malaysia is NR latex. And, over 1991-2002 exports to Malaysia from Thailand of NR have risen to 350,000 from below 30,000 tonnes (Figure 16).

Figure 16: Thai exports of NR to Malaysia and share of total Thai exports, 1991–2002

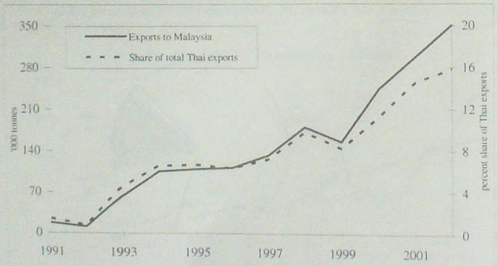
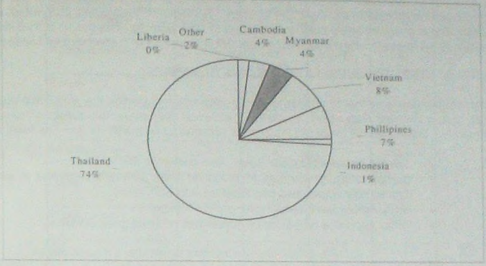


Figure 17 gives a breakdown of Malaysian NR imports by origin in 2002, underlining the importance of Thailand as a supplier of NR latex to Malaysia There has been a steady rise since that time, which, as we will see, is due to trade between Malaysia and Thailand

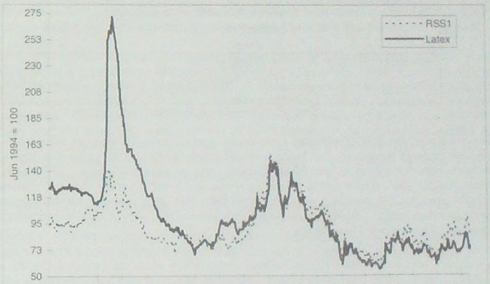
Figure 17: Malaysian Imports of NR by origin, % shares 2002



PRICES

The price of latex does not move independently of the fundamentals of the rubber industry. This means that latex prices move in line with the overall trend of the benchmark rubber price, that of RSS1. This is seen in Figure 18. Of course, the obvious exception to this rule has been over the period 1988-89. Over the first half of 1988, the latex price increased by 140% while RSS1 rose by only 28%. What was the reason for this monolithic difference in price movements? This is simply due to a substantial rise in demand in 1988 when approximately 571,000 tonnes of latex was consumed compared to 439,000 tonnes in 1987, an increase of 30%. Although latex had carried a premium over RSS1 throughout the mid-1980s and into the early 1990s, this has since been replaced by a discount.

Figure 18: Latex and RSS1 prices, Jan '86 –May '03



SYNTHETIC RUBBER LATICES

At this point, attention is switched to the synthetic side of the equation, and we put forward a brief – non-technical – overview of the SR-latex sector, providing a description of the major elastomer types and their uses, touching on the issue of data availability, before focusing on broad trends in SR-latex markets, using the information available. The overview is intended to provide an indication of the importance of these materials in the context of the world SR industry. It should be recognised, and noted, as a segment of the industry that is often not adequately covered due to data scarcity. The upshot is that individuals and parties sometimes fail to appreciate the significance of SR lattices in both market size and scope of applications.

MAJOR SYNTHETIC RUBBER LATTICES AND THEIR USES

The intention here is neither to provide in-depth information regarding the production process for SR lattices nor to give a detailed discussion surrounding technical properties and molecular structure of the various elastomers. There are four major SR lattices, as recognised by the IRSG, and are listed as follows:

- *Styrene-butadiene rubber latex*: Also known as **SBR-latex**;
- *Carboxylated styrene-butadiene rubber latex*: sometimes referred to as **XSBR-latex** (trade data usually aggregates this together with SBR-latex);
- *Nitrile rubber-latex*: also known as **NBR-latex**;
- *Polychloroprene rubber latex*: sometimes referred to as **CR-latex**.

Table 1: Major end use sectors for synthetic rubber lattices

Natural and Synthetic Rubber Lattices	**Major End Use Sectors**
NR Latex	Examination, household and surgical gloves; Balloons; Condoms; Thread
XSBR latex	Paper coating; Carpet adhesives; Impregnations and adhesives
SBR latex	Foam products; Carpet foam; Binder/adhesives
CR Latex	Household and industrial gloves; Adhesives; Coatings
NBR latex	Industrial gloves; Textile industry

Source: International Rubber Study Group

A few years ago, the IRSG conducted an in-depth study examining the uses of both NR and SR lattices and some brief findings are provided in Table 1. Solid forms of NR and SR enjoy a multitude of markets ranging from tyres right through to simple mats, shower caps, seals and gaskets. SR lattices also serve a great number of end use sectors owing to the very many rubber products that are manufactured. The most important uses for SR lattices are listed below (with NR latex included for the purposes of comparison). Taking coverage further, Table 2 provides an indication of the relative size of competing end use sectors for SR lattices in percentage share terms.

Table 2: Relative size of competing end use industries, % share

Type of Application	**NR**	**X/SBR**	**NBR**	**CR**
Dipped products	65	-	30	15
Adhesive binders	12	11	20	50
Thread	9	-	-	-
Carpets and rugs	5	40	-	-
Moulded foam	7	1		10
Paper	-	44	30	5
Non wovens	-	4	20	20
Other	2	-	-	-

Source: T D Pendle, IRSG International Rubber Forum, 1989.

Table 3: End Uses of SBR lattices and % share of total demand, 2001

End Uses	**% Share of total demand**
Paper coating	35
Carpet backing	51
Other uses	14

Note: Information available from the American Plastics Council, by kind permission of the IISRP.

There are a few observations to make from the above information. Dipped products – in particular, examination, surgical and household gloves – account for by far the largest share of overall demand for NR latex. With respect to SBR lattices, these materials do not tend to compete greatly with NR latex for market share, and instead largely serve the markets for paper coating and backings for carpets and rugs.

As is commonly appreciated, with the latex allergy having been given wide coverage in the press in recent years, there has been a great degree of interest in synthetic alternatives. This is particularly the case with regard to dipped products – notably in glove applications which are used in a variety of ways in everyday life. NBR-latex is the major alternative to NR-latex in glove applications, with CR-latex taking a smaller share of that particular market. The market for paper applications is also a particularly important one for NBR latex. Both NBR latex and CR latex are used, similarly to SBR lattices, in paper and non-woven applications. However, adhesive applications represent the key use for CR latex. This is not particularly surprising when one considers the perceived high costs of producing CR latex. It is therefore excluded from medium- to large-volume applications such as the industry for dipped goods.

Of course, a number of years have passed since the original market assessment was undertaken. And Tables 3 and 4 provide supporting evidence. According to information presented by BMS (Table 4), an international market research company with specialist knowledge of the latex industry, paints, coatings and paper-products account for the largest share of global demand. One note of caution is, however, advised here, in that demand figures in Table 4 include a portion of SR-lattices that are deemed outside the traditional area of rubber – and hence, rubber statistics. Nonetheless, this information is useful in showing the sheer size of end use sectors for SR lattices.

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SBR latex	Foam products; Carpet foam; Binder/adhesives
CR Latex	Household and industrial gloves; Adhesives; Coatings
NBR latex	Industrial gloves; Textile industry

Source: International Rubber Study Group

A few years ago, the IRSG conducted an in-depth study examining the uses of both NR and SR lattices and some brief findings are provided in Table 1. Solid forms of NR and SR enjoy a multitude of markets ranging from tyres right through to simple mats, shower caps, seals and gaskets. SR lattices also serve a great number of end use sectors owing to the very many rubber products that are manufactured. The most important uses for SR lattices are listed below (with NR latex included for the purposes of comparison). Taking coverage further, Table 2 provides an indication of the relative size of competing end use sectors for SR lattices in percentage share terms.

Table 2: Relative size of competing end use industries, % share

Type of Application	NR	X/SBR	NBR	CR
Dipped products	65	-	30	15
Adhesive binders	12	11	20	50
Thread	9	-	-	-
Carpets and rugs	5	40	-	-
Moulded foam	7	1		10
Paper	-	44	30	5
Non wovens	-	4	20	20
Other	2	-	-	-

Source: T D Pendle, IRSG International Rubber Forum, 1989.

Table 3: End Uses of SBR lattices and % share of total demand, 2001

End Uses	% Share of total demand
Paper coating	35
Carpet backing	51
Other uses	14

Note: Information available from the American Plastics Council, by kind permission of the IISRP.

There are a few observations to make from the above information. Dipped products – in particular, examination, surgical and household gloves – account for by far the largest share of overall demand for NR latex. With respect to SBR lattices, these materials do not tend to compete greatly with NR latex for market share, and instead largely serve the markets for paper coating and backings for carpets and rugs.

As is commonly appreciated, with the latex allergy having been given wide coverage in the press in recent years, there has been a great degree of interest in synthetic alternatives. This is particularly the case with regard to dipped products – notably in glove applications which are used in a variety of ways in everyday life. NBR-latex is the major alternative to NR-latex in glove applications, with CR-latex taking a smaller share of that particular market. The market for paper applications is also a particularly important one for NBR latex. Both NBR latex and CR latex are used, similarly to SBR lattices, in paper and non-woven applications. However, adhesive applications represent the key use for CR latex. This is not particularly surprising when one considers the perceived high costs of producing CR latex. It is therefore excluded from medium- to large-volume applications such as the industry for dipped goods.

Of course, a number of years have passed since the original market assessment was undertaken. And Tables 3 and 4 provide supporting evidence. According to information presented by BMS (Table 4), an international market research company with specialist knowledge of the latex industry, paints, coatings and paper-products account for the largest share of global demand. One note of caution is, however, advised here, in that demand figures in Table 4 include a portion of SR-lattices that are deemed outside the traditional area of rubber – and hence, rubber statistics. Nonetheless, this information is useful in showing the sheer size of end use sectors for SR lattices.

Table 4: Demand for SR-latex by major application, 2001 ('000 tonnes)

Market Segement	Demand ('000 tonnes)
Paints and coatings	2160
Paper and paperboard	1840
Adhesives and sealants	1700
Carpets	880
Non-wovens	330
Textiles	330
Other applications	735

Source: BMS, Rapra Conference Proceedings, Latex 2002

COVERAGE OF WORLD SYNTHETIC RUBBER STATISTICS

Before proceeding, a short note on the Group's focus and its role with regard to statistics is deeme necessary. As an international commodity body, the activities of the IRSG are centred on providing bot economic and statistical information regarding developments in the world rubber industry. This is primaril achieved through two monthly regular products, namely:

- *Rubber Industry Report:* this key publication builds on the Group's statistical expertise and analytica strengths and provides a monthly overview of developments in the world rubber industry.
- *Rubber Statistical Bulletin*: this publication provides a complete overview of trends in the worl rubber industry. Free of words and running commentary, the monthly bulletin provides statistics o rubber production and consumption trade and prices at the country, regional and global level.

In recent years, the Secretariat of the IRSG has been able to expand its database of rubber statistics using an independent approach, whereby statistics are sourced from governments, statistical agencies, industry and the internet. The interaction with industry has been especially useful for the collection and dissemination of SR statistics in recent years, while industry and the use of internet based databases has facilitated growth in the IRSG's database of international trade flows in NR and SR.

Since the Group's inception, the recording of NR and SR statistics has been conducted on an aggregate basis. That is, total synthetic rubber production in Japan, for example, would encompass all grades of SR produced in that country – inclusive of SBR, BR, EPDM, all synthetic rubber lattices and carbon black master-batch, etc (for a full list of individual SR products, refer to Annex A1). However, it is, in large part, governments, statistical agencies and industry that supply data to the IRSG, and it is usually collected or received in aggregate format.

SOME SPECIFICS ON SYNTHETIC RUBBER LATTICES

CAPACITY AND DEMAND

While the IRSG's coverage of world statistics has improved dramatically in recent years, an area which has become increasingly hazy is that relating to SR lattices. Until 2000, perhaps the best available information available in the public sphere was that published by the International Institute of Synthetic Rubber Producers (IISRP), based in the USA.

Table 5: Capacity for major SR latex types, 1999, ('000 tonnes)

Region	SBR latex	Carbox'd SBR latex	NBR Latex	Sub Total	**Total SR Capacity**	*Share of all Capacity*
North America	105	584	22	711	**3,750**	*19.0*
Western Europe	170	577	40	787	**2,683**	*29.3*
Central & Eastern Europe	159	-	-	159	**3,087**	*5.2*
Latin America	18	50	2	70	**669**	*10.5*
Asia	146	200	26	372	**3,114**	*11.9*
Others	5	7	1	13	**106**	*12.3*
Global	**603**	**1,418**	**91**	**2,112**	**13,409**	*15.7*

Source: International Institute of Synthetic Rubber Producers.

However, after encountering some difficulties with regard to data disclosure, the IISRP elected to discontinue its coverage of this sector of the SR industry. Consequently, information regarding capacity and demand trends is no longer available. But, in order to provide an indication of the importance of the SR lattices sector, capacity listings for SBR-latex, carboxylated-SBR latex and NBR-latex are given in Tables 5–6, together with capacity for all SR and the relevant share of latex capacity in the respective regions and at the global level.

Table 6: Share of latex capacity by region, 1999, % share

Region	SBR latex	Carbox'd SBR latex	NBR Latex
North America	17.4	41.2	24.3
Western Europe	28.2	40.7	44.0
Central & Eastern Europe	26.4	-	-
Latin America	3.0	3.5	2.2
Asia	24.2	14.1	28.4
Others	0.8	0.5	1.1
Global	**100.0**	**100.0**	**100.0**

Excluding poly-chloroprene (CR) latex, for which information was not available, SBR-latex and XSBR lattices appear most important, accounting for the lion's share of global capacity. Furthermore, it would seem that capacity is located in Western Europe, North America and Asia, in particular Japan, Korea and Taiwan. This situation essentially mirrors that which prevails for solid SR, which includes: SBR, BR and EPDM. This is not surprising when one considers that the costs of producing SR lattices are understood to be very high.

In order to assess the importance of lattices in total SR consumption, again we make use of information accredited to the IISRP. The information refers to the market situation in 1998, with no updates available in the public sphere since that time. In order to use this data in estimating the market share of lattices in aggregate consumption of SR, it is first necessary to assume that there have been no drastic structural changes in the industry since that time. This is likely to be true for the mature markets of North America, Western Europe and Japan.

Table 7: Elastomer market volumes in selected regions, 1998 ('000 tonnes)

	W. Europe	N. America	Asia	L. America	C. Europe	Aggregate
SBR	612	952	770	380	152	2,866
SBR-latex	**116**	**90**	**145**	**9**	**5**	**365**
XSBR-latex	**720**	**696**	**270**	**55**	**12**	**1,753**
BR	363	565	536	147	47	1,658
EPDM	259	301	168	25	6	759
CR	64	71	88	20	12	255
NBR (solid + latex)	**102**	**106**	**92**	**21**	**19**	**340**
Others	285	456	261	56	60	1,118
Grand Total	**2,521**	**3,237**	**2,330**	**713**	**312**	**9,113**

Note: Data above excludes that which relates to China, the former CIS and other planned economies (according to IISRP definitions).

Figure 19: Synthetic rubber market shares, World

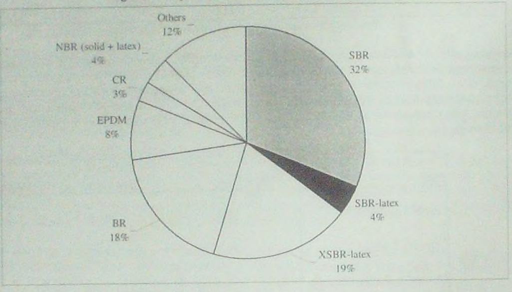


Figure 20: Synthetic rubber market shares, Western Europe

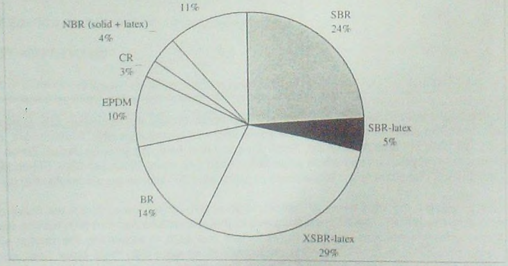


Figure 21: Synthetic rubber market shares, North America

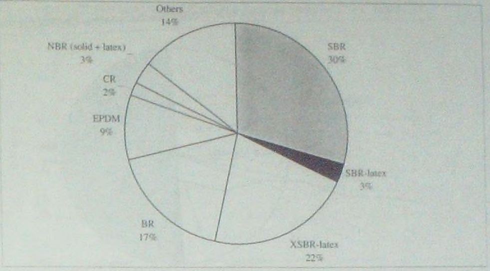
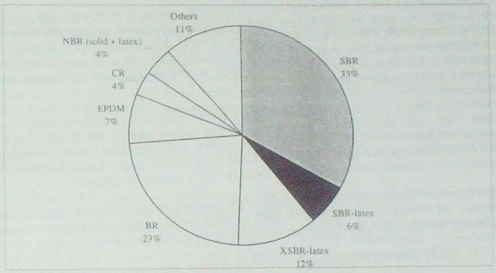


Figure 22: Synthetic rubber market shares, Asia



23: Synthetic rubber market shares, Latin America

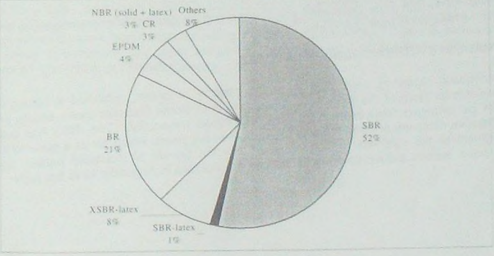
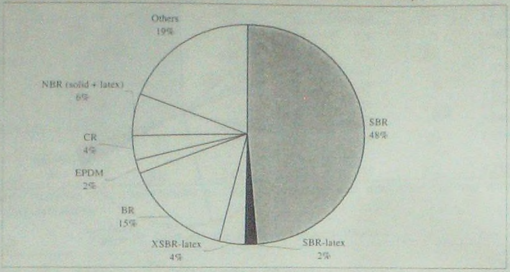


Figure 24: Synthetic rubber market shares, Central Europe



Immediately apparent from the above is the significant share of SBR-latex and XSBR-latex in demand for all SR. Excluding data for NBR (which lumps together demand for solid product and lattices) the markets for SBR-latex and XSBR-latex took a 23% share of world demand for all SR. It would appear, on the basis of the information available, that XSBR-latex is an important market, second in size to that of the solid-SBR market. Of course, aggregating industry data across regions can often mask differing trends between regions and this case is no different.

What one finds is that the largest markets for lattices appear to be those in North America, Western Europe and Asia. Data suggests that in Western Europe lattices of SBR and XSBR take a significant share – in excess of 30% – of the overall market for synthetics, with significant, but relatively smaller, shares indicated for North America and Asia. Lattices account for a smaller proportion of overall demand in Latin America and Central Europe, where demand for these products is less developed.

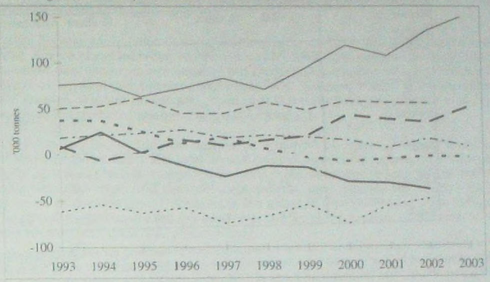
If one recalls that the lion's share of capacity is generally located in those regions, it is not entirely surprising to find the importance of lattices in total demand for SR increasing in regions such as North America, Western Europe and Asia. Some possible explanations may include:

- The perceived high costs of production of latex products;
- The relative size of end use sectors in the regions;
- The high costs associated with transporting the product from one country to another, especially with respect to inter-continental freight.

TRADE IN SYNTHETIC RUBBER LATTICES

Information regarding trade data is, in the majority of cases, published in disaggregated format. It is available for many of the major trading countries in Customs Statistics books, usually on a monthly basis, or can be extracted from internet facilities, mentioned previously. The IRSG has built up a reliable and extensive database of trade flows in SR latex over the years, which act as a guide to the importance of this segment of the synthetic rubber industry. For the benefit of interested parties, aggregate trade flows (imports, exports and net trade) in SR lattices are included in Appendix A2 to this paper.

Figure 25: Net exports of SR lattices for selected countries, 1993–2003[5]



The above figure depicts the trend in net exports for various selected countries. The general theme does seem to be one of key producers also being net exporters – albeit of relatively small amounts – of SR latex. Germany is the notable exception with net exports averaging around 95,000 tonnes per year over the period in question. China, meanwhile, remains a large net importer of material, suggesting that capacity there remains underdeveloped. However, with Chinese demand for rubber having increased strongly in recent years and expected to continue doing so in further years, imports are likely to continue expanding unless capacity is built to reduce the country's reliance on imported material.

According to industry sources, however, trade in lattices is bounded to a certain degree owing to cost issues and practicalities. However, there are some notable exceptions, dependent on geographical location and the product involved (see Table 7).

In the case of NR latex, it is acknowledged that production is usually located close to where the market and processing facilities are to be found, that is in South East Asia, particularly in Malaysia. The situation is rather similar for SR lattices, in that transportation costs are usually much higher than those incurred when moving sheet or block rubber from one country to another. In normal circumstances, as we noted earlier, a special container or vessel is required in order to safely and effectively transport the product. Such apparatus entails much higher costs.

Table 8 is constructed using information available from the US Rubber Manufacturers Association and the US International Trade Commission (USITC), Department of Commerce. US exports by destination, for SBR-latex (including carboxylated lattices), SBR and BR are presented below. The idea here is to show that each product serves different export markets owing to transportation issues. It should, however, be noted that the evidence is anecdotal, and must remain so in the absence of information on trade flows by destination for a high number of different markets.

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[5] Both French and German figures are only up to November 2003, but included in the graph. But, the UK data was not available at the time of writing and the Canadian and the Benelux figures were only up to April and June 2003, as such they were left out of the graph. However, all figures have been included in the table in the Appendix.

Table 8: US gross exports of SBR, solid BR and SBR-latex, 2002 ('000 tonnes)

Exports to Region	SBR	% share	BR	% share	SBR-latex	% share
NAFTA	103.3	52.2	45.4	19.6	54.1	78.2
Latin America	15.0	7.6	34.7	15.0	3.0	4.4
Europe	41.8	21.1	105.5	45.7	10.1	14.6
Asia	26.9	13.6	36.1	15.6	0.7	1.0
Others	11.0	5.6	9.3	4.0	1.4	2.0
Total	**198.1**	**100.0**	**230.9**	**100.0**	**69.2**	**100.0**

The immediate observation is that the external pattern of demand for BR (and to a lesser extent for SBR) is determined to a higher degree by a larger number of markets. Notably, while US exports of BR in total are more than three times greater than those of SBR-latex, the NAFTA partner countries – Canada and Mexico – are the final destination for more than 75% of all US exports. It would appear that significant amounts are also shipped to Latin America and Europe, the latter being the largest regional market for US product. More than 82% of all exports of SBR-latex related products move to NAFTA or Latin America. This provides some slender support for the notion that due to high costs of production and issues regarding transportation, markets for SBR-latex tend to be closer to where the material is manufactured.

Of course, there will be exceptions to this rule, with one example relating to US exports of NBR-latex. In 2002, according to information from US ITC, total US exports of NBR-latex stood at 18,600 tonnes, of which around 85% headed for Asia – with close on 5,000 tonnes moving to both Malaysia and Thailand and further volumes serving the markets of Sri Lanka, China and Indonesia. While NR is the dominant material used in glove production, when synthetic rubber is utilised, NBR-latex is the usual material of choice. Consequently, the pattern of overseas demand for US exports is most likely determined by glove making operations in parts of Asia.

FINAL NOTES AND CONCLUSIONS

This paper has focused on rubber lattices – both NR and SR lattices. What we have found is that the centre of gravity of the NR latex sector, like that of the solid NR and SR industries, is increasingly to be found in Asia. With Malaysia home to the largest national latex goods industry, it is also the world's leading NR latex consumer, a position which it is likely to enjoy for the foreseeable future, despite diversifications downstream by other Asian producing countries. We have also seen that Thailand is the largest supplier of raw NR latex to the Malaysian market accounting for well over 70% of all arrivals in 2002 – and underlining Thailand's position as the largest producer of raw latex. Increasing shipments to Malaysia can, of course, be partly explained by declining output in Malaysia throughout the 1990's.

Malaysia is a prime example of a NR producing country, which has strived to add value to its rubber industry through the manufacturing and exporting of rubber goods. For example, in 2001 Malaysia opened the Washington office of the Malaysian Rubber Export Promotion Council to promote the low-protein, high quality Standard Malaysian Glove. This course of action is designed to promote greater use of NR latex gloves in the US amidst increasing anti-latex legislation in the US in recent months. Additionally, scientists at the John Hopkins University School of Medicine recommended to the Food and Drug Administration that all new medicine bottle stoppers be changed from NR latex to SR in the same year.

Increasingly, other NR producing countries, apart from Malaysia, have adopted policies to increase domestic consumption of locally produced rubber by increasing rubber goods, particularly latex goods, production. In Thailand, for example, rubber related departments are now geared towards promoting such policies. The Chairman of the Federation of Thai Industries, Erwin Muller, has called on the government to proceed with the operation of 'Comprehensive Rubber Development Strategies'. The government policy is aimed at increasing domestic rubber goods production from the current rate of growth of 10% to 20% per year. Thai rubber product exports have been increasing steadily in recent years. Sri Lanka was also reported to be keen on establishing an industrial park for the manufacture of finished rubber goods, with the government aiming to increase the country's share of the world rubber market to 1% from its current level, estimated to be less than 0.1% according to industrial sources.

Our survey of the SR latex sector has considered a different app roach, necessitated by some limitations due to data scarcity. From our brief excursion into the industry for SR lattices, we have certainly found that these products are indeed very important, with capacity and production accounting for a significant share of total SR at the global level. We have surmised that capacity is, however, located in the developed regions, notably, North America, Western Europe and Japan, and that trade flows are bounded to a degree by the high costs associated in producing and transporting latex products.

Future growth in markets for SR latex will depend on a number of issues. Amongst these are demand prospects in markets such as China and India as well as other developing regions. We have already seen that capacity for SBR based lattices is largely to be found in the developed regions, where markets exhibit a high degree of maturity. With long distance trade unlikely, new capacity will possibly be required in developing markets as demand grows. Additionally, the extent to which NBR latex gains market share will, of course, be related to the inroads that this elastomer makes at the expense of NR latex in response to continued concern surrounding the latex protein allergy.

ACKNOWLEDGEMENT

We would like to thank the Secretary-General and our colleagues at the International Rubber Study Group for their helpful comments.

Appendix A1: Synthetic rubber and corresponding HTS (six digit) codes used in international trade

400211	**Latex of styrene butadiene rubber**
400219	Styrene butadiene rubber
400220	Polybutadiene rubber
400231	Isobutene-isoprene rubber
400239	Halo-isobutene-isoprene rubber
400241	**Latex of chloroprene rubber**
400249	Chloroprene rubber
400251	**Latex of acrylonitrile-butadiene rubber**
400259	Acrylonitrile-butadiene rubber
400260	Isoprene rubber
400270	Ethylene-propylene-nonconjugated diene rubber
400280	Synthetic rubber mixtures
400291	**Other synthetic rubber latex**
400299	Synthetic rubber and fatice derived from oils
400510	Compounded rubber, not vulcanised, with carbon black or silica

Appendix A2: Aggregate trade in SR lattices for selected countries

Table A3-1: Aggregate imports of SR lattices for selected countries, 1993–2002 ('000 tonnes)

	Canada	USA	France	Germany	Belux	UK	China	Japan
1993	17.7	22.5	40.3	29.6	75.9	27.1	...	0.6
1994	21.1	38.0	41.7	28.6	68.7	33.1	...	0.4
1995	27.3	29.5	52.6	25.3	74.7	28.8	...	0.4
1996	34.3	24.5	52.0	22.9	73.2	33.0	...	0.3
1997	56.4	30.4	56.1	20.9	101.0	26.8	...	2.8
1998	45.1	29.6	53.7	28.6	98.5	26.9	...	3.4
1999	51.6	31.9	51.7	20.6	92.6	32.1	...	7.6
2000	60.0	23.3	58.8	48.1	106.0	37.2	73.1	14.7
2001	49.7	20.6	48.8	53.9	92.4	24.4	67.4	21.9
2002	55.2	18.5	46.0	49.3	84.2	30.0	67.4	27.6
2003	17.1	18.1	41.5	32.3	36.4	...	76.0	31.3

Table A3-2: Aggregate exports of SR lattices for selected countries, 1993–2002 ('000 tonnes)

	Canada	USA	France	Germany	Belux	UK	China	Japan
1993	24.4	31.3	77.8	105.3	14.1	77.3	...	18.6
1994	45.7	31.2	79.0	107.3	14.5	85.8	...	21.8
1995	29.3	31.9	78.0	88.8	11.6	90.5	...	23.8
1996	22.3	40.6	64.7	95.3	15.5	78.2	...	27.4
1997	32.7	40.6	74.9	104.0	26.4	71.6	...	21.1
1998	33.0	45.1	60.1	99.5	31.4	83.6	...	24.6
1999	37.6	51.9	49.1	114.5	38.5	80.8	...	26.8
2000	30.2	66.0	51.1	166.7	30.8	95.0	0.9	30.0
2001	18.1	58.6	43.7	161.0	36.7	80.0	1.5	28.5
2002	16.4	52.5	43.1	183.7	34.9	85.0	1.9	43.7
2003	5.2	68.6	37.4	184.7	17.7	...	2.3	39.0

Table A3-3: Aggregate net exports of SR lattices for selected countries, 1993–2002 ('000 tonnes)

	Canada	USA	France	Germany	Belux	UK	China	Japan
1993	6.7	8.8	37.5	75.7	-61.8	50.2	...	18.0
1994	24.6	-6.8	37.3	78.7	-54.2	52.7	...	21.4
1995	2.0	2.4	25.4	63.5	-63.1	61.7	...	23.4
1996	-12.0	16.1	12.7	72.4	-57.7	45.2	...	27.1
1997	-23.7	10.2	18.8	83.1	-74.6	44.8	...	18.3
1998	-12.1	15.5	6.4	70.9	-67.1	56.7	...	21.2
1999	-14.0	20.0	-2.6	93.9	-54.1	48.7	...	19.2
2000	-29.8	42.7	-7.7	118.6	-75.2	57.8	-72.2	15.3
2001	-31.6	38.0	-5.1	107.1	-55.7	55.6	-65.9	6.6
2002	-38.8	34.0	-2.9	134.4	-49.3	55.0	-65.5	16.1
2003	-11.9	50.5	-4.1	152.4	-18.7	...	-73.7	7.7

GLOBAL LATEX TECHNOLOGIES AND MARKETS

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ABSTRACT

This paper reviews the current state of the latex industry, examines recent trends within the industry and reviews the factors behind these trends.

The natural and synthetic latex industry is in a dynamic state at the present time. Inter-materials competition has intensified as new materials become available to challenge the incumbent materials.

The synthetic latex supply industry has undergone restructuring with continuing concentration and has considerable overcapacity in some polymers.

The supply of natural rubber has been transformed by shifts in the supply base in Asia as well as the International Rubber Consortium Limited (IRCo) between Indonesia, Malaysia and Thailand.

On the demand side a number of important trends have impacted traditional applications sectors, such as medical gloves.

New challenges face the industry such as increased cost and price pressures as well as the continued allergy concerns about natural rubber latex.

INTRODUCTION

Latex is a colloidal dispersion of a rubber or plastic material in an aqueous medium. Latex can be obtained from trees or from oil-derived chemicals.

A wide range of polymer latices is available commercially including:

- Styrene butadiene copolymers
- Acrylonitrile butadiene copolymers
- Polychloroprene
- Acrylic polymers, including styrene acrylics
- Vinyl acetate polymers
- Vinyl acetate –ethylene copolymers
- Polybutadiene
- Synthetic polyisoprene
- Natural rubber

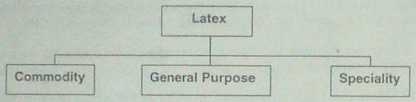
In contrast to Mother Nature who gives us natural rubber straight from a tree, the production of synthetic latices is often a sophisticated process involving free radical emulsion polymerization in water, whereby a monomer is polymerized by itself or combined with another monomer (co-monomer) to create a high molecular weight polymer. The latex dispersion also has surfactants, stabilizers, and other additives.

Synthetic latices can vary from soft rubbery materials, similar to natural rubber, to hard cross-linked solids that are used for durable coatings. In general, latex is more expensive on a dry basis than dry polymer. However, since it is a liquid, it is usually easier to process. Some latex production processes can be readily automated such as glove manufacturing. Latex polymers tend to have better physical properties and to be less prone to contamination that dry polymers. However, many elastomers cannot be manufactured in latex form and must be re-dispersed to make a latex, thus increasing their cost.

Use of polymer lattices is restricted to the manufacture of articles or components up to a few millimeters thick or products with an intercommunicating cellular structure because of the need to remove water during processing. The cost of water removal and the attendant effects of shrinkage, are important and sometimes limiting factors on the use of latex.

The fact that latices are based on water also gives these products several benefits over alternative solvent-based products. For example, the legislation issues associated with health and flammability of solvents are eliminated, or at least mitigated, by using latex. Also, the fact that the polymers in latex are emulsified, rather than dissolved, allows the preparation of very high solids latices (over 70%) without a large increase in viscosity. This enables formulators to make systems comprising a combination of high polymer content and high filler content, something that is very difficult to achieve with solvent-based systems.

It is useful to classify the wide range of commercial polymer latices into three categories, viz. commodity, general purpose and specialty:



Commodity	General Purpose	Speciality
Natural rubber	Polychloroprene (CR)	Butyl (IIR)
SBR	Nitrile (NBR)	Polyisoprene (IR)
	Polybutadiene	Ethylene-Vinyl Chloride
	Acrylic	Chlorosulphonated PE (CSM)
	Vinyl acrylic	Polyvinylidene chloride
	Styrene acrylic	Polyvinyl Pyridine
	Vinyl acetate	Fluoroelastomers
	Ethylene-vinyl acetate	

Commodity Latex

Commodity latices are natural rubber and styrene-butadiene copolymers
The characteristics of these latices are:

- Used in very large quantities
- Narrow applications e.g. paper coating, carpet backing
- Large global overcapacity
- Low prices
- Low profit margins

General Purpose Latex

General-purpose latices include rubber latices, such as polychloroprene and nitrile, plus thermoplastic products such as acrylics and vinyl acetate.
The characteristics of these latices are:

- Used in high volume e.g. textiles, paints, adhesives
- Medium priced
- Used in a wide range of applications

Speciality Latex

Specialty latices are generally produced in small volumes.
The characteristics of these latices are:

- High performance, such as high temperature resistance or enhanced barrier properties
- High price –often produced by re-dispersion of solid rubber
- Tailored to specific functions and manufacturing processes
- Generally only used when specific in-use conditions dictate this

DEMAND FOR LATEX

The overall latex market is dominated by the two commodity rubber latices; natural rubber and SBR.

The consumption of natural latex is just over 7 million tons but most of this is converted to solid rubber, with over 70% being used in tyres. The amount used in latex form is around 1 million tons.

Figure 1 shows the global consumption of latex polymers.

Figure 1 Global consumption of synthetic and natural latex (Ref. 1)

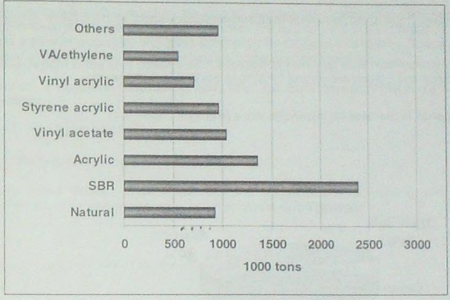
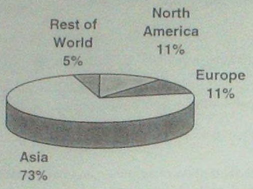


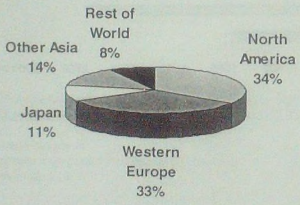
Figure 2 shows the regional demand for 1 million tons of natural latex.

Figure 2 Regional % demand for natural latex (Ref.1)



Global demand for synthetic latex polymers is around 8 million metric tons with a market value of $15 billion, with North America and Europe accounting for 67% of the demand (Figure 3)

Figure 3 Regional % demand for synthetic latex (Ref.1)



COMMODITY LATEX

Natural Rubber Latex

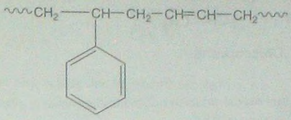
Natural latex (NRL) (cis 1,4-polyisoprene) is the concentrated, purified form of the latex extracted from the rubber tree, Hevea brasiliensis, cultivated in tropical regions, notably South East Asia.

Hevea is indigenous to the Amazon Basin where it grows within 5° of the equator. It was taken from the Amazon to South Asia (Sri Lanka) and South East Asia (Singapore and Malaysia) by the British, where it is now grown on plantations. Cultivation has now spread throughout suitable climatic regions of South East Asia. Plantations can be found within +/-20° either side of the equator.

The traditional hub of the plantation business was Malaysia. More recently Thailand has emerged as the largest producer of natural rubber followed by Indonesia. The investment in plantations in the traditional countries of Malaysia and Thailand has peaked, while it continues to develop in Vietnam and other lower cost countries. Overall, the epicentre of production of rubber in Asia appears to be shifting north eastwards towards Indo-China.

Styrene butadiene (SBR or SB Latex)

SBR is a random copolymer produced by the copolymerisation of butadiene with styrene, either in emulsion or solution.



The most common styrene content is 23-25% for SBR used in the tyre industry but styrene contents of 50 to 70% are common in products for other applications.

Copolymers with more than 45 percent butadiene are usually referred to as SBR latex; products with more styrene may be referred to as SB latex.

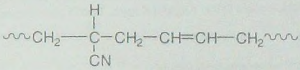
Many SB latices are carboxylated by the use of co-monomer unsaturated acids such as maleic, fumaric, acrylic or methacrylic (these copolymers are often referred to as X-SBR). Carboxylation generally leads to enhanced adhesive properties and gives alternative methods of crosslinking. These type of emulsions are widely used in the paper coating, carpet binding and adhesives industries.

There are many worldwide producers of SBR latex, but BASF and Dow Reichhold have by far the leading market shares.

GENERAL PURPOSE LATEX

Acrylonitrile Butadiene Copolymers (NBR Latex)

Commonly called "Nitrile", these elastomers are copolymers of acrylonitrile and butadiene. They are produced by emulsion polymerization in batch or continuous processes.



$$\sim CH_2-\underset{CN}{\overset{H}{C}}-CH_2-CH{=}CH-CH_2\sim$$

Nitrile used in latex form is actually a terpolymer of acrylonitrile, butadiene and methacrylic acid and known as carboxylated NBR latices (commonly referred to as X-NBR). Methacrylic content is typically 3-6%, with butadiene at 55-70% and acrylonitrile at 25-50%.

Nitrile rubber latices give products that exhibit excellent resistance to solvents, fuels, oils and greases, are abrasion resistant, bond to a wide variety of substrates and exhibit a high degree of toughness.

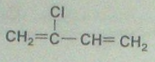
Nitrile latices are the currently the major competitor to natural rubber in the manufacture of disposable latex gloves and are also used as textile and non-woven reinforcement, including the manufacture of synthetic leather. Global production of nitrile latex is estimated at 90,000 tons.

Other applications include blending with phenolic and epoxy resin emulsions for adhesive and coating applications, caulks and sealants, additives for coal tar and asphalt.

Manufacturers of nitrile latices are BASF, PolymerLatex, Dow Reichhold, Zeon, Noveon and Synthomer.

Polychloroprene (CR Latex)

Polychloroprene is the linear polymer of chloroprene (2-chloro-1,3-butadiene).

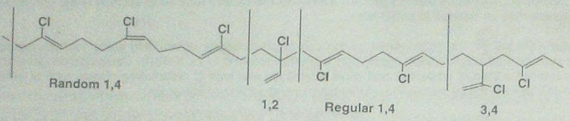


$$CH_2{=}\overset{Cl}{\overset{|}{C}}{-}CH{=}CH_2$$

Chloroprene

Polychloroprene is made by a free-radical emulsion polymerization, either in a batch or a continuous system

Polychloroprene consists of four different structural units, stereoisomers cis-1.4 and trans-1,4, 3,4 and 1,2. The 1,2 units exist at about 1.5 % in the polymer and are the primary sites for crosslinking of the elastomer.

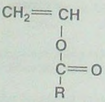


The major applications for polychloroprene latices are in contact adhesives and in dipping operations for the manufacture of industrial, chemical resistant gloves.
Global production of polychloroprene latex is estimated at 20,000 tons but should increase as better technology allows replacement of solvent based adhesive products and demand for gloves increases. The high price of polychloroprene limits its growth.

There has been considerable consolidation of manufacturers and plants in recent years with DuPont Dow Elastomers being the only manufacturer in North America with Polimeri Europa and Bayer, the only ones in Europe. Japanese producers are Denki Kagaku Kogyo, Tosoh and Showa DDE.

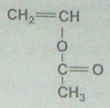
Vinyl Ester Polymers

Vinyl esters are esters of monocarboxylic acids :



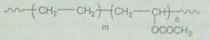
$$\begin{array}{l} CH_2{=}CH \\ \quad\quad\ \ | \\ \quad\quad\ \ O \\ \quad\quad\ \ | \\ \quad\quad\ \ C{=}O \\ \quad\quad\ \ | \\ \quad\quad\ \ R \end{array}$$

The most common and largest volume commercial product is vinyl acetate (VA):

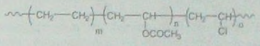


$$CH_2{=}CH{-}O{-}C({=}O){-}CH_3$$

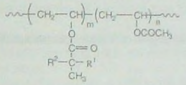
Vinyl ester latices also include several random copolymers, e.g



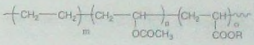
Vinyl acetate/ethylene



Vinyl acetate/vinyl chloride/ethylene



Vinyl acetate/versatate



Vinyl acetate-ethylene-acrylate

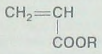
Vinyl ester homopolymers and copolymers are manufactured by free-radical emulsion polymerization.

The largest single market for VA homopolymer and copolymer emulsions is adhesive applications, offering low cost systems with very fast adhesive build-up on many surfaces, particularly paper substrates. The paint industry is also a major user of these latices.

National Starch and Air Products Polymers are the leading manufacturers of vinyl acetate emulsions. Air Products Polymers is the global market leader in vinyl acetate/ethylene emulsions with Celanese holding the leading share in Europe.

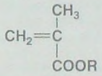
Acrylic Polymers, including Vinyl Acrylics and Styrene Acrylics

Acrylics are homopolymers and copolymers of acrylic and methacrylic monomers



$$CH_2{=}CH{-}COOR$$

Acrylate Monomer



$$CH_2{=}C(CH_3){-}COOR$$

Methacrylate Monomer

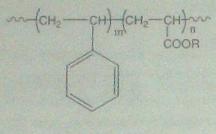
They are the most versatile of the synthetic latices, because of the wide range of monomers and co-monomers available, however, their relatively high cost, compared to vinyl esters has limited their market penetration somewhat.

They are manufactured by free-radical emulsion polymerization using batch or semi-batch processes. There are numerous monomer combinations to produce copolymers or terpolymers or higher combinations, leading to a very large number of possible variations in final properties.

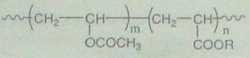
Typical monomers include; acrylates such as methyl acrylate, ethyl acrylate, n-butyl acrylate, t-butyl acrylate, 2-ethyl hexyl acrylate; and methacrylates such as methyl methacrylate and butyl methacrylate.

Pure acrylic latices are the best technical solution for preparing high quality exterior household paint systems and industrial finishes, and can be formulated to give outstanding weatherability and chemical resistance.

Less expensive latices can be prepared by using copolymers of acrylics with styrene, known as styrene acrylics and with vinyl acetate, called vinyl acrylics.



Styrene acrylic



Vinyl acrylic

Styrene acrylics in particular have become successful as low cost resins, yet with many of the advantages of pure acrylics - low water absorption, high alkali resistance and low dirt pick-up of the coating.

Although many acrylic latices were originally developed for coating applications, they enjoy many uses in several industries including adhesives, floor polishes, paper coatings and printing inks.

BASF is the leading global producer of acrylic emulsions. Rohm and Haas and Dow Chemical are also major suppliers.

Ethylene-Vinyl Chloride copolymers (EVCL)

Vinyl chloride and ethylene can be copolymerised by free-radical emulsion polymerisation at high pressures to produce ethylene –vinyl chloride copolymers (EVCL). Variations include a third monomer such as vinyl acetate or monomers with pendant carboxyl or amide groups. These halogen-containing polymers are particularly suitable as flame retardant adhesives for bonding and coating fabrics.

Air Products and Chemicals is the leading supplier of these emulsions.

Polybutadiene

Polybutadiene was first manufactured in Russia and Germany in the 1920s by polymerizing butadiene with sodium and called "Buna" rubber. Today most polybutadiene is produced in solution with alkyl lithium catalyst and is used in tyre production.

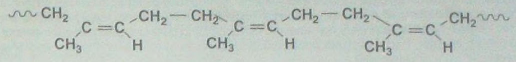
Latices of polybutadiene are still manufactured and most are used captively for the production of acrylonitrile-butadiene-styrene plastics (ABS), where styrene and acrylonitrile are free-radically polymerized in a polybutadiene latex to produce a graft copolymer. The leading companies in this area are General Electric, BASF and Bayer.

Polybutadiene is a very tacky polymer with a very low Tg of –79 °C and latices are also used for manufacturing low temperature tape and label pressure sensitive adhesives, mastics and specialty coatings.

SPECIALTY LATEX

Synthetic Polyisoprene (IR Latex)

The major component of natural rubber (99%) is cis 1,4 polyisoprene, and the development of synthetic polyisoprene was always a very desirable objective for rubber chemists.



cis 1,4 polyisoprene

In contrast to the materials produced by the Hevea brasiliensis tree, emulsions of high cis 1,4 content polyisoprene cannot be prepared directly by emulsion polymerization. All attempts to date to polymerize isoprene free-radically give low molecular weight, predominantly trans 1,4 polymers.

However, high cis 1,4 polymers can be prepared in solution using organometallic Ziegler-Natta catalysts or alkyl lithiums [2] and must then be converted into emulsions.

The Ziegler Natta IR is very similar to natural rubber, with a cis 1,4 content of 96%, a wide molecular weight distribution and high gel content except that it has a lower molecular weight and does not contain the proteins found in NR. The alkyl lithium IR is somewhat different with a cis 1,4 content of 91%, no gel, a high molecular weight and a narrow molecular weight distribution. Furthermore, this polymer is very pure, colorless and contains no ammonia. It has been shown to be an alternative to NR in several applications, including dipping and sheeting applications.

Although the synthetic alkyl lithium IR is expected to gain several high-value niche applications where its purity and controlled properties are important, it will be a tough battle to counter the huge advantage of the low cost of natural rubber in commodity applications.

Polyvinylidene chloride polymers (PVDC)

Several copolymers of vinylidene chloride are produced commercially. The most well known is a copolymer with methyl acrylate which was invented by Dow Chemical in the 1930s and marketed under the Saran® brand name.

Other co-monomers that are used are vinyl chloride, acrylonitrile, methacrylonitrile and methyl methacrylate. Several of these copolymers are available as latices (e.g., Haloflex® latex from Avencia, Diofan® from Solvay, Polidene® from Scott Bader). PVDC copolymers have the best combination of a high gas barrier and low moisture permeation of any commercial packaging plastic. They are frequently used as a thin layer between cellophane, paper and plastic packaging to improve barrier performance. Their ability to provide packaging with a barrier against gases, odors, water, water vapor, oils and fats and their extraordinary ability to be easily heat-sealed has made them a widely used polymer in the food and medical packaging industries. By coating aluminum foil with PVDC, heat sealing can be achieved without causing a weak point in barrier properties. The latices can be applied by reverse gravure coating, air knife coating, spray coating or dip coating. There are numerous applications in the food industry where the PVDC coating is frequently used as the outside barrier layer in a multilayer package, e.g. stand-up pouches, cracker boxes, dried fruit packages, candy wraps, meat packaging trays and flour packaging. PVDC emulsions are used widely as high moisture barrier coatings in pharmaceutical packaging.

PVDC copolymer latices are also used in high performance industrial paints, fire-resistant coatings, primers for blasted steel and rust preventative coatings.

Polyvinyl Pyridine

Latex copolymers of SBR and 2-vinyl pyridine are used to improve adhesion between rubber and fabric reinforcement material. Typical applications are in tyres, conveyor belts, hoses and other industrial rubber reinforced products. Vinyl pyridine content is typically 10-15%. Companies like Omnova Solutions are key suppliers of these latices.

Butyl Rubber

Butyl rubber is a polymer of isobutylene, containing small amounts (1-3%) of isoprene as a co-monomer.

Butyl latices are available, which combine the outstanding material properties of butyl rubber, namely resistance to acids, alkalis, solvents and oil and, in particular, gas impermeability, with the advantages of an aqueous dispersion. To do this, butyl rubber, which after polymerization exists in dissolved form in a hydrocarbon, is converted into an aqueous secondary dispersion, which then no longer contains any organic solvent. This "redispersion" is necessary because the corresponding polymerization reaction cannot be performed directly in water. Because of this additional processing, butyl latices tend to be expensive (over$11/wet kg.)

Butyl latex is supplied by Lord Corporation and PolymerLatex.

InMat Inc. has developed butyl latices containing nanoparticles of exfoliated silicas. These latices give coatings that have gas impermeabilities some 30 to 100 times lower than butyl rubber and are being used as coatings in tennis balls and evaluated as highly chemical resistant gloves and tyre innerliners.

Fluoropolymers

Tecnoflon ™ Latex (Ausimont Solvay) is a highly concentrated water based emulsion of a fluoroelastomer terpolymer. Tecnoflon ™ Latex is solvent free and therefore can be an environmentally friendly alternative for solvent-based fluoroelastomer dispersions. This latex can be used for coating applications whenever superior chemical resistance and excellent thermal stability are required. It can be applied by spraying, dipping or using any other conventional coating technology.

Chlorosulfonated Polyethylene Latex (CSM Latex)

Lord Corporation (US) and Sumitomo Seka Chemicals (Japan) have developed an emulsion process for the polymerisation of chlorosulfonated polyethylene – this is essentially polyethylene with pendant chlorine and chlorosulfonyl groups.

These latices are used to prepare water-based CSM adhesives and coatings to replace solvent based ones for bonding ethylene-propylene rubber to reinforced textiles, particularly in the applications of manufacturing belts and hoses.

Latices of 40% solids content are available, which show good adhesion to nylon, polyester and aramid fibres.

APPLICATIONS FOR LATEX

Latex products are used in a wide range of industries as shown in Table 1. Natural latex is still used for the manufacturing of many products. However, it has been replaced, wholly or partly by synthetic latices in a number of applications since about 1960.

Table 1 Typical applications for latex

Paints & Coatings Interior paints Exterior paints Industrial finishes Release coatings Sports surface coatings	***Construction*** Floor adhesives PVC tile adhesives Ceramic tile adhesives Concrete additives Wallboard joint compounds Cellulose insulation binders Mastics & sealants Asphalt modification	***Packaging*** Bags Envelopes Paper cores & tubes Corrugated boxes Paperboard cartons Flexible packaging Can & bottle labels Pressure sensitive labels
Textiles & Nonwovens Non woven fabric binders Flocking adhesives Coatings Back coatings Pigment binders "Hand" builders	***Furniture*** Foam pillows Foam mattresses High pressure laminates Paper & film overlays Flocking adhesives	***Consumer*** Paper/PVC wall coverings Paper adhesives Wood adhesives & fillers Tile adhesives Paper adhesives Caulks Floor polishes
Paper Binders in pulp process Coatings Saturants Sizes	***Miscellaneous*** Disposable gloves Chemical resistant gloves Ink vehicles Soil stabilizers	

The major markets for **natural latex** are medical gloves and foams. Figure 3 shows the global breakdown of markets

Figure 3 Global natural latex markets (Ref.1)

Medical Gloves

Medical gloves is the by far the largest market application for natural latex. Medical gloves are defined as protective gloves used in the healthcare sector.

End markets include: hospitals, ambulant care, laboratories, dental and medical practices, emergency services etc.

For medical gloves, one country, the USA, is the dominant consumer. Moreover, it is in this national market that the most dynamic events have occurred relating to the use of NRL gloves.

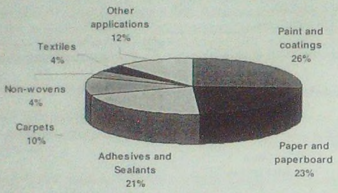
Foams

Foams is a significant market for natural latex and is growing significantly as foam rubber mattresses and pillows continue to gain market share in both Europe and North America. Natural latex is frequently blended with SBR latex for these applications

The major markets for **synthetic latex** are (Figure 4):

- Paint and Coatings
- Paper and paperboard
- Adhesives and Sealants
- Carpets
- Textiles and Non-Wovens

Figure 4 Global Synthetic latex market (Ref. 1)



Paint and Coatings

The paint and coatings market is usually categorized into three segments:

- Architectural or decorative coatings
- Product finishes for original equipment manufacture (OEM)
- Special-purpose coatings

The overall market share of latex paints across Europe is about 70% and close to 100% for architectural paints in some countries. The percentage of latex paint in architectural coatings in the US is 80%. Latex continues to penetrate the market for OEM and special-purpose coatings.

Paper and Paperboard

Latex is used extensively for the coating and treatment of paper products.

Container board and paperboard are widely used to make corrugated boxes and cartons. They can be impregnated or coated with latices to enhance water resistance, grease and oil resistance, add flame retardancy or lower moisture vapour transmission rate.

Paper is coated for various reasons: to upgrade the paper, to make it whiter or more printable and to provide varying degrees of resistance to water or grease. Latex binders play a vital role in the performance properties of coated paper and paperboard. They "bind" coating pigments to the sheet, and impart specific printing capabilities and optical properties to paper and paperboard. Typical coated products include catalogs, magazines, mail inserts, and packaging for cosmetics, pharmaceuticals and food.

A wide range of latices can be used, depending on the specific properties required including SBR, acrylics, styrene-acrylonitrile-acrylate, vinyl acetate and vinyl acrylics. SBR is the most widely used latex, with over 80% of the market, because of its good performance and low cost. SBR does have some limitations, notably its poor resistance to many of the organic solvents used in printing inks.

Adhesives and Sealants

Applications in adhesives and sealants comprise around 20% of all synthetic latex sales globally (this does not include non-woven, textile and carpet applications)

Latex polymers are widely used as the polymeric base for a variety of water-based adhesives and sealants. They are attractive to customers because of their non-flammable nature and low content of volatile organic components (VOCs).

Packaging is the largest single market for latex adhesives with over 50% of latex used in this market segment. The largest application is packaging adhesives used for rigid packaging applications like paper and paperboard packaging, including boxes and folded cartons. Vinyl acetate, vinyl acetate–ethylene and SBR emulsions are the major types used for these applications. Label and tape applications for both liquid and pressure sensitive adhesives are also major applications and acrylics are very important raw materials in these products. Emulsions compete with other environmentally acceptable technologies for these applications, particularly hot melt adhesives.

Although water-based latex adhesives have been used for many years in flexible packaging applications like paper bags and sacks, they are becoming increasingly important in packaging applications for laminating plastics and foils. Adhesives play an integral role in the production of this flexible packaging. The main function is to bond two or more substrates together to form a lamination having more useful properties than the sum of its parts. Adhesives, although usually only a small portion of the entire lamination when compared to the wide range of films, foils, papers or printing inks used in flexible packaging, are vital for maintaining the end use properties of a finished package. Adhesives are generally applied in one of the last steps of the converting process and are often given the task of overcoming inherent shortcomings of the other flexible packaging materials. Acrylic emulsions are the basis of adhesives in this area and are proving to be cost-effective alternatives to one- part and two-part polyurethanes.

Latex adhesives are important in furniture manufacturing including edge-banding, panel bonding and application of veneers. Crosslinkable acrylics are the major adhesive bases and compete with high performance hot melts for many applications.

Emulsions, particularly vinyl acetate, also are major raw materials in the production of construction adhesives, household glues and DIY woodworking glues. Acrylics are used widely in consumer and professional caulks and sealants because of their excellent water resistance.

Other latices also find applications in adhesives, for example, polychloroprene is used in contact adhesives for furniture, kitchen cabinets, custom display cabinets, interior and exterior panels and partitions, footwear, automotive trim, roofing membrane attachment, and a wide variety of related applications where quick, high strength permanent bonds are needed. In contact adhesives polychloroprene has a similar property as natural rubber, viz. "auto adhesion." Auto adhesion means that the substrates are coated with adhesive, allowed to dry, and then combined under light to moderate pressure. This results in an instant bond. The bond strength of the assembled components is often sufficient to enable additional finishing operations without clamping or fixturing.

Carpets

Latices are key components in the production of modern carpets. Carpet construction methods include weaving, tufting, needlepunching, flocking and knitting. Most of the carpet made in the United States and Europe is tufted. During tufting, face pile yarns are sewn (or punched) into a primary backing by a wide multineedled machine. Tufts are inserted lengthwise in tufted carpeting, rather than widthwise, as woven carpet is constructed. Tufts are anchored in place with a layer of latex compound, which also attaches the secondary backing (Fig.5). The backing layers give the carpet added dimensional stability and strength.

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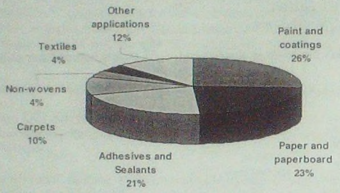
Figure 4 Global Synthetic latex market (Ref. 1)



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Container board and paperboard are widely used to make corrugated boxes and cartons. They can be impregnated or coated with latices to enhance water resistance, grease and oil resistance, add flame retardancy or lower moisture vapour transmission rate.

Paper is coated for various reasons: to upgrade the paper, to make it whiter or more printable and to provide varying degrees of resistance to water or grease. Latex binders play a vital role in the performance properties of coated paper and paperboard. They "bind" coating pigments to the sheet, and impart specific printing capabilities and optical properties to paper and paperboard. Typical coated products include catalogs, magazines, mail inserts, and packaging for cosmetics, pharmaceuticals and food.

A wide range of latices can be used, depending on the specific properties required including SBR, acrylics, styrene-acrylonitrile-acrylate, vinyl acetate and vinyl acrylics. SBR is the most widely used latex, with over 80% of the market, because of its good performance and low cost. SBR does have some limitations, notably its poor resistance to many of the organic solvents used in printing inks.

Adhesives and Sealants

Applications in adhesives and sealants comprise around 20% of all synthetic latex sales globally (this does not include non-woven, textile and carpet applications)

Latex polymers are widely used as the polymeric base for a variety of water-based adhesives and sealants. They are attractive to customers because of their non-flammable nature and low content of volatile organic components (VOCs).

Packaging is the largest single market for latex adhesives with over 50% of latex used in this market segment. The largest application is packaging adhesives used for rigid packaging applications like paper and paperboard packaging, including boxes and folded cartons. Vinyl acetate, vinyl acetate–ethylene and SBR emulsions are the major types used for these applications. Label and tape applications for both liquid and pressure sensitive adhesives are also major applications and acrylics are very important raw materials in these products. Emulsions compete with other environmentally acceptable technologies for these applications, particularly hot melt adhesives.

Although water-based latex adhesives have been used for many years in flexible packaging applications like paper bags and sacks, they are becoming increasingly important in packaging applications for laminating plastics and foils. Adhesives play an integral role in the production of this flexible packaging. The main function is to bond two or more substrates together to form a lamination having more useful properties than the sum of its parts. Adhesives, although usually only a small portion of the entire lamination when compared to the wide range of films, foils, papers or printing inks used in flexible packaging, are vital for maintaining the end use properties of a finished package. Adhesives are generally applied in one of the last steps of the converting process and are often given the task of overcoming inherent shortcomings of the other flexible packaging materials. Acrylic emulsions are the basis of adhesives in this area and are proving to be cost-effective alternatives to one- part and two-part polyurethanes.

Latex adhesives are important in furniture manufacturing including edge-banding, panel bonding and application of veneers. Crosslinkable acrylics are the major adhesive bases and compete with high performance hot melts for many applications.

Emulsions, particularly vinyl acetate, also are major raw materials in the production of construction adhesives, household glues and DIY woodworking glues. Acrylics are used widely in consumer and professional caulks and sealants because of their excellent water resistance.

Other latices also find applications in adhesives, for example, polychloroprene is used in contact adhesives for furniture, kitchen cabinets, custom display cabinets, interior and exterior panels and partitions, footwear, automotive trim, roofing membrane attachment, and a wide variety of related applications where quick, high strength permanent bonds are needed. In contact adhesives polychloroprene has a similar property as natural rubber, viz. "auto adhesion." Auto adhesion means that the substrates are coated with adhesive, allowed to dry, and then combined under light to moderate pressure. This results in an instant bond. The bond strength of the assembled components is often sufficient to enable additional finishing operations without clamping or fixturing.

Carpets

Latices are key components in the production of modern carpets. Carpet construction methods include weaving, tufting, needlepunching, flocking and knitting. Most of the carpet made in the United States and Europe is tufted. During tufting, face pile yarns are sewn (or punched) into a primary backing by a wide multineedled machine. Tufts are inserted lengthwise in tufted carpeting, rather than widthwise, as woven carpet is constructed. Tufts are anchored in place with a layer of latex compound, which also attaches the secondary backing (Fig.5). The backing layers give the carpet added dimensional stability and strength.

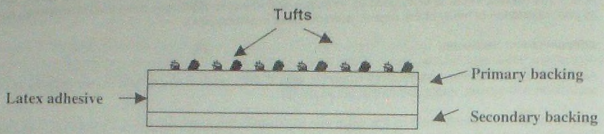

Figure 5 Construction of tufted carpet

Latex is the product that holds the entire system together by securing the face fibres to the primary backing and then bonding the secondary backing to it. The latex typically comprises 40-60% of the total weight of a carpet.

High styrene-content carboxylated SB latex is the most frequently used backing and laminating compound, although other compounds, such as polyvinyl chloride, amorphous resin, ethylene vinyl acetate, polyethylene, and polyurethane, are used. Natural latex is used only on small, washable rugs.

Textiles and Non-Wovens

Latices are key materials in the manufacturing of both textiles and nonwoven fabrics. The latices comprise from 5% to 60% of the weight of the fabric on a dry basis. Thus, they are not merely adhesives but contribute many of the important characteristics to the fabric.

Textiles are woven from yarns made of natural or synthetic fibres and then "finished" to make the final product.

Polymer latices are used widely in these finishing operations and function as:

- Coatings and backcoatings
- Hand builders
- Pigment binders
- Flocking adhesives

Latex coatings give increased tensile strength to the fabric, stiffness and abrasion resistance. Back coatings using latex enhance strength, durability and wear resistance.

Nonwoven fabrics, as their name implies, are not woven in the classical sense of textiles but comprise a web or continuous sheet of fibers laid down mechanically. The fibers may be deposited in a random manner or oriented in one direction. Most widely used fibers include cellulosics, polyamides, polyesters, polypropylene and polyethylene. The spun fibers, which may be drawn, are laid down directly onto a belt by carding, air-laying or wet-laying. Latex has traditionally been the adhesive that holds these fibres together.

Vinyl acetate and acrylics are the main latices used in non-woven manufacturing. As polymer technology for manufacturers of synthetic binder systems improved, a greater variety of chemical building blocks became available with much greater flexibility in terms of binder strength, durability, and other properties. The introduction of cross-linkable and self-crosslinking binder polymers turned out an entirely new range of fabric properties. This was particularly noteworthy in durable nonwovens where such durability features as washability and dry cleanability were important.

Depending on the end-use of the fabric, the binder can influence strength, softness, adhesion, firmness, durability, stiffness, fire retardancy, hydrophilicity, hydrophobicity, anti-microbial properties, organic compatibility, surface tension, dimensional stability and solvent, wash and acid resistance.

PRODUCTION OF LATICES

The production of natural rubber is controlled by the governments of East Asia. Figure 6 shows the value chain. The value chain for natural rubber gloves is quite complex. Moreover it is international since some 90% of medical gloves are actually manufactured in Asia and the majority of these are then exported to the USA or Europe. The supply side is complicated by the significant degree of cross selling and subcontracting that occurs. The major suppliers of medical gloves generally own some glove production facilities but also subcontract production to a considerable extent.

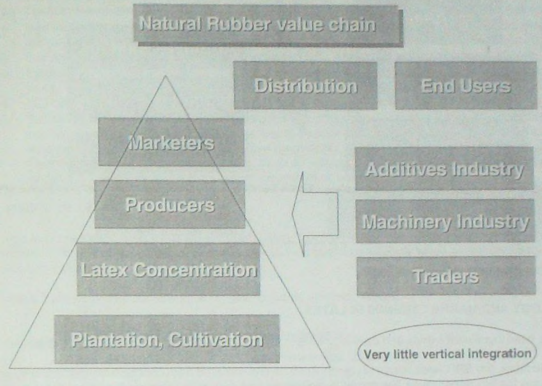

Figure 6 The natural rubber latex value chain

Synthetic latex is produced by large chemical and rubber companies and world capacity is controlled by the investment decisions of these companies. Figure 7 show the value chain.

Three large companies dominate the global latex industry, Dow Chemical, BASF and Rohm and Haas, each with sales of over $1billion and a combined market share of just over 20%.

Dow and BASF are major global styrene producers and Dow is also a major butadiene manufacturer. Rohm and Haas and BASF are both major global acrylic manufacturers.

There is also a large group of suppliers with annual sales of emulsion polymers in the $300-million to $600-million range in 2000. This group includes Air Products Polymers, Celanese, Polimeri Europa, National Starch and Chemical, Omnova Solutions, PolymerLatex and Rhodia. Many of these companies are forward integrated into end products. For example, Dow, Rohm and Haas, Air Products and National Starch are major manufacturers of adhesives.

Other major suppliers of emulsion polymers include Avecia, Eastman, JSR and Noveon.

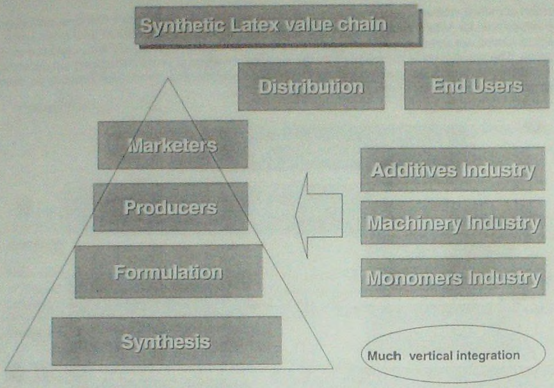

Figure 7 The synthetic latex value chain

TECHNOLOGY AND MARKET TRENDS IN LATEX

There have been significant trends and developments in the synthetic and natural rubber latex industries.

In **synthetic latex**, the SBR latex market in North America has suffered from considerable overcapacity and cost pressures but key applications like coatings, adhesives and carpet bonding have continued to grow. Less efficient producers have struggled to survive and Ameripol Synpol went bankrupt and sold its SBR business to ISP.

An encouraging note is that UCAR Emulsion Systems (UES), part of Dow Chemical Co, plans to invest $100 million to construct a "next-generation" latex facility in Hahnville, Louisiana to manufacture SBR and other latices.

In Europe, two factors have influenced the demand for SBR latex. On the one hand the carpet sector is in a time of change. Consumers have followed the fashion trend and replaced carpeted floors with hard surfaces made from wood or laminate. Tufted carpet production reached a peak in Europe in 1997, and has been declining at around 3.5 percent annually [3]. This has led to a very large decrease in the consumption of SB and carboxylated SBR. On the other hand there has been a large increase in the demand for moulded, foamed latex products, such as mattresses and pillows and this has had a positive effect on SB latex consumption. However, overall there has been considerable cost cutting and retrenchment. Dow Chemical Co. has announced plans to idle its emulsion SBR plant in at Pernis, in the Netherlands.
China is a current and future growth market for both natural and synthetic latex and both BASF and Dow have recently opened SBR latex plants the country.

Other developments in synthetic latex include:

- Celanese purchased the Clariant emulsions business.
- DuPont Dow and Showa Denko terminated a polychloroprene manufacturing and marketing joint venture in Asia. Showa Denko will continue to manufacture and market polychloroprene in that region.
- Bayer and Degussa AG sold PolymerLatex, their 50:50 joint venture, to the financial investor Soros Private Equity Partners.

In **natural latex**, the most significant developments have been the more than two-fold increase in price of latex in the last two years, the formal implementation of the tri-partite agreement between Indonesia, Malaysia and Thailand, now called International Rubber Consortium Limited (IRCo), and designed to control the production and price of natural rubber, and the increased usage of gloves due to the SARS and bird flu outbreaks.

Other developments in natural latex include:

- Viet Nam announced plans for large increases in the planted areas of rubber trees and that shipments of latex will be made directly to the US, avoiding intermediate traders.
- Tillotson Healthcare Corp., the US maker of a variety of medical gloves, went out of business
- Medline Industries Inc. bought Maxxim´s medical products operation, which includes its examination and surgical glove lines, while RoundTable Healthcare Partners acquired its vascular goods business.
- French glove producer Comasec S.A. purchased SSL´s Marigold industrial glove business.
- Yulex announced the completion of a 750 ton pilot plant for the production of Guayule natural rubber latex.
- The USDA are using genetic engineering to boost the yield of rubber from sunflowers
- The Malaysian Rubber Board, in collaboration with other countries, is currently investigating planting transgenic rubber trees that display a variety of desired agronomic traits, be they concerned with disease resistance, high rubber and timber productivity, or even the production of protein pharmaceuticals. The transgenic rubber tree has already shown itself capable of producing a bacterial enzyme, an antibody and human serum albumin in its latex.

PRICES OF LATEX

Prices of synthetic latices have always been higher than NR latex. The relative pricing of synthetic and natural latices is of great interest to end-users and suppliers, particularly when substitutions can be made on the basis of price.

Table 2 shows typical US bulk price ranges for some synthetic latices:

Table 2 US bulk price ranges for synthetic latex

Type of Latex	**Price range US$/wet kg**
SBR	1.05 – 1.10
Vinyl Acetate	1.12 – 1.17
Vinylacetate-ethylene	1.15 – 1.35
Vinyl acrylic	1.20 – 1.30
Acrylic	1.35 – 1.50
Ethylene-vinyl chloride	1.35 – 1.45
Nitrile	1.05– 1.30
Polychloroprene	6.60 – 7.70
Butyl	11-12

At the end of December 2001, centrifuged Malaysian NR latex was priced at $0.385 /wet kg and the price rose dramatically to 0.935 by March 2004 Synthetic latices have shown some increases over the same period with increased costs of raw materials such as butadiene and styrene. However, the price differential between NR and synthetics has narrowed significantly over the last 2 years.

FORECAST FOR SYNTHETIC LATEX

World demand for synthetic latex polymers is forecast to increase 4.5 percent per year to 9.9 million tons in 2005 as the market continues to outpace growth in the global economy. Market value is forecast to rise 6.1 percent per year to more than $20 billion, benefiting from shifts in product mix toward higher-priced emulsions, particularly acrylics [4]. Table 3 shows global and regional forecasts through 2005.

Table 3 Global Synthetic Latex Polymer Forecast (1000 tons)

Region	2000	2005	% annual growth
North America	2654	3200	3.8
Western Europe	2595	3225	4.4
Japan	995	1145	2.8
Other Asia	1070	1495	6.9
Rest of world	661	880	5.9
Total global demand	**7975**	**9945**	**4.5**
Source: data from Ref. 4			

Table 4 shows the major market drivers and restraints expected to affect the different latex technologies.

Table 4 Market Drivers (D) and Restraints (R) for Latex

Latex	Trend	Market Drivers (D) and Restraints(R)
SBR	Moderate growth	**D** Steady growth in paper coatings, adhesives and asphalt **D** Significant growth in Asia **R** Decline of carpet business in Europe **R** increase in costs of styrene and butadiene
Natural	Moderate growth	**D** Significant growth in Asia **D** Continued growth in gloves **R** Current high price of this latex **R** Decrease in planted area of trees
Nitrile	High growth	**D** High growth in gloves
Acrylic	High growth	**D1** Growth in latex paints **D2** Growth in adhesives and sealants **R** High price compared to other latices.
Vinyl acetate	Solid growth	**D** Growth of adhesives market
Styrene acrylic	Moderate growth	**D** Growth in latex paint **R** Competition from acrylics
Vinyl acrylic	Moderate growth	**D** Growth in latex paint **R** Competition from acrylics
VA/ethylene	Solid growth	**D1** Growth of adhesives market **D2** Growth in latex paint
Polychloroprene	Moderate growth	**D1**. Replacement of solvent-base adhesives **D2**. Increased use in gloves **R**. Continued government legislation and activist pressures on chlorine-containing materials **R**. High price of this latex

Overall growth in latex polymers will be influenced by increases in the global GDP and by the growth of the individual end-user market segments. Over 50% of the market for latex polymers is in industries like medical, food packaging and paper coatings, which are relatively recession proof.

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ADDITIVES FOR THE LATEX INDUSTRY

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In the course of the last two to three decades the latex industry has seen big changes. These have greatly influenced the production of latex articles and almost totally transformed the business.

The quality of the products has greatly improved, machinery is much more sophisticated, the output of the machinery is much higher and last but not least a lot of regulation regarding health, safety and environment has been passed and must be observed by producers today.

All these changes have been achieved by numerous improvements, innovations and developments, mostly in the area of machinery, processing and work-flow. But one important area of the industry has remained almost stagnant during all this time: The chemicals and raw materials!

The raw materials and chemicals used today are still almost the same as those used a quarter of a century ago, in no way optimised for today's equipment and needs.

With new chemicals for the latex industry, designed for today's needs, a further leap in the productivity and profitability of the operations should be possible, similar to the one seen in the past.

This paper aims to introduce some of these newly developed additives, give insight into their benefits and discuss their impact on the latex article production.

MAKING NR-LATEX NITROSAMINE FREE AND SKIN FRIENDLY – WITH STRUKTOL

In natural rubber producing countries the use of a combination of Tetra Methyl Thiuram Disulphide (TMTD) and Zinc Oxide as a preservative for field latex has become virtually universal since its introduction as a secondary preservative for low ammonia latex in about 1975.

This preservative system has proved very popular because it is highly effective and also relatively cheap and easy to use.

Nonetheless, for *some* years now it has been evident that this system suffers from two major disadvantages relative to consumer requirements for certain types of products: TMTD is an allergen causing contact dermatitis in susceptible persons and it is the source of the *nitrosamines* and nitrosatable amines found in raw rubber and lattices.

Notwithstanding these facts, the EU requires that nitrosamines are *limited* to *less* than 10 ppb in baby feeding teats and soothers and in toy balloons. Similar legislation exists in several other countries. And most probably this legislation will be further extended to encompass other latex and rubber products.

In our view, there is a clear need for grades of raw rubber and latex concentrates that are not only free of nitrosamines and nitrosatable amines but are also skin friendly.

Therefore we at Schill +Seilacher have spent considerable effort in the past years to find solutions that overcome the mentioned drawbacks of the ZnO/TMTD system.

It has been demonstrated that it is possible to produce commercially *acceptable* HA and LA Latex concentrates, containing no nitrosamines or nitosatable amines, if the new bactericidal chemicals of STRUKTOL are used to replace the TMTD.

Such HA (high ammonia) and LA (low ammonia) lattices are currently being used successfully for the production of balloons, gloves, other dipped products and latex thread.

The absence of the nitrosamines, nitrosatable amines and the contact dermatitis causing TMTD together with the fact that the STRUKTOL bactericide has FDA approval for food use means that latex concentrates pr‥ced with these additives will have no trouble finding their way into the currently very sensitive European and American markets.

It is believed that the development of a new, more *"user friendly"* and *"environmentally friendly"* type of natural latex is not only economically sensible and timely but can only help improve the *"image" of* natural latex witch has been severely damaged in many countries by protein allergy problems.

EXPERIMENTAL AND RESULTS

The latex concentrates referred to in this paper were produced in Malaysia at the end of the rainy season. They were made in the conventional manner using the production facilities of Latex Industrias s.a. The preservative chemicals used in this work were Tetra Methyl Thiuram Disulphide (TMTD) and Zinc Oxide, both in the form of aqueous dispersions, and the new preservative Struktol LB219 (Schill+ Seilacher) which is a 50 (weight) % solution of synthetic carboxylates. The Struktol LB219, if used, was added directly to the latex without dilution,

For the production of conventional HA (high ammonia) and LA (low ammonia) lattices 0.025 pbw each of TMTD and Zinc Oxide were added in the field together with 0.28% of ammonia. For the new type of latex LB219 was simply used to replace the TMTD and was added, at the level of 0.02 pbw, to the field latex together with an 0.03 pbw zinc oxide (in dispersion) and 0.28 % of ammonia. For HA lattices the extra ammonia required was added after concentration. For the production of conventional LA lattices 0.02 pbw each of TMTD and zinc oxide were added after concentration. For the new type of latex 0.02 pbw each of LB 219 and zinc oxide was added after the concentration.

If necessary, the MST levels of the lattices made with LB219 were boosted by the addition of low amounts of Struktol LS100 (Schill+Seilacher), an aqueous solution of synthetic soap. This was used at a half the level normally considered necessary - because LB219 also functions as a colloidal stabiliser and reduces the necessity for additional stabilisation.

In all cases below the lattices designated with the letter **'A'** were preserved with TMTD and Zinc Oxide and those with the letter **'B'** were preserved with LB219 and Zinc Oxide.

To evaluate the relative performance of the different preservative systems various characteristics of field Latex (during 7 days) and (during storage) of the concentrate latex. The results are shown in Tables 1, 2 and 3. clearly demonstrate that there is a positive influence of the Struktol LB 219 lattices and virtually no difference in the quality of preservation of the concentrate lattices during storage for 2 month.

Table 1:
VFA Numbers: Changes on field latex

Time days	Latex A	Latex B
0	0,029	0,029
1	0,029	0,035
2	0,041	0,035
3	0,071	0,041
4	0,084	0,041
5	0,112	0,041
6	0,112	0,048
7	0,112	0,048

Struktol LB 219.

Stabilizer - struktol LB [illegible]

Table 2:
HA Latex - development of properties on Storage

Time	Latex A MST	pH	VFA	KOH	Latex B MST	pH	VFA	KOH
6 days	400	10,5	0,009	0,45	400	10,52	0,009	0,45
1 month	1100	10,51	0,018	0,50	1200	10,5	0,017	0,49
2 month	1200	10,5	0,018	0,55	1200	10,5	0,017	0,55

Table 3:
LA Latex- development of properties on storage

Time	Latex A MST	pH	VFA	KOH	Latex B MST	pH	VFA	KOH
10days	600	10,1	0,009	0,42	520	10,0	0,009	0,40
1 month	800	10,1	0,014	0,43	870	10,0	0,014	0,42

To confirm that the new preservative is free of nitrosatable amines prior to use, a sample was analysed by the Rubber Consultants Analytical Laboratory in the UK. In addition, cast raw rubber films made from these lattices were tested to determine the amounts of nitrosatable amines present. Measurements were made using the procedure prescribed by the BGVV (Bundesgesundsheitsamt) i.e. with extraction by artificial saliva. The results obtained are shown in Tables 4 and 5

Table 4:
Nitrosamine Analysis of TMTD & LB219

	NDMA(ppb) Nitrosodimethylamine	NDEA(ppb) Nitrosodiethylamine)
TMTD*	100-430	1-5
Struktol LB 219	nd (not detectable)	nd

*the range of quantities found in commercial sample from four different suppliers

Table 5:
Nitrosatable Amines present in HA Lattices

	NDMA (ppb)	NDEA (ppb)
HA Latex*	167-400	0-13
HA Latex -LB219	39	nd
MHA (SP)**	10-20	5

*HA.Latex Range of values found in 5 samples of latex

**MHA (Sp) An HA latex prepared in Malaysia and preserved solely with ammonia

The results in Table 5 clearly show that, in contrast to TMTD, LB219 is completely free of nitrosamines as measured by the BGVV test procedure. This is not surprising since there is no nitrogen in the molecule but the measurements also serve to confirm that no contamination with amines occurs during manufacture. The values obtained demonstrate that the addition of 0.02 phr of the worst sample of TMTD (i.e. that containing 430 ppb), would contribute almost 9 ppb of nitrosamines to the rubber, (assuming no losses in processing) <u>before</u> addition of accelerators- and thus render the task of meeting a maximum level of 10 ppb of nitrosamines almost impossible.

The measurements made on films from lattices HA.UK clearly show the effects of the presence of TMTD in the very high levels of nitrosatable amines, particularly nitrosodimethylamine, present. It must be emphasized that <u>none</u> of the 5 commercial HA latex samples tested here could meet the requirements of the EU specifications for nitrosatable amines even before the addition of vulcanising agents. In contrast, both the special, non-commercial TMTD-free Malaysian latex and the TMTD-free, the new Latex with Struktol LB 219.were well below the nitrosatable amine limits. The fact that both of the TMTD-free lattices showed the presence of small amounts of nitrosatable amines and even minute amounts of nitrosamines is attributed to contamination: both lattices were prepared in concentrate factories which regularly produce TMTD preserved latex and cross contamination of amines, at these concentrations, is known to occur readily, even between samples sealed in polyethylene bottles.

It is possible that the use of a different preservative might affect the colloidal properties of latex compounds made from it. It is also possible, though less likely, that it could affect the physical properties of vulcanisates made from the compounds. To determine whether these possibilities were significant, latex compounds were according to the formulation in Table 6.

Table 6:
Formulation Used for Compound Preparation from Lattices A and B

	pbw, wet	pbw, dry
NR Latex	167.0	100.0
10% KOH	4.0	0.4
50% Stabiliser[1]	0.4	0.2
50% ZDEC	2.0	1.0
42% Antioxidant[2]	2.4	1.0
50% Zinc Oxide	1.0	0.5

1. Struktol LS100 (Schill+ Seilacher Germany)
2. Struktol LA229 (Schill+ Seilacher Germany)

* Films vulcanised for 25 minutes at 120°C.

Comparative measurements of certain of the characteristics of the compounds made from the above formulation were performed, to assess whether the preservation system had any effect. The results are shown in Table 7 and clearly indicate that there was no detectable difference between the two lattices.

Table 7:
Properties of Compounds from Lattices A and B

	Latex A	Latex B
DRC (%)	49.4	49.5
Viscosity (Ford Cup #3)	25.3	25.3
MST (sec)	1720	1780
pH	11.4	11.3

Vulcanised films prepared from these compounds were examined for their physical properties and the data obtained are listed in Table 8. Again, the tensile strength, modulus and elongation at break figures in Table 8 show that vulcanisates made from the two lattices are virtually identical.

Table 8:
Tensile Properties of Vulcanisates from Lattices A and B

	Latex A	Latex B
TS (MPa)	28.2	27.6
Mod. 300% (MPa)	1.7	1.7
EB (%)	870	870

SUMMARY

It has been demonstrated that it is possible to produce commercially acceptable HA Latex and LA Latex concentrates, containing no nitrosamines or nitrosatable amines, if the bactericidal chemicals Struktol LB219 is used to replace TMTD. The absence of the nitrosamines and nitrosatable amines from these lattices together with the fact that LB219 has FDA approval for food use should mean that latex concentrates produced in this way will allow easy entrance into the highly regulated markets of Europe and US.

Soaps of C16 - C18 → [illegible] + ↑ Zinc sensitive
+ good colloid

DEVELOPMENTS IN STABILISERS FOR NATURAL RUBBER LATEX COMPOUNDS

Stabilising additives for natural latex compounds are usually based on the potassium or sodium salts of *natural* fatty acids, particularly those acids having from 10 to 18 carbon atoms. These natural fatty acids are obtained by hydrolysis of vegetable oils and their composition varies greatly depending on the origin of the oil. For application in latex technology only the technical, *i.e.* unpurified, grades of these acids are used so the actual soap employed is a mixture of various fatty acids, the detailed composition depending on the source of the oil.

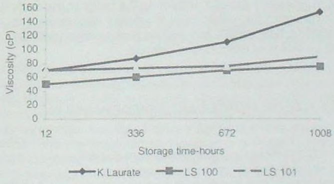
These fatty acid soaps are quite effective and relatively cheap but suffer from certain disadvantages. The higher molecular weight (C16 or C18), unsaturated fatty acid soaps (*e.g.* oleates) are good stabilisers for uncompounded latex but have a strong tendency to foam and are very sensitive to the presence of zinc oxide. (The high molecular weight *saturated* fatty acids are rarely used because they have rather low solubilities in water and are not effective stabilisers). Soaps based on caprylic (C10) acid have a low foaming tendency and good resistance to zinc oxide but do not give very high stability. Soaps of lauric acid (C12) are widely used because they represent a compromise between these extremes: they are more effective stabilisers than caprylates but less sensitive to zinc oxide than the C18, unsaturated, soaps. The industry today is just becoming aware that there are alternatives to these natural fatty acid soaps which have clear processing advantages, these alternatives are soaps based on synthetic fatty acids.

Research and development work done by **Schill & Seilacher** has shown that soaps made from certain of these synthetic fatty acids have an interesting and technically useful combination of properties which makes them good alternatives to the natural products for the preparation of compounds from natural latex. Their advantages should be particularly useful in the production of dipped goods, latex thread, and adhesives. The Struktol stabiliser (LS 100 and LS 101) exhibit a combination of high solubility in water, high mechanical stability, long term colloidal stability, low foaming tendency, and good resistance to destabilisation by zinc oxide.

EXPERIMENTAL AND RESULTS

Figure 1 compares the viscosity stability of a prevulcanised latex prepared with potassium laureate with that of similar lattices prepared using two synthetic fatty acid soaps (Struktol LS100 and Struktol LS101).// The results clearly show that the lattices prepared with the Struktol stabiliser shows much better stability of viscosity over a storage period of 6 weeks at room temperature.

Figure 1. **Effect of soaps on the storage viscosity increase of prevulcanised lattices.**



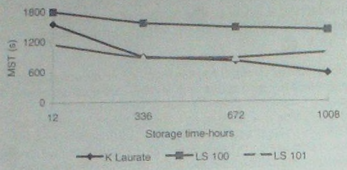
× good sensitivity
C12 → (~~high~~ no foaming
C16 + C18)
+
C14 C

The viscosity increase of a latex on storage is one measure of its colloidal stability. Similarly, the changes occurring in mechanical stability time (MST) during storage is another measure of the stability of the system. The mechanical stability values of the **prevulcanised lattices** mentioned above were measured during six weeks' storage and are shown in Figure 2, it is clear that the LS100 and LS 101 are measurably superior to potassium laureate.

K - laurate }
LS 100 LS101 } →

K - Caprylate (soap) →
best chemical stability

Figure 2. **Changes in MST on storage of prevulcanised lattices stabilised with various soaps**



Other work has shown that the superiority of these stabilisers is not confined to prevulcanised lattices but, as would be expected, is also true for vulcanisable latex mixes and in raw latex, where they could be used to replace the laureate soap commonly added to ensure adequate MST values.

The major use of these new soaps is expected to be in the dipping industry where it is important to obtain good colloidal stability without causing foaming.

Table 1:
Comparison of different Stabilisers: ZnST and MST

	Relative Mechanical Stability	Relative Zinc Stability
Control (without stabiliser)	1,00	1,00
K-Caprylate	1,89	1,07
Struktol LS100	> 2,00	1,64
Struktol LS 101	2,44	1,50

SUMMARY

It has been shown that certain synthetic fatty acid soaps offer superior colloidal stabilising performance to the commonly used laureate soaps and therefore represent a useful addition to the range of materials available to the latex compounder. These products permit the technologist to prepare latex mixes and prevulcanised lattices with improved colloidal stability, both initially and on long term storage, with no technical penalty in terms of increased foaming problems or difficulties in gelation.

THE INFLUENCE OF DISPERSION PARTICLE SIZE ON ANTIOXIDANT PERFORMANCE IN VULCANISED LATEX

This chapter presents results demonstrating that the particle size of an antioxidant dispersion can have a major influence on its effectiveness in protecting vulcanised latex products.
The development of dispersions of phenolic-type antioxidants having both a very small average diameter and a very narrow size range, which we call "superfine dispersions", has permitted experimental comparisons with conventionally milled dispersions showing that greatly improved performance is obtained. In many cases the improvement is such that as little as half the amount of antioxidant is required if a superfine dispersion is used. A further, and very important, characteristic of superfine dispersions is that they are virtually free of sedimentation problems.

This means, that when a superfine antioxidant dispersion is added to a latex mix the user can be sure that the amount added is the amount present in the product, even after prolonged storage. The improvement in antioxidant performance is attributed to the increased uniformity of distribution of the antioxidant throughout the rubber.

EXPERIMENTAL AND RESULTS

Ball milled dispersions were prepared using a laboratory-size, mill (800 ml capacity) with a grinding time of 72 hours. Superfine dispersions were prepared using the proprietary method established by Schill + Seilacher.

Measurements of particle size and size distribution were carried out using a "Mastersizer micro +." Ver.2.U particle size measuring machine (ex Malvern Instruments.) which utilises low-angle laser scattering techniques.

Measurements of tensile properties were carried out by standards methods and made at intervals during oven ageing at 70° C for up the eight weeks.

Vulcanised latex films were prepared by coagulant dipping processes using the following base formulation:

	pbw (wet)	pbw (dry)
Natural Rubber Latex (60% DRC)	166,7	100,0
10% Potassium hydroxide solution	3,0	0,3
50% Solution of Struktol LS 100	0,4	0,20
50% Sulphur dispersion	3,0	1,5
50% ZDEC dispersion	2,0	1,0
50% ZnO dispersion	2,0	1,0
Antioxidant dispersion	---as indicated---	---as indicated---

The phenolic antioxidant used in this study was a butylated *p* cresol derivative. The stabiliser used for the latex compounds was Struktol LS 100, a fatty acid soap solution supplied by Schill + Seilacher.

I. Particle size distributions

The results of particle size measurements of a ball milled dispersion of the phenolic antioxidant are shown in Figure I. This process has resulted in a dispersion having a wide range of particle sizes - in this case from as low as 0.1 micron to as high as 30 microns (a ratio of largest to smallest of 300) - with two, poorly defined, modal peaks at 6.2 and 1.6 microns. The majority of the particles lie in the range 0.7 -11.0 microns.

This value is one of the larger of the commonly used measures of average particle diameter and in a highly polydisperse system, such as the above dispersion, is significantly larger than the number average diameter. (In a perfectly monodisperse system, of course, all measures of average particle size are identical).

It should be noted here that Gorton and Pendle (4) published the particle size distributions of dispersions of many latex compounding ingredients, including antioxidants. Their dispersions were obtained using a high speed disperser, rotational ball mills, vibrational ball mills, and an „Attritor" and their size measurements were made using a "Coulter Counter". The Coulter method, under the conditions used by them, could not measure particles less than I micron diameter so that the size distributions are less complete than those obtained from the "Mastersizer". However, it is possible to make some degree of comparison. Gorton & Pendle presented volume average diameters, among others, and these can be compared directly with the Mastersizer data. They found that one phenolic antioxidant, when dispersed using a high speed dispersing machine, showed a volume average diameter of 5.8 microns and a particle size ranging from 2 to 6 microns. They also found similar results for two other commercial phenolic antioxidants and showed that vibrational ball milling (which is, generally, 2-3 times faster than rotational ball milling) of these antioxidants for 24 hours reduced the average particle diameter to about 2.5 microns but had little effect on the *range* of size present and that the best antioxidant dispersions they could obtain still retained significant numbers of large (*i.e.* greater than 10 microns diameter) particles. Therefore one can say the particle size distribution show in Figure 1, obtained for the phenolic antioxidant used in this work, is broad1y similar to previously published data on antioxidant dispersion partic1e size distributions and is not in any way untypical. It is clear therefore, that although conventionally milled dispersions may have reasonably fine *average* diameters they also possess a wide range of particle sizes and that they are, effectively, much coarser than they appear - because a disproportionately large proportion of the mass lies in the larger sized particles.

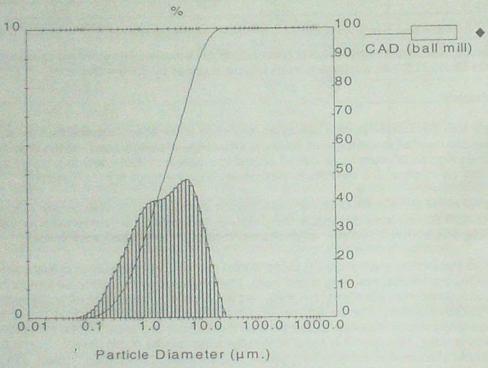
The particle size distribution of a superfine dispersion is shown in Figure 2. This dispersion can be seen to be unimodal in nature and to have a volume/ volume average diameter of 0.34 microns and a size range from 0.11-0.7 microns - a ratio of largest to smallest of only 7. To illustrate that the results obtained are readily reproducible Table 1 summarises the information for this dispersion and for three others, of the same antioxidant, produced by the same technique.

Table 1.
Consistency of Superfine Dispersion Properties

Preparation	Distribution Type	Modal size (micron)	Size range (micron)	Specific surface area sq. m/ g
A	Unimodal	0.32	0.15- 0.62	17.83
B	Unimodal	0.33	0.15- 0.69	17.20
C	Unimodal	0.33	0.15- 0.62	17.40
D	Unimodal	0.33	0.15- 0.62	17.5

The data in Table I show that this production method consistently yields products which are virtually identical in respect of both average diameter and spread of sizes.

Figure 1.



Result: Derived Diameters Table

ID: CAD (ball mill)	Run No: 1	Measured: 14.2.2003 14:38
File: PR-TGV	Rec. No: 14	Analysed: 14.2.2003 14:38
Path: C:\SIZERMP\DATA\		Source: Analysed

Sampler: Internal		Measured Beam Obscuration: 14.1 %
Presentation: 5OHD	Analysis: Polydisperse	Residual: 1.750 %
Modifications: None		

Conc. = 0.0050 %Vol	Density = 1.000 g/cm^3	S.S.A.= 5.2399 m^2/g
Distribution: Volume	Span = 3.788E+00	Uniformity =1.186E+00

A.S.T.M Derived Diameters (um)

N	3	2	1	0
D[4, N]	4.19	2.19	1.18	0.73
D[3, N]		1.15	0.63	0.41
D[2, N]			0.35	0.24
D[1, N]				0.17

Distribution Moments

	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	4.19	4.308	1.6291	2.6774
Surface	1.15	1.866	4.2850	25.3014
Length	0.35	0.526	9.1528	157.2136
Number	0.17	0.173	9.1978	272.2068

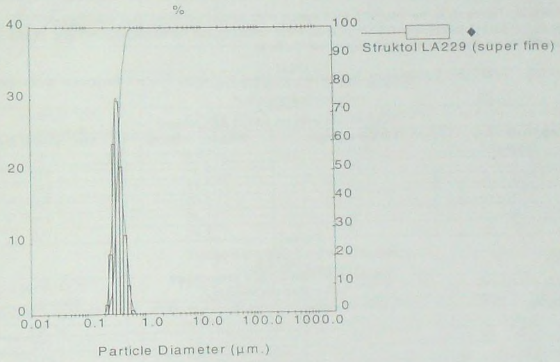
Distribution Percentiles (um) -- Volume

Percentile	Size	Percentile	Size
10.0 %	0.46	80.0 %	7.10
20.0 %	0.80	90.0 %	10.28
50.0 %	2.59	100.0 %	26.20

Distribution Modal Sizes (um)

Mode	Size	Mode	Size
1	5.99		

Figure 2.



Result: Derived Diameters Table

ID: STRUKTOL LA 229
File: PR-TGV
Path: C:\SIZERMP\DATA\

Run No: 1
Rec. No: 12

Measured: 5.2.2003 12:30
Analysed: 5.2.2003 12:31
Source: Analysed

Sampler: Internal
Presentation: 5OHD
Modifications: None

Analysis: Polydisperse

Measured Beam Obscuration: 16.2 %
Residual: 1.798 %

Conc. = 0.0033 %Vol
Distribution: Volume

Density = 1.000 g/cm^3
Span = 5.526E-01

S.S.A.= 17.8358 m^2/g
Uniformity =1.650E-01

A.S.T.M Derived Diameters (um)

N	3	2	1	0
D[4, N]	0.35	0.34	0.34	0.33
D[3, N]		0.34	0.33	0.32
D[2, N]			0.32	0.32
D[1, N]				0.31

Distribution Moments

	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	0.35	0.075	0.7810	0.5811
Surface	0.34	0.070	0.8449	0.9050
Length	0.32	0.066	0.8764	1.1796
Number	0.31	0.062	0.8737	1.3717

Distribution Percentiles (um) -- Volume

Percentile	Size	Percentile	Size
10.0 %	0.27	80.0 %	0.41
20.0 %	0.29	90.0 %	0.46
50.0 %	0.34	100.0 %	0.69

Distribution Modal Sizes (um)

Mode	Size	Mode	Size
1	0.32		

Ageing performance

The following Tables show the results of oven ageing tests carried out using latex vulcanisates made with no added antioxidant (Table 2), with 0.5 phr of antioxidant added as ball milled dispersion (Table 3) and with 0.5 phr of antioxidant added as superfine dispersion (Table 4)

Tables 5, 6, 7 and 8 give the corresponding results for mixes containing different dosages of antioxidant

Table 2:
Vulcanisate with no added Antioxidant

ageing@ 70°C (weeks)	Tensile strength (MPa)	Modulus @ 300% (MPa)	Elongation at Break (%)
0	26	2,50	910
2	23	1,77	860
4	16	2,00	790
6	15	1,45	770
8	14	1,40	750

Table 3
Vulcanisate with 0,5 phr Antioxidant
ball-milled dispersion

ageing@ 70°C (weeks)	Tensile strength (MPa)	Modulus @ 300% (MPa)	Elongation at Break (%)
0	25	1,51	885
2	22	1,45	887
4	20	1,67	820
6	18	1,65	800
8	14	1,35	780

Table 4
Vulcanisate with 0.5 phr Antioxidant superfine dispersion

ageing@ 70°C (weeks)	Tensile strength (MPa)	Modulus @ 300% (MPa)	Elongation at Break (%)
0	24	1,6	840
2	23	1,55	830
4	22	1,50	825
6	19	1,78	810
8	18	1,45	780

Table 5:
Vulcanisate with 1.0phr of Antioxidant ball-milled dispersion

ageing@ 70°C (weeks)	Tensile strength (MPa)	Modulus @ 300% (MPa)	Elongation at Break (%)
0	25	1,75	900
2	23	1,72	890
4	21	1,71	800
6	18	1,85	760
8	14	1,34	770

Table 6
Vulanisate with 1.0 phr Antioxidant superfine dispersion

ageing@ 70°C (weeks)	Tensile strength (MPa)	Modulus @ 300% (MPa)	Elongation at Break (%)
0	26	1,61	850
2	26	1,61	840
4	21	1,8	775
6	20	1,8	770
8	17	1,5	762

Table 7
Vulcanisate with 2.0 phr Antioxidant ball milled dispersion

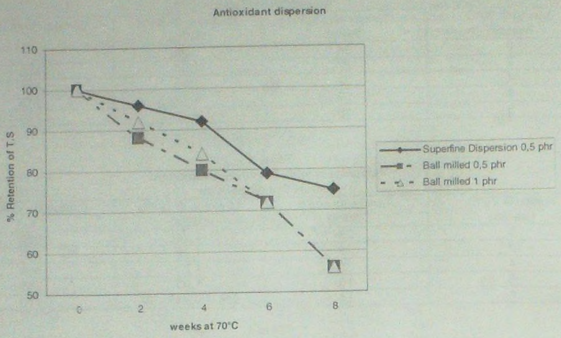
ageing@ 70°C (weeks)	Tensile strength (MPa)	Modulus @ 300% (MPa)	Elongation at Break (%)
0	27	1,43	925
2	26	1,40	890
4	19	1,76	855
6	16	1,45	834
8	13	1,09	811

Table 8
Vulcanisate with 2.0 phr Antioxidant superfine dispersion

ageing@ 70°C (weeks)	Tensile strength (MPa)	Modulus @ 300% (MPa)	Elongation at Break (%)
0	27	1,70	856
2	26	1,55	836
4	24	2,21	786
6	20	1,93	768
8	16	1,56	763

Selected data from these tables is reproduced in Figures 1 where the values presented are the percentage retentions of the unaged values plotted against time of ageing. This has been done to make the differences and trends more readily observable.

Figure 3.



Examination of the data in these Tables and Figure leads to the following conclusions:

(a) the antioxidant used is an effective protectant for the vulcanisates prepared in this work (when aged at 70°C)

(b) that there is very little advantage to be gained in adding more than 0.5 phr of the antioxidant (NB. This conclusion applies only to the vulcanisates and conditions of ageing used in this study, there is every reason to expect that under more severe ageing conditions higher levels of antioxidant would be beneficial)

(c) that "superfine" dispersions give better ageing resistance that the ball milled dispersions - even if the latter are added at higher levels,

The improved ageing of the finer particle size dispersions may be attributed to the improved distribution of the antioxidant throughout the product due to the vastly increased number of particles
A dispersion with an average particle diameter of 0.34 micron has 1000 times more particles (per gramme of dispersed material) as a dispersion with an average particle diameter of 2.6 micron.

SUMMARY

Significant improvements in the performance of a phenolic antioxidant in latex vulcanisates, have been obtained by the use of aqueous dispersions having a very small average particle diameter and a very narrow size range. It is believed that the improved performance is a consequence of the more homogenous distribution of the antioxidant throughout the product (resulting from the smaller particle size) which permits the additive to be more readily available to the site of oxidation.

Additionally, it is clear that superfine dispersions have other significant advantages in addition to improved antioxidant performance. The superfine dispersions of the antioxidant used in this study do not sediment (for all practical purposes) and this means than the amount of antioxidant added to the latex at the compounding stage will be the amount present in the products. If conventional ball-milled dispersions are used this is not necessarily true because their larger particles sediment very rapidly (during maturation or in the dipping tank) and. for this reason, the amount in the product may be less that the amount added to the latex.

Furthermore, the very large particles (those greater than 10 microns diameter) present in ball milled dispersions may form significant points of weakness in very thin products, such as condoms.

For example, particles of this diameter at the extreme elongations involved in the air-burst test would be similar in magnitude, or greater than, the thickness of the rubber itself and could therefore be one of the factors contributing to premature failure in that test.

For all these reasons we believe that the advent of superfine dispersions represents a significant advance in latex technology which will promote the production of better ageing and better performing latex products

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ZMTI SLURRY AND ITS EFFECT ON FIVE PHENOLIC ANTIOXIDANTS

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BIOGRAPHICAL NOTE

Ms. Webster received her Bachelor of Science in Chemistry from the University of Nevada. Immediately following graduation, she began work in Research and Development at Microflex Corporation in Reno, Nevada. She worked on the design and development of multiple medical exam glove projects over the three years she was with Microflex. Ms. Webster joined R.T. Vanderbilt Company, Inc. in January 2004 as the Latex Chemist in Waterborne Technologies, a division of the Rubber and Plastics Department.

ABSTRACT

The formulation of new ideas rarely starts with totally new technology. Zinc 2-mercaptotolumidazole (ZMTI) has been a reliable antioxidant synergist in the dry rubber industry for many years. It has only recently been available in dispersion form for use in the latex industry. Initial research has shown that the use of ZMTI in conjunction with popular phenolic antioxidants used in the glove and thread industries will greatly improve antidegradant protection. The increased performance is reflected in significantly improved aging, shelf life, and heat resistance. Additionally, the use of ZMTI greatly improves the whiteness and brightness of latex films. This paper is a continuation of previous investigations on ZMTI. It considers five different phenolic antioxidants and the effect that ZMTI has on their performance when used in natural and synthetic latex films. The latex films were evaluated for the following: 1) original physical properties, heat and aging resistance (measured by the retention of original physical properties), and 3) cost-effectiveness.

Introduction

Formulating a new compound consists of much more than just selecting the best performing chemical. Before finalizing a new product formulation, a good latex chemist looks at the cost and benefits of each additive. Often the best additive is neither the lowest nor the highest priced. Additionally the correct choice is not always the one that gives the best technical results. The correct additive is the one that is most cost-effective. Nowhere else is this more the case than with antioxidants. Exporters of latex products know that products are often sealed in containers for weeks after production. Temperatures in these containers are normally around 38°C. According to ASTM D 573 the oxidation rate doubles for every 10°C increase in temperature. That means that under these conditions, the oxidation rate is easily twice and possibly three times the oxidation rate at room temperature (23°C). This could mean the difference between gloves that pass and do not pass FDA requirements.

This paper will evaluate five different phenolic antioxidants and the effect that ZMTI has on their performance when used in natural and synthetic latex films. The films were evaluated for original physical properties and heat and aging resistance (measured by the retention of original physical properties). Additionally the cost-effectiveness of each antioxidant was assessed.

All the antioxidants used in this study are available from R.T. Vanderbilt Company, Inc. (RTV), and the RTV Price List was used as the basis for evaluating cost-effectiveness.

Identification

For the purposes of this paper, the following abbreviations will be made:

Table 1

Abbreviation	Chemical[1] Name
Antioxidant 1 (AO1)	Tris-(3,5-di-t-butyl-4hydroxybenzyl) isocyanurate
Antioxidant 2 (AO2)	3,5-di-tert-butyl-4-hydroxy-hydrocinnamic acid triester of 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6-(1H,3H,5H)-trione
Antioxidant 3 (AO3)	2,2'-methylene bis 4-methyl-6-tert-butylphenol (o-MBp14)
Antioxidant 4 (AO4)	Butylated Reaction product of p-cresol and cyclopentadiene
Antioxidant 5 (AO5)	Alkylated (butyl and styryl) Bisphenol A
ZMTI (Z)	Zinc 2-mercaptotoluimidazole

Procedure

This study was designed to look at different antioxidants in a generic aqueous setting. Because the various antioxidants used have different characteristics in different applications and different latexes, this study is only a general assessment and not to be used as a conclusive statement on cost-effectiveness. However, it can still be used as a guide when starting the design process. In order to maximize the usefulness of the study, both Carboxylated Acrylonitrile latex and Hevea Natural Rubber latex were used.

The initial compound was made using a conventional Carboxylated Butadiene-Acrylonitrile (XNBR) accelerator system.

Table 2

Ingredient	DRY (PHR)	WET (PHR)
41.5% XNBR	100	241
33% Sodium Lauryl Sulfate	0.25	0.8
4% Potassium Hydroxide Solution	1	25
50% Sulfur Dispersion	1	2
33% Zinc Oxide Dispersion	1	3
50% TMTD Dispersion	1	2
50% ZDBC Dispersion	1	2
Sulfated Methyl Oleate	0.5	1.5
Antioxidant (variable)	1	2

The antioxidant and ZMTI were added according to Table 3. All of the quantities are in DRY Parts per Hundred Rubber (PHR).

Table 3

Compound	ZMTI	AO1	AO2	AO3	AO4	AO5
XNBR 1	--	1				
XNBR 1Z	1	1				
XNBR 2	--		1			
XNBR 2Z	1		1			
XNBR 3	--			1		
XNBR 3Z	1			1		
XNBR 4	--				1	
XNBR 4Z	1				1	
XNBR 5	--					1
XNBR 5Z	1					1

The films were coated on glass plates and allowed to dry for 24 hours. These films were then placed in the oven for vulcanization. The oven was allowed to rise to temperature for 4 minutes. The films were then cured for 30 minutes at 121°C. After cooling, half of the samples were placed back in the oven for

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[1] When using any chemical product, obtain and comply with the precautions and warnings on the Material Safety Data Sheet and utilize good industrial handling procedures.

accelerated aging. These samples were aged for 144 hours at 85°C. All samples were tested on a T-10 Tensometer Machine using standard ASTM test method D6319-00.

The master batch was made using a traditional Natural Rubber Latex (NRL)) acceleration package (see Table 4).

Table 4

Ingredient	DRY (PHR)	WET (PHR)
67% High-Ammonia NRL	100	150
33% Sodium Lauryl Sulfate	1	3
10% Potassium Hydroxide Solution	0.5	5
50% Sulfur Dispersion	1	2
33% Zinc Oxide Dispersion	0.5	1.5
60% ZMBT Dispersion	1	1.7
50% ZDEC Dispersion	1	2
33% Sulfated Methyl Oleate	0.5	1.5
Antioxidant (variable, see below)	1	2

The antioxidants and ZMTI were added according to the following scheme (see Table 5). All amounts are in DRY (PHR).

Table 5

Compound	ZMTI	AO1	AO2	AO3	AO4	AO5
NRL 1	--	1				
NRL 1Z	1	1				
NRL 2	--		1			
NRL 2Z	1		1			
NRL 3	--			1		
NRL 3Z	1			1		
NRL 4	--				1	
NRL 4Z	1				1	
NRL 5	--					1
NRL 5Z	1					1

These compounds were coated and prepared for vulcanization in exactly the same process as the nitrile. The films were then cured for 20 minutes at 100°C. They were allowed to cool, and half the films were aged at 85°C for 132 hours. Both sets of samples were then tested on a T-10 Tensometer Machine for aged and unaged 300% Modulus, Ultimate Elongation, and Tensile according to ASTM D3578-00.

Results

Natural rubber films and synthetic rubber films degrade differently. Natural rubber films undergo chain scission, causing a decrease in tensile strength and an increase in elongation. On the other hand, synthetic rubber films continue to crosslink as they oxidize. They become hard and brittle. This means that the retention of tensile strength is a good indicator for the aging profile of natural rubber films, and elongation in combination with tensile strength is a good indicator of the nitrile aging profile.

RTV is not an expert in glove manufacturing and makes no warranties with respect to the results set forth here.[2] These results should only be used as a guideline for starting bench work.

Nitrile Results

Most glove-makers want to maximize tensile while minimizing modulus. Figure 1 shows the best aged tensile results were produced with AO2. NBR-4Z also has high tensile strength. This film was made with AO4 and ZMTI.

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[2] The information presented herein, while not guaranteed, was prepared by technical personnel and, to the best of our knowledge and belief, is true and accurate as of the date hereof. No warranty, representation or guarantee, expressed or implied, is made regarding accuracy, performance, stability, reliability or use. This information is not intended to be all –inclusive, because the manner and conditions of use, handling, storage, and other factors may involve other or additional safety or performance considerations. The user is responsible for determining the suitability of any material for a specific purpose and for adopting such safety precautions as may be required by R.T. Vanderbilt Co. does not warrant the results to be obtained in using any material, and disclaims all liability with respect to the use, handling, or further processing of any such material. No suggestion for use is intended as, and nothing herein should be construed as, a recommendation to infringe any existing patent or to violate any federal, state, local law or regulation.

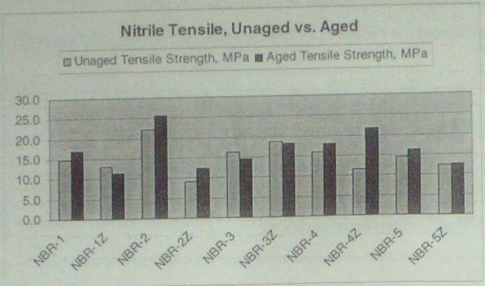

Figure 1

As is typical in nitrile, the elongation of the films decreased greatly upon aging (Figure 2).

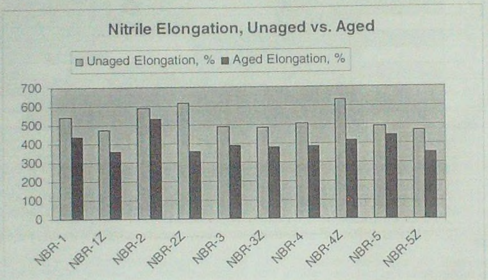

Figure 2

Figure 3 shows the modulus of the films before and after aging. As was expected, these compounds hardened as they aged. Figure 3 clearly shows that the smallest increases in modulus were observed in NBR-2, NBR-3, and NBR-3Z.

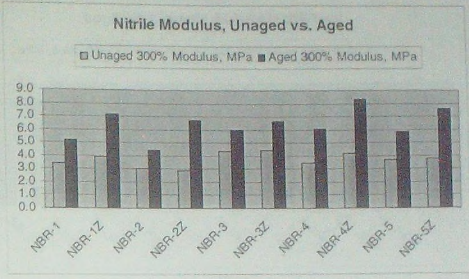

Figure 3

<u>Natural Rubber Latex</u>

As noted above, natural rubber latex has a completely different vulcanization curve than nitrile. Rather than hardening like nitrile during aging, NRL films lose tensile strength. Figure 4 shows how the films decrease in tensile strength upon aging.

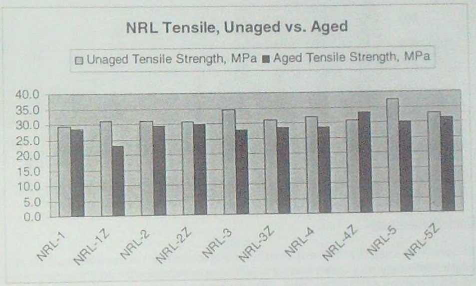

Figure 4

The only two samples to maintain a tensile of 30MPa were NRL-4Z and NRL-5. The rest of the results for the natural rubber latex are presented below. All films meet or exceed ASTM requirements as stated in standard D3578-00 (see Figures 5 and 6).

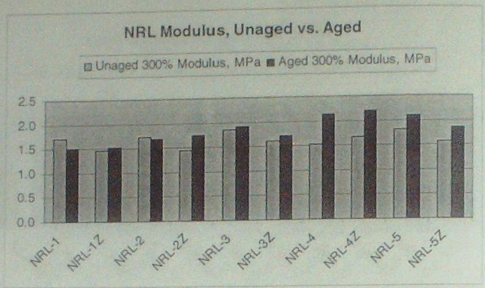

Figure 5

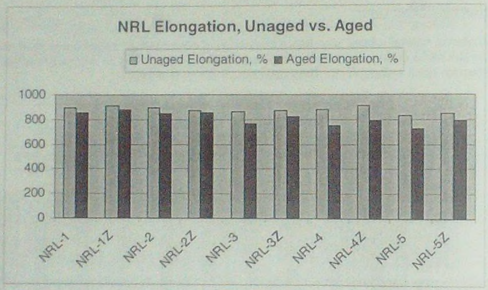

Figure 6

Cost-effectiveness

In order to determine cost-effectiveness, a minimum standard for the samples must be set. Although the aged testing in this study was much harsher than the specifications for ASTM testing, it is important that these films still meet the ASTM standards. Gloves imported to the United States are required to meet this standard upon arrival. This means that the aged testing of 7 days at 70°C is often not a stringent enough standard to use when choosing antioxidant protection for a latex product. With all this in mind, the following standards were used in determining cost-effectiveness.

Table 6

Latex	Tensile (MPa)	Elongation (%)
Carboxylated Acrylonitrile	19	400
Hevea Natural Rubber	30	N/A

Based on these minimum standards, the following graphs for nitrile were prepared.

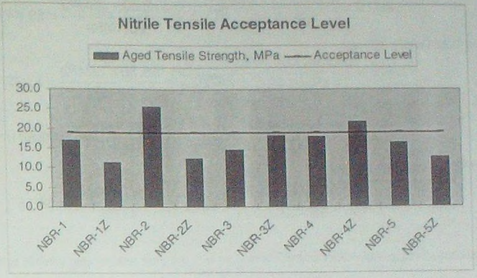

Figure 7

Using the minimum standard of 19MPa for tensile strength, NBR2 and NBR4Z are the only two samples that meet or exceed the level.

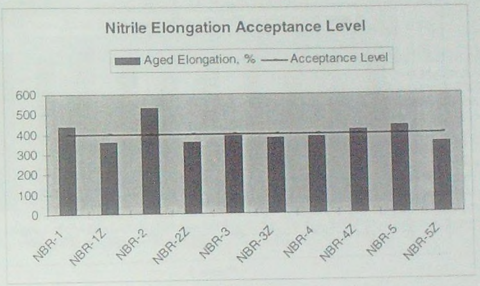

Figure 8

Again using the minimum standard determined above, the films that meet or exceed 400% elongation are NBR1, NBR2, NBR4Z, and NBR5.

In order to determine cost-effectiveness, an equation is used to determine the relative cost. This equation takes into account the performance of the additive, as well as its actual cost.

$$\text{Relative Cost} = \frac{\text{Actual Cost} \times \text{Minimum Standard}}{\text{Performance}}$$

The only two common samples for nitrile were made with AO2 and AO4 with ZMTI. The data from these films were used in the relative cost equation as shown below:

$$RC_{AO2} = \frac{\$13.00 \times 19MPa}{25.1MPa} = \$9.84$$

Relative Cost Tensile (Nitrile)

$$RC_{AO4+Z} = \frac{\$8.50 \times 19MPa}{23MPa} = \$7.02$$

$$RC_{AO2} = \frac{\$13.00 \times 400\%}{529\%} = \$9.82$$

Relative Cost Elongation (Nitrile)

$$RC_{AO4+Z} = \frac{\$8.50 \times 400\%}{417\%} = \$8.15$$

The most cost-effective antioxidant or the antioxidant with the best relative cost in nitrile is AO4 with ZMTI.

Using the same procedure, the following graph was prepared for natural rubber latex.

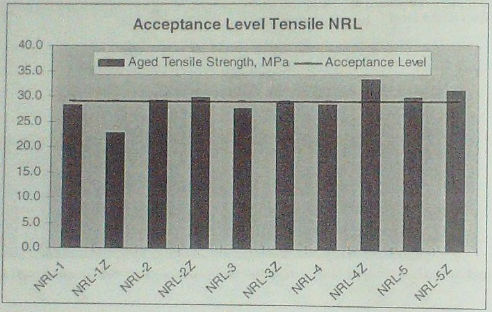

Figure 9

Although slightly harder to determine, the films that meet or exceed the standard for natural rubber latex tensile are NRL2, NRL2Z, NRL4Z, NRL5, and NRL5Z. Using the relative cost equation, the following relativ costs were determined.

$$RC_{AO2} = \frac{\$13.00 \times 29MPa}{29.2MPa} = \$12.91$$

$$RC_{AO2+Z} = \frac{\$19.00 \times 29MPa}{29.8MPa} = \$18.49$$

Relative Cost Tensile (NRL)

$$RC_{AO4+Z} = \frac{\$8.50 \times 29MPa}{33.4MPa} = \$7.38$$

$$RC_{AO5} = \frac{\$3.03 \times 29MPa}{29.9MPa} = \$2.93$$

$$RC_{AO5+Z} = \frac{\$9.03 \times 29MPa}{31.1MPa} = \$8.42$$

Clearly the product with the lowest relative cost is AO5. At a relative cost of $2.93, this emulsion is clearly the most cost-effective. For those that do not like working with emulsions (myself included), the second most cost-effective antioxidant based on relative cost is AO4 with ZMTI.

Conclusion

In this paper, we investigated five different phenolic antioxidants, the effect that ZMTI has on these antioxidants, and the cost-effectiveness or relative cost of these different antioxidant systems. Based solely on relative cost, the best antioxidant in the study for Carboxylated Acrylonitrile is AO4 with ZMTI. For the natural rubber latex, the best relative cost antioxidant is AO5. Unfortunately this value does not include ease of use. It is also important to remember that AO5 is only available as an emulsion. With this in mind, the most cost-effective antioxidant (including ease of use) for natural rubber latex is AO4 with ZMTI.

In a compound, one of the most integral and most often overlooked ingredients is the antioxidant. It is important to remember that cheaper is not always better. A company can usually save money by choosing the most cost-effective chemical. It is important to consider all the factors including technical feasibility, ease of use, and relative cost. This is the case with an antioxidant system. The right antioxidant maintains the physical properties of the product, and allows the product to be transported long distances with a formula designed not to degrade during transportation.

Acknowledgements

NR Latex: Getahindus, Sdn Bhd, Malaysia – LATZ
XNBR Latex: Noveon IP Holdings, Inc– HYCAR® 1570x79 Latex
Sodium Lauryl Sulfate: R.T. Vanderbilt Company, Inc. – DARVAN® WAQ Additive
ZMBT: R.T. Vanderbilt Company, Inc. – ZETAX® Accelerator
ZDEC: R.T. Vanderbilt Company, Inc. – ETHYL ZIMATE® Accelerator
TMTD: R.T. Vanderbilt Company, Inc. – METHYL TUADS® Accelerator
ZDBC: R.T. Vanderbilt Company, Inc. – BUTYL ZIMATE® Accelerator

AO1: R.T. Vanderbilt Company, Inc. – VANOX® GT Antioxidant

AO2: R.T. Vanderbilt Company, Inc. – VANOX® SKT Antioxidant

AO3: R.T. Vanderbilt Company, Inc. – VANOX® MBPC Antioxidant

AO4: R.T. Vanderbilt Company, Inc. – VANOX® L Antioxidant

AO5: R.T. Vanderbilt Company, Inc. – AGERITE® SUPERLITE® Antioxidant

ZMTI: R.T. Vanderbilt Company, Inc. – VANOX® ZMTI Antioxidant

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A HIGH PERFORMANCE MICROBIOCIDE SYSTEM FOR LATEX PROTECTION

Bernd Unterweger
Biomontan, Austria

BIOGRAPHICAL NOTE

Bernd Unterweger Biomontan Enns/Austria

Born 1950 in Austria

Studied Chemistry at the university of Graz / Austria

27 years experience in the application of specialty chemicals in different industries such as paper industry, board industry and latex industry.

Specialty chemicals include biocides, flocculants and special treatments in the paper industry.

ABSTRACT

Microorganisms are always present during the production of synthetic latex emulsion.
Without treatment, they may increase their population dramatically. They may destroy the polymer and cause other problems.

A new environmental friendly biocide system to protect latex emulsions from microorganism will be introduced.

Polymer emulsions, such as SBR latex, are aqueous fluids, which present an excellent medium for the multiplication of micro organisms.
As the emulsions are used for the production of high quality products, including those coming in contact with food, they have to be in a clean condition, when used.
When selecting an appropriate micro biocide for the protection of the product, one has to know the conditions these micro organisms are growing:

- type of polymer emulsion
- pH value
- expected stability
- final use of the product

The temperature mainly that of the injection point of the biocide, plays an important roll for the selection of the biocide.
Of course, the biocide must not react with the polymer emulsion or have a negative input on it.

What are bacteria and where do they come from?
Bacteria are microscopic tiny single cell organisms without nucleus.
They multiply by splitting the cell. Their size is between 1 and more microns, but there are bacteria having a size of 0,75 mm.
They are the true-life artists:
Some kinds of them can multiply at a temperature of −17°C
Some kinds grow in hot springs at more than 100°C.
Smoke chimneys in the deep sea give food to bacteria. They can use the exhausted sulphur for their own growth.
It is not surprising, that bacteria are extremely resistant against x-rays.

Bacteria live everywhere. They live in the soil, in the water and in the air. They attack food stuff and most of the organic compounds.

The presence of elemental oxygen is not essential for many species of bacteria. Anaerobic bacteria can survive without it.
It is possible, that these bacteria were the first species living on our planet before free oxygen was produced by photosynthesis.

In this connection it is interesting to know that free oxygen is poisonous for this type of bacteria.

Classification of bacteria:

Generally, bacteria are classified due to specific properties.
Based on their appearance:

Coccen are spherical

Coccen 1

Bacillus is rot-shaped

Bacillus 1

Spirochetes are like a spiral

Spirochetes 1

Based on the different behaviour against iodine/crystal violet
Those, which cannot be stained in this way, are gram-negative.
Those, which are stainable with the dye stuff, are gram-positive.

gram-positive 1

Bacteria increase by cell division. The genetic material is doubled; the bacteria expand and pinch off in the middle.

The frequency can be very high. It is said, that bacteria can double their number under good conditions every 20 minutes.

Good life conditions for bacteria are:

- Sufficient food
- Sufficient humidity
- Temperature around 37°C, but could be also much higher
- pH at around 7
- Aerobic bacteria's need also free oxygen dissolved in the water

Based on above calculation, the number of bacteria may increase from 1 to 33 million within 8 hours.

The food offer is sufficient for them:

- ✓ all kind of natural and synthetic latices
- ✓ dispergators
- ✓ wetting agents

A high number of bacteria may cause tremendous problems in the industry:

- decrease in pH value and decrease of redox potential
- bad odour based on the reduction of Sulphur to S^{2-}
- formation of rust due to the oxidation of iron
- formation of slime
- destroying the raw material, the intermediate or the final product.

Nevertheless, bacteria are very important in different industrial areas:

They are responsible for the biodegradation of biological material. They are furthermore responsible for the fermentation during the production of cheese, Yoghurt or Sauerkraut.
Bacteria are also very important for the production in the leather industry, tobacco, pharmaceuticals and washing detergents.

Based on what we have said before, that bacteria may cause a lot of problems in the production of latex, the total count of micro organisms must be kept low.

Therefore, chemical products are used and they are called biocides. They belong to different chemical compound classes:

- alcohols
- formaldehyde and formaldehyde releasing compounds
- phenol products
- biocides based on acetic acid and its derivates
- Carbamates and derivates
- Miscellaneous

The biocide may be added as single component product or as blend. In this case, synergistic effects are sometimes achieved.

Biocides attach bacteria by destroying the cell wall.
They also intervene in the metabolism of the bacteria and destroy the food balance.

Mainly, they act as quick killer that means, they kill the bacteria immediately, but their effect does not last very long.

Further, there are conservation biocides on the market, which do not act so fast but their effect is long lasting.

Of course, the requirements for biocides are nowadays very strict:

- They have to be efficient and have to be effective already in small amounts
- They have do be biologically degradably
- They have to be in accordance with the EC guidelines and the guidelines of different organisations

Biocides are normally added discontinuously as shock during the production process. They can be also added batch by batch for the conservation of the product.

Of course, there are also disadvantages because of the addition of biocides:

- Biocides are always poisonous
- The cost of treatment may be significant
- Micro organisms may become resistant against the biocide
- The use of biciodes become more and more problematic due to environmental reasons

We from Biomontan are therefore developing a method to significantly decrease the amount of biocide needed in the industry to act as a quick killer during the production process:

As described above, in the first step several biocides have to be screened to find out the most effectives on.

The selected biocide has to be added discontinuously. Additionally, a second product is added discontinuously based on different parameters controlled. pH and redox potential are under constant control and are increased due to the addition of the second product.

The trials in one industrial plant have to be continued, but there are strong indications, that a large quantity of biocide can be saved.

Furthermore the system will allow the end user to better monitor the system and act more quickly mainly during the hot summertime, if necessary.

SAFER ACCELERATORS FOR THE LATEX INDUSTRY

Khirud B Chakraborty and **Roger Couchman**
Robinson Brothers Limited, West Bromwich B70 0AH UK

BIOGRAPHICAL NOTE

Roger Couchman has a degree in Polymer Technology and Chemistry to LRSC. Polymer research and development. Experience was gained with BTR Industries (5 years- rubber, PU, environmental and analytical chemistry) followed by Production (3 years - compounding, manufacture of hose, escalator handrail and print blankets.)

Roger Couchman has worked for Robinson Brothers Limited for 19 years in sales and marketing of Robac polymer chemicals. He has covered the global market working with both distributors and their customers in technical and commercial situations.

Whilst with Robinson Brothers he has worked on market introduction of new accelerator systems offering solutions to the nitrosamine problem and reduced Type IV skin allergy. Numerous technical papers being presented including International Latex conferences in USA and Germany.

ABSTRACT

It is accepted that many widely used latex vulcanisation accelerators: dithiocarbamates, thiurams and thiazoles are capable of producing Type IV allergic response in certain individuals within the population and may also possess increasingly unacceptable eco-toxic and acute toxicity profiles.

Thiurams and dithiocarbamates (derived from secondary amines) can also produce potentially harmful N-nitrosamines when used.

The paper describes three safer accelerators developed and commercialised by Robinson Brothers Ltd. They are designed to reduce or eliminate the impact of the above problems using sustainable technology. The paper describes their technological affect particularly in synthetic polyisoprene applications. It also covers Natural Rubber and SBR latex blends for foam applications. Results show equivalent technological performance to those seen with widely used conventional materials. Mechanisms of action will also be discussed.

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1. INTRODUCTION

The unique characteristics of natural rubber such as high levels of stereo regularity, highly branched polymer with a high molecular weight and a wide molecular weight distribution result in vulcanised rubber film products having a unique combination of strength and elasticity. These characteristics also make natural rubber particularly useful for the preparation of barrier protection products. As a result natural rubber latex is used in a wide range of industries and applications including personal protective equipment (surgical and examination gloves), medical devices (catheters), condoms, food contact and child related products (nipples and pacifiers), mattresses, carpet backing, binders in non woven fabrics, paper, water based paints and many others.

However, increased concerns have been reported over the past 20 years of allergic responses[1] to products, particularly personal protective equipment, food contact and child related products manufactured from latex derived polymers. Based on various studies and practical evidence[2,3] it is now widely accepted that two types of allergic responses are associated with natural rubber latex products: Type I and Type IV allergy.

Type I allergy is also known as 'Type I hypersensitivity or immediate contact dermatitis'. Exposure produces symptoms such as itching, urticaria, swelling, breathlessness and rhinitis. In extreme cases a serious condition known as anaphylactic shock may occur. This allergic reaction has been linked to the presence of water extractable proteins (WEP) which are present in natural rubber latex. This is well documented and various action/standards developed to control and regulate the amount of proteins e.g. SMG scheme and ASTM Standards.

Type IV allergy is by far the most common allergic reaction associated with latex based products and manifests itself as localised itching, redness, swelling, blistering and cracking. This is often referred to as 'delayed contact dermatitis'. This type of allergic response has been linked closely with the chemicals used to vulcanise natural rubber latex.

Another area of great concern is potential formation of nitrosamines from the latex based products: Over the last few decades, toxicological work[4,5] has clearly indicated that nitroso compounds in general and N-nitrosamines in particular have severe carcinogenic effects on various life forms, including primates. Many of them are suspected human carcinogens as documented by the International Agency for Research on Cancer (IARC[6,7]). The source of these nitrosamines have been found to be due to secondary amine derived accelerators (such as dithiocarbamates, thiurams, mercaptobenzthiazole and some sulphenamides - the vulcanisation workhorses of the rubber industry). Various legislations[8,9] already exist on the levels of N-nitrosamines and nitrosatable substances for 'special' category products e.g. nipples, pacifiers.

From the above discussion it is quite clear that both potentially harmful concerns (Type IV allergy and nitrosamines) are due to the conventional accelerators widely used in the manufacture of latex products.

Environmental concerns are also growing with the use of conventional accelerators. They mostly require higher energy consumption during compounding and processing. Moreover, the presence of heavy metals usually associated with the use of conventional accelerators may either contaminate the product giving recycling problems and/or pollution of the leach water.

Over the last two decades, synthetic lattices such as SBR, nitrile, neoprene, vinyl etc have made significant inroads into markets traditionally dominated by NR latex. In some cases there has been an almost total shift to synthetic latex such as carpet backing and foam products. In others, such as gloves, synthetic lattices now account for a significant share of total demands. Although synthetic lattices do not contain natural proteins as in NR latex and hence free from Type I allergy, they still require conventional accelerators such as thiurams, dithiocarbamates and thiazoles to vulcanise them. Hence Type IV allergy and nitrosamine problems do exist with synthetic latex products.

More recently synthetic polyisoprene (same monomer unit isoprene as in NR) has been developed to provide a material with the benefits of natural rubber and eliminate the potential for protein allergy. However, due to synthetic variants typically having a lower level of stereo regularity and different molecular weight characteristics has resulted in synthetic polyisoprene films having an inferior balance of properties than those of vulcanised natural rubber films. Vulcanisation of synthetic polyisoprene latex using a conventional cure package such as dithiocarbamates, thiurams, zinc oxide and sulphur yields poor shelf stability, typically coagulating within a few days of compounding and inferior physical properties including surface defects[10]. Moreover, Type IV allergy and nitrosamine issues still remain in latex articles.

Robinson Brothers Limited's response has been to develop sustainable and toxicologically less hazardous accelerators. They not only reduce/eliminate Type IV allergic and potentially carcinogenic nitrosamines but will also improve the vulcanisate properties.

The present work will demonstrate an ability to provide synthetic polyisoprene vulcanised films with absence of Type IV allergy, a safer nitrosamine content and have improved desired properties.

It also describes how the newer accelerators are capable of producing foam based on Natural Rubber and SBR blends with the absence of mercapto benzthiazole, reduction of both Type IV allergy and potentially carcinogenic nitrosamines.

2. EXPERIMENTAL

Commercially available low ammonia natural rubber latex (LATZ), SBR latex (index – HSL/LSL) and polyisoprene (Kraton™ IR-RP401) were used in the present study.

Prevulcanisation of the latex was carried out at 65°C for 6 hours unless otherwise specified. Latex films were prepared by casting on glass plates and dried for 72 hours in a humid atmosphere at room temperature. Post vulcanisation studies were carried out using room temperature dried films just after mixing and then heated in an air oven for 30 to 45 minutes at 120°C.

The determination of cross-link density in compounded rubber latex during pre-vulcanisation studies was carried out using a modified solvent swell test[11].

A Brookfield LVT viscometer operating at 60 rev/min was used to determine the compound viscosity. All physical tests were carried out using an Instron 4302 Tensile testing machine.

Please refer to Appendix 1 for glossary of abbreviations.

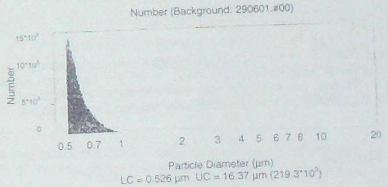
3. RESULTS AND DISCUSSION

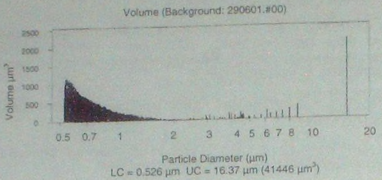
Synergistic combination of nitrogen free DIXP (Robac AS100) and safer accelerator ZDNC (Arbestab Z) in synthetic polyisoprene latex.

DIXP is diisopropyl xanthogen polysulphide, the structure of which is completely free from nitrogen, phosphorous and metallic elements. It is completely used up during cross-linking process leaving no residue in the product. It has been approved by the FDA in the USA under regulation 21CFR177.2600 as a component of rubber articles intended for repeated use in contact with food and also approved by the French Ministry of the Economy under NOR:ECOC9400131A as a component of rubber materials in contact with food stuffs, alimentary products and drinks. DIXP is employed as 60% emulsion which is easily miscible in the latex medium.

ZDNC is based on highly branched and longer alkyl chain safer secondary amine. It is highly involatile, thermally stable and soluble in rubbers.

Due to the chemical nature of the molecule, ZDNC seems to possess very balanced hydrophobic and hydrophillic character resulting in easy migration from the aqueous phase to the non polar latex micelle. Smaller particle size enhances the above process to ensure high effectivity as an accelerator. Robinson Brothers Limited has developed a technique to produce a 35% dispersion of ZDNC showing very small particle size distribution. (0.2 - 1µ).





ZDNC has undergone thorough toxicity testing and has been found to be significantly less hazardous than conventional dithiocarbamate accelerators. (Contact Robinson Brothers Ltd for details)

ZDNC has been approved by the BGVV in Germany under special category of recommendation XXI, articles based on natural and synthetic rubbers.

3.1 Effect of DIXP/ZDNC in combination on prevulcanisation of polyisoprene latex – surgeons glove type formulation:

Formulation (wet weight):

Polyisoprene latex (Kraton IR-RP401)	167.0
30% K Coprylate	1.7
20% KOH	2.5
50% ZnO	1.0
60% Sulphur	2.5
50% 2246 AO	1.0
40% MMBI AO	1.25
Water	80.0

Accelerator

1.	50% ZDEC	1.0
	50% MBT	1.0
2.	60% DIXP	0.67
	35% ZDNC	1.15

The effectiveness of DIXP and ZDNC at 0.4 phr each in prevulcanisation of polyisoprene latex at 65°C for 6 hours is compared with conventional accelerators, ZDEC/MBT at 0.5 phr each, see *figure 1*. Measuring percentage linear swelling in toluene assessed the rate and degree of prevulcanisation. Almost full prevulcanisation occurs when the percentage linear swelling value reaches between 80-84.

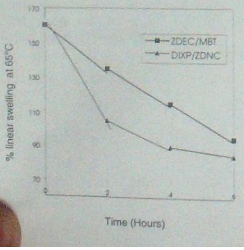


Figure 1

Plot of linear swelling against time 65°C

Effective prevulcanisation was found to occur with DIXP/ZDNC between 5-6 hours at 65°C while ZDEC/MBT was not as effective under the same conditions.

After 6 hours of prevulcanisation, films were flowed and dried for 72 hours at room temperature followed by leaching in still water for 4 hours. One set of films were dried overnight at 30°C and another set dried for 30 minutes at 120°C. *Tables 1 and 2* respectively show tensile properties of the above dried films. All tensile samples are E type dumbbell. Thickness 1.0 – 1.1nm.

Table 1

Tensile properties of the films dried overnight at 30°C

	ZDEC/MBT at 0.5phr each	DIXP/ZDNC at 0.4phr each
300% Modulus (MPa)	0.75	0.77
Tensile strength (MPa)	9.58	12.5
Elongation at break (%)	980	>1050

Table 2

Tensile properties of the films dried for 30 minutes at 120°C

	ZDEC/MBT at 0.5phr each	DIXP/ZDNC at 0.4phr each
300% Modulus (MPa)	1.20	0.92
Tensile strength (MPa)	12.0	15.0
Elongation at break (%)	971	>1050

NB It may be mentioned that tensile specimens containing DIXP/ZDNC did not break due to high elongation. Tensile strength values are estimated.

Both *tables 1 and 2* show the better tensile properties of vulcanisates containing DIXP/ZDNC compared to ZDEC/MBT although molecular mass of ZDNC is approximately 2 times greater than ZDEC.

3.2 *Maturation of polyisoprene latex at 35°C*

DIXP and ZDNC in combination (0.4phr each) can effectively mature polyisoprene latex at 30°C without destabilising or increasing the viscosity of the compounded latex to any significant extent. ZDEC/MBT combination showed an increase in viscosity of the compounded latex and appeared to destabilise to some extent at the same time. (*Figures 2 and 3*)

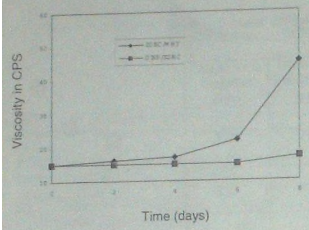


Figure 2

Changes in viscosity of compounded latex during maturation at 30°C

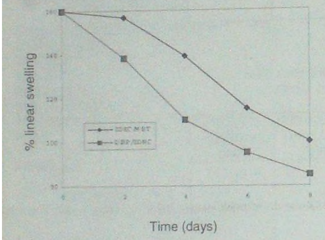


Figure 3

Plot of % linear swelling against time at 30°C

Figures 2 and 3 clearly show that effective vulcanisation of compounded latex occurred at 30°C with DIXP/ZDNC combination after 8 days.

After 8 days of maturation, films were prepared as before followed by final cure for 30 minutes at 120°C. *Table 3* shows the physical properties of the cured films.

Table 3

	ZDEC/MBT	DIXP/ZDNC
300% Modulus (MPa)	0.93	1.16
Tensile strength (MPa)	17.20	22.0
Elongation at break (%)	930	>1050

3.3 *Discussion*

It can be seen from the above results that under similar technological conditions DIXP/ZDNC combination is more effective in vulcanising polyisoprene latex compared to conventional accelerator system ZDEC/MBT. More effective vulcanisation was found to take place during maturation at ambient temperatures indicating that cross-linking of polyisoprene might not be significantly temperature dependent *cf* natural rubber latex. Time of reaction appears to be more important on affecting properties. This could be due to the fact that synthetic polyisoprene is purely non ionic and non polar *cf* NR latex containing natural rubber proteins and other semi polar products (eg TMTD). As a result the migration of added sulphur and accelerators is slower to the reaction site. Since DIXP is non polar and ZDNC very weakly polar due to long alkyl chain, they are more soluble in the latex medium resulting in better migration to the reaction site and hence optimised properties can be achieved.

DIXP, although a sulphur donor, does not behave like traditional sulphur donors eg TMTD. In general TMTD produces predominantly mono and disulphidic cross-links in elastomers. Determination of the nature of cross-links using chemical probe technique[12] has found that DIXP produces all three types of cross-links – poly, di and mono sulphidic almost in equal proportion. ZDNC, an accelerator, like other dithiocarbamates also produces di and polysulphide cross-links. As a result this combination is capable of producing very balanced physical properties.
Since DIXP does not contain nitrogen in its chemical structure it is impossible to generate n-nitrosamines. As it is largely consumed during vulcanisation process leaving no residue to induce Type IV allergic response.

ZDNC is highly thermally stable (no decomposition occurs below 250°C) and does not produce parent diisononylamine easily. Diisononylamine, moreover, has been shown to be difficult to nitrosate, and if nitrosated, its nitrosamine is involatile and also toxicologically much less hazardous in terms of both acute toxicity and metabolic activity.

Genotoxic tests on N-nitrosdiisononylamine show it to have negative metabolic activation and is not mutangenic. ([+]HRC RSN46A/891630)

Due to high solubility of ZDNC in rubber very little migration, if at all, occurs to the surface of articles in normal use. Skin sensitisation and delayed contact hypersensitivity test carried out on ZDNC by Huntingdon Research Centre[+] (Report No 83499D/RSN 17199) showed no evidence of dermal reactions or delayed contact hypersensitivity. These data, together with its high solubility in rubbers and consideration of migration data, lead us to believe that ZDNC has considerable potential to alleviate health concerns, type IV allergic reactions in particular.

4. Effectivity of PTDC dispersion (Robosol) in NR/SBR latex blend

PTDC dispersion or Robosol is a proprietary aqueous dispersion based on primary thioamine dithiocarbamate. Chemically PTDC is 2,2'-dithio(diethylammonium)-bis (dibenzyl dithio carbamate) also known as SAA30 – which does not contain any metal ion. PTDC is classed as an ultrafast accelerator and capable of replacing conventional thiurams and dithiocarbamates on a weight to weight basis althougth its molecular weight is significantly higher compared to most conventional accelerators.

4.1 Results

ZDEC and ZDBC in combination with MBT and DPG are the most widely used accelerators for compounding SBR/NR latex blend. These are highly efficient and their performances are difficult to match by using other accelerators. However, they can produce a significant amount of regulated and harmful nitrosamines in the products. Moreover, they are also of great concern regarding Type IV chemical allergens. Hence there is a demand for an accelerator to replace the above in order to reduce or eliminate harmful effects associated with ZDEC, ZDBC and MBT. In this context the effectivity of PTDC dispersion in combination with DPG was examined in SBR/NR latex and compared with ZDEC/MBT/DPG system. It may be mentioned here that PTDC is mainly developed for production of latex articles to be used in the non health care sector (e.g. examination gloves, mattresses, carpet backing etc.). No approvals have yet been sought nor will be in the near future due to the high cost involved and regulatory needs of the envisaged market.

The following formulations were examined:

	Dry Weight	
	1	2
SBR latex (2720)	60	60
LANR latex	40	40
Potassium caprylate	0.5	0.5
KOH	0.5	0.5
ZnO	2.5	2.5
Sulphur	2.0	2.0
MMBI antioxidant	1.0	1.0
ZDEC	1.0	-
MBT	1.0	-
DPG	0.5	0.5
PTDC	-	1.5

All ingredients were mixed into the latex either as aqueous solutions or dispersions under slow stirring for approximately 30 minutes. The compounded latex was then allowed to stand for at least four hours. Films were then flowed and dried at ambient temperature under humid conditions for 4 days. Films were then tested for rheological cure performance in a Monsanto Moving Die Rheometer at 120°C (MDR 2000) with the following properties:

Formulation:

	TSI (mins)	T_{90} (mins)	RH rate (lb – in/min)	M_H (lb – in)
Control (no accelerator)	20	17.93	0.2	5.5
ZDEC/MBT/DPG	1.73	11.93	1.4	10.94
PTDC/DPG	1.1	9.8	2.3	12.54

The previous table indicates that although the molecular weight of PTDC (698) dispersion is almost twice that of ZDEC (361), the rate and state of cure associated with PTDC is higher than ZDEC system on equal weight basis. It is also noted that ZDEC requires use of thiazole (MBT) to vulcanise effectively.

New films from the above compounded latex were then cured for 40 minutes at 120°C and tensile properties measured in the table below:

Formulation:

	300% Modulus (MPa)	Tensile strength (MPa)	Elongation Break (%)
Control (no accelerator)	0.52	4.5	>1000
ZDEC/MBT/DPG	1.27	14.2	520
PTDC/DPG	1.10	16.4	590

Vulcanisate containing PTDC/DPG showed slightly better tensile properties.

4.2 Latex foam (moulded)

Attempts have been made to produce latex foam with the previous formulations using the method discussed in Natural Rubber Technical Information sheet, Latex Series L42, 1981. In the present study accelerators were mixed in masterbatch and left to stand overnight at room temperature followed by expanding the original volume to 5-6 times using high speed stirrer. Swelling agent, sodium silico-fluoride was then added and the foam stirred for 1 minute. Foam was then poured into the warm mould (30°C) and cured for 90 minutes at 100°C in hot air circulating oven. After cooling the mould the foam rubber was squeezed to remove excess water and dried at 70°C for 6 hours. Good dimensional foam structure was achieved with Robosol/DPG system (see *Figure 4*)). Formulation containing ZDEC/MBT/DPG required 120 minutes curing time to achieve the similar foam structure below.

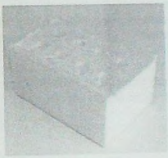


Figure 4

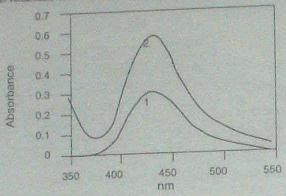
4.3 Discussion

The effectivity of PTDC dispersion in NR/SBR latex blend is clearly evident by the rate of cross-linking and state of the cure. These properties are very similar if not better to that of ZDEC on an equal weight basis. In the post vulcanisation process PTDC dispersion gave superior tensile properties compared to ZDEC system. Well structured latex foam with NR/SBR latex blend can successfully be produced using PTDC dispersion in a shorter curing time.

In order to gain an insight into the mechanisms of action of PTDC, the vulcanisate cured with PTDC was extracted (Soxhlet) with methanol and hexane respectively. The extracts were analysed by various analytical techniques including HPLC, FTIR and UV Spectroscopy. Neither the diaminoalkyldisulphide component of PTDC nor its possible derivatives were detected in the extracts. However, the hexane extract showed the presence of ZBEC and it confirmed by reacting the extract with aqueous copper sulphate solution. Typical brown colour characteristic to copper dithiocarbamate was observed. The resultant solution was then analysed by UV Spectroscopy and compared with standard ZBEC solution in hexane under the above conditions (*Figure 5*). Both solutions gave similar absorption maxima at 430 – 440 nm indicating the presence of ZBEC in the hexane extract.

Figure 5

UV Spectra of Copper dibenzyl dithiocarbamate in hexane



1 = Standard ZDEC solution in hexane reacted with copper sulphate
2 = Hexane extract of natural rubber vulcanisate cured with SAA30 and reacted with copper sulphate

It may be mentioned that in June 1994 ZBEC was approved by the BGA in Germany for category 1 (food contact use) and special category 2.5 (nipples, soothers and toy balloons). It is also approved by the FDA under regulation 21CF177.2600 as a component of rubber articles intended for repeated use in contact with food.

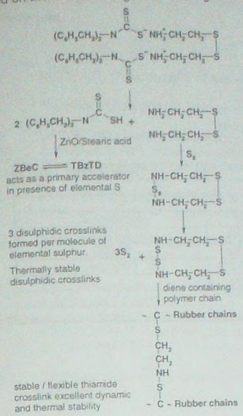
The above extraction work tends to suggest that during vulcanisation the diaminoalkyldisulphide component of PTDC becomes integrated into the polymer network which resists extraction.

Estimation of the nature of cross-links in the pure gum vulcanisatres, using selective chemical probes, indicates that PTDC predominantly produces disulphide cross-links with a lower proportion of polysulphidic cross-links (approximate ratio of dipolysulphidic to polysulphidic cross-links is 60-40).

As PTDC becomes fully integrated into the polymer network during vulcanisation, it is unlikely that PTDC will migrate to the surface. Hence it is highly possible to reduce/eliminate Type IV allergic reaction utilizing PTDC as an accelerator.

Determination of nitrosamine in the natural rubber latex vulcanisates cured with PTDC dispersion did not show more than 3ppb of combined nitrosamines and less than 10ppb nitrosatable amines.

Based on the above findings the following mechanism of action of PTDC is proposed.



General Conclusion

The present paper discusses the issues of Type IV allergy and nitrosamines particularly relevant to the latex industries. The three safer accelerators developed at Robinson Brothers, DIXP (Robac AS100), ZDNC (Arbestab Z) and PTDC dispersion (Robosol) have been shown to greatly minimise the concerns relating to the above health issues, whilst maintaining desirable properties in the latex products for their end users.

Appendix 1

List of abbreviations used in text

Abbreviation	Chemical Name	Trade Name
ZDEC	Zinc diethyldithiocarbamate	
ZDBC	Zinc dibutyldithiocarbamate	
ZDNC	Zinc diisononyldithiocarbamate	Arbestab Z
DIXP	Diisopropylxanthogen polysulphide	AS100
PTDC	Primary thioamine dithiocarbamate	SAA30
PTDC dispersion	Aqueous dispersion containing PTDC	Robosol
LANR	Low ammonia natural rubber latex	
SBR	Styrene butadiene rubber	
ZnO	Zinc oxide	

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DE-AERATION TECHNOLOGY AND APPLICATIONS

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BIOGRAPHICAL NOTE

Dipl.-Ing. (FH) Johannes Popp, NETZSCH-Feinmahltechnik GmbH, was studying machine construction at the Fachhochschule Coburg. Since 1987 he is working at NETZSCH-Feinmahltechnik GmbH in the construction department, engineering and sale in Germany and England with the focal point mixing technology.

ABSTRACT

Besides grinding and mixing equipment NETZSCH-Feinmahltechnik GmbH also manufactures machines for the de-aeration of various products. With the NETZSCH De-Aerator it is possible to simply remove micronised gas and air pockets of liquids with different viscosities or of viscous masses and pastes.

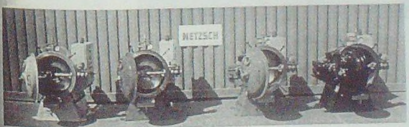
According to the VDR principle (Vacuum-Thin layer-Rotational procedure) different products with low viscosity to flowable masses are processed with minimum product loss. Depending on the machine size and viscosity of the products throughput rates of 50 – 10000 kg per hour can be achieved. The NETZSCH De-Aerator can be used to de-aerate both small quantities using changeable tanks in batch operation or large processes in continuous operation.

A variety of applications in the food, cosmetics, pharmaceutical, paint or chemical industry will also be presented.

Introduction

When processing liquid to high-viscosity products, cause air or gas pockets often difficulties. The embedding of air and so oxygen can lead to negative effects on the product. These could be e.g. oxidation, fats or oils becoming frowsty, discoloration or interference of smell and taste of the products and for coated materials it could lead to porous and holey surfaces. In contrast, de-aerated products are normally chemically more stable and longer living.

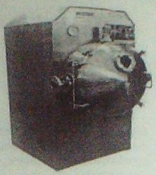
With the NETZSCH-Vacuum-De-Aerator it is easily possible to continuously de-aerate flowable products. Even micronized gas and air pockets of liquids of different viscosities or of viscous masses and pastes are removed with that machine. The De-Aerator can be used for processing small quantities in batch operation as well as for large batches in continuous operation.



Pict. 1: NETZSCH-Vacuum-De-Aerator

Machine Description

The NETZSCH-Vacuum-De-Aerator impresses by a compact, enclosed construction with smooth outer surfaces. The drive and the vacuum pump are integrated in the machine stand. In the IP design, the switch box is also mounted in the machine stand and so the machine can be put into operation immediately after assembly. Additional special equipment such as condenser with scraper in the vacuum line, cooling of product-wetted parts, automatic valves in the product supply or a filling level safety control provide flexibility for the use in many fields of application. All product-wetted parts are designed in stainless steel.



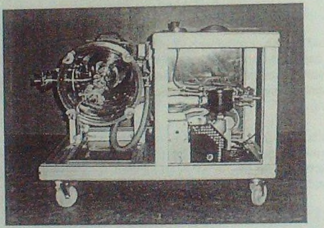
Pict. 2: NETZSCH-Vacuum-De-Aerator DA 602

The throughput is dependent on the product and its viscosity and can vary depending on the machine size – from laboratory machine *MINIVAC* (pict. 3) to production sized models – between 50 and 10,000 kg product per hour (see table 1).

The De-Aerator can be linked to an existing atmospheric process system, whether it be a bulk mixer or a change pan type mixer and de-gas the product prior to usage. Furthermore, an automatic operation with automatic valves in the product line and a level, vacuum and flow control is possible.

Table 1: Machine sizes

Machine type	**Drive [kW]**	**Throughput [kg/h]**
series 600 (601, 602)	18.5	500 – 10,000
series 400 (401, 402)	11	250 – 2,500
MINIVAC	2.2	50 – 220



Pict 3: Laboratory-De-Aerator *MINIVAC*

Function Principle

Pict. 4: Function principle of the NETZSCH-Vacuum-De-Aerator

According to the VTR principle (Vacuum-Thin layer-Rotational procedure, pict. 4) different products with low viscosity to flowable masses can be processed at a minimum product loss. The continuous operation places highest technical demands on the product feeding and collection line with possibly leakage-free outlet.

The necessary vacuum in the vacuum chamber is produced by a vacuum pump. Due to the vacuum the product is sucked via the product feeding line and transported to the center of a rotating bowl. The product feeding quantity is adjustable by a valve in the feeding pipeline. The required product layer thickness on the rotating bowl can be changed by an easily adjustable inlet gap.

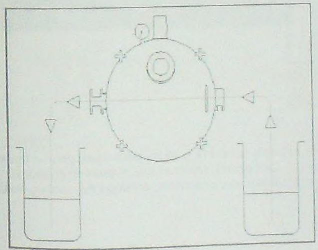
Due to the centrifugal forces the product is spread over the rotating bowl and hereby de-aerated. Because of the shell-like formation of the rotating plate the product is collected in the outer area and is discharged out of the machine via a product pick-up pipe. The product's residence time in the de-aerating chamber, which is extremely short, is controlled by non-return valves and valves. A very thin product film with a large surface is formed. Thus it is guaranteed that the enclosed air or gas bubbles can leak completely.

Further advantages of the NETZSCH-De-Aerator include the easy operation, the uncomplicated and quick cleaning of the machine as well as the simple maintenance. Furthermore, a quick product change at a minimum product loss is possible. Depending on the product viscosity the compact machine requires no additional feed or transfer pump and can be arranged in series with a filling machine to accommodate shorter production times directly from a mixer into barrels.

Modes of operation

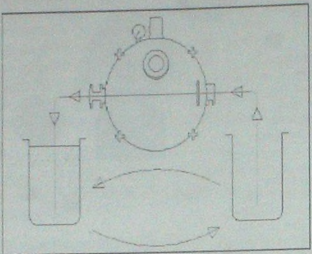
There are different modes of operation how the De-Aerator can be operated.

In the single pass mode (picture 5) the product is fed to the machine via the graduated inlet valve of the machine. The product is then de-aerated and evacuated into the process vessel.



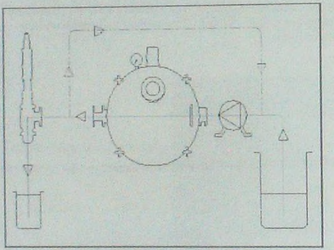
Pict. 5: Single Pass Mode

If one pass is not enough you have to use the multi pass mode (picture 6). Like in the single pass mode, the product is fed to the machine via the graduated inlet valve and is then de-aerated and evacuated into process vessel. After completion of the pass the vessels are cycled in order that the product is passed through the De-Aerator once more.



Pict. 6: Multi Pass Mode

An automatic discharge (picture 7) of the NETZSCH-De-Aerator is also possible. In this operation mode the discharging of de-aerated product takes place as described above. If the container is full or an increase of the pressure is being noted then the product is recirculated until a new container is put in position or the line pressure drops.

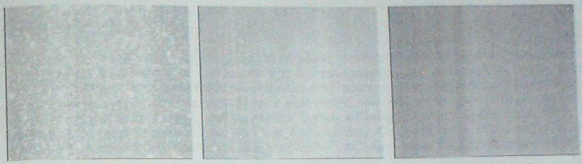


Pict. 7: Automatic Discharge

Applications

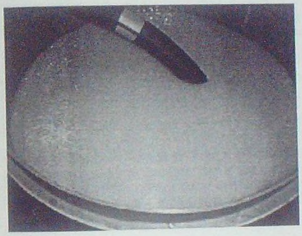
The NETZSCH-Vacuum-De-Aerator can be used for example in food (e.g. sirup, beverages, peanut butter), cosmetics (e.g. soaps, hand washing paste, shower gel, toothpaste), pharmaceutical, paint or chemical industry. The machine is being used to de-aerate products like inks and paints, printing inks, sealing masses, adhesives, plastic, lubricants, and latex-compounds.

In watery aging protection dispersions, the contained micronized air must be removed to guarantee a consistent viscosity of different batches. Here, the product may not be negatively influenced in the de-aeration process neither regarding its store stability nor its particle size distribution. Picture 8 shows microscope pictures of a dispersion sample before and after the De-Aerator. The use of the De-Aerator additionally provides time and space-saving as a direct filling of the dispersion into the corresponding sale barrels is possible.

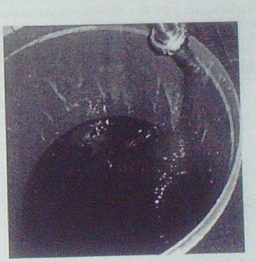


Pict. 8: Sample before de-aeration (left), middle and right: sample after de-aeration (3000 kg/h, 50 mbar abs., different adjustments)

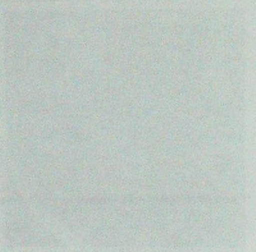
The following pictures show a further example: The de-aeration of a shower gel. While originally the de-aeration was achieved by leaving the product, the company's benefit from the use of the De-Aerator was saving time and space.



Pict. 9: shower gel before de-aeration



Pict. 10: shower gel after de-aeration



COMPOUNDING AND MANUFACTURE OF THIN-WALL LATEX PRODUCTS

Ray Russell-Fell
Retired Rubber Technologist

BIOGRAPHICAL NOTE

Ray's career in dipped rubber technology spans 50 years, of which 29 were in London International Group's R & D Division, developing latex compounds and process methods, until retirement as Senior Scientist in 1991. He has researched and published several articles on reduction in the allergenic potential of skin-contact rubber products, and on other aspects of latex technology.. He was a member of three relevant British Standard Committees for 38 years, and the Medical Society's Contact Dermatitis Group since 1978; also, by invitation, a co-opted member of an All-Party Parliamentary Group on Skin (1994-1996), a technical consultant to Thailand's Dept. of Medical Science (1993 – 1997), and to the US AID Program (1999 – 2003), advising on quality improvement of locally manufactured & imported NRL medical products.

From 1957 to 1963, he was Technical Manager of the Chichester Rubber Company, where specialised, high-value natural and synthetic dipped and press-moulded rubber products were manufactured for the Ministry of Defence and other critical applications..

ABSTRACT

Chemical aspects of raw latex concentrate Lots need equal consideration with mechanical stability, and a numerically-quantifiable method of chemical stability measurement is outlined. Choice and preparation of compounding ingredients, and heat versus room-temperature prevulcanisation of NRL compounds is discussed. Correction of some common dipped product production problems are also discussed, and the critical balance of temperature/time in heat vulcanisation in relation to dipped NRL products' potential shelf - life illustrated. Benefits of statistical process control are also discussed. Effects of different, final process methods on skin-contact products' Type I & Type IV allergenic potential are illustrated. Two little-known but useful aspects of physical test result interpretation are also illustrated.

INTRODUCTION

An attraction of NR latex technology is the challenge of its variable – often frustrating – behaviour, and that it can be used to make products with a range of specific physical properties to meet particular requirements. The variance of NRL concentrate with season, rainfall and delay between tapping and delivery to dipped product factories makes it difficult to set hard and fast formulations and processes, but it is possible to set guidelines that reduce manufacturing problems.

Synthetic rubber latices have more consistent properties but, many aspects of NRL technology similarly apply, particularly those which affect wet-gel strength. A fundamental rule in working with all rubber latices is, test and record every aspect that can practicably be tested – those test results will create a yardstick when production goes well, from which variation in subsequent NRL Lots or compounded latex can be identified as a possible cause when problems arise.

CHEMICAL PROPERTIES OF NRL CONCENTRATE

Apart from obvious interest in rubber content of an NRL concentrate Lot, many consider its mechanical stability time (MST) to be the most important factor. Chemical stability is usually relegated to the background, possibly because time-consuming test methods – such as zinc oxide thickening time – were previously the only practicable route to measure that. But, the relative chemical stability of latex concentrate can have profound effect on dipping characteristics of compounds made from it, and indirectly also influence product quality during heat vulcanisation, so measurement of it is highly advisable.

Technologists often find that NRL Lots of similar MST value behave very differently when put into dipped production, and few have not at some time had problems attributable to excessive or low chemical stability. To form NRL coatings or gels that dry into a uniform layer, it is necessary for the rubber particles to lose individual stability and form a continuous mass. If the surface of a thin, 'straight dipped' latex film dries out before rubber particles below it have completely agglomerated, trapped moisture will subsequently cause uneven gel shrinkage and surface cracking. Problems occur in coagulant-dipped products when that entrapped moisture turns to steam during vulcanisation, to form blisters; in rolled cuffs ('Beads') of medical gloves, blistered beads can initiate tearing during glove donning. Excessive chemical stability of the latex, rather than mechanical fault, is a common cause of that defect..

Published research by Blackley [1] into NRL particle stability and electrophoretic mobility modified by addition of various chemicals concluded that – providing an essential minimum is present – the particle's charge (its chemical stability) can remain unchanged despite electrolyte-induced decrease or stabiliser-induced increase in its mechanical stability. He hypothesised that mechanical destabilisation is due primarily to change in nature and extent of the particle's surface hydration. Blackley visualised latex particles as being protected against mechanical destabilisation by a tightly-bound layer of water molecules at the interface between particle surface and the aqueous phase, bound by hydrogen bonding of water to sites that confer negative charge to the particle. And, he interpreted the effect of added electrolytes as modifying the extent and 'tightness' of the particle's hydration, rather than modifying its charge. His conclusion was that magnitude of the charge carried by rubber particles is not the principle factor that determines its mechanical stability, as MSTs can be artificially changed without varying that charge.

Also, work by Calvert [2] showed that between one-quarter and one-half of the ammonium salts of non-volatile fatty acids in ammonia-preserved NRL concentrate are of a type that would be expected to be adsorbed at the rubber-aqueous interface to contribute to the particle's charge.

In basic terms, the rubber particle's charge reflects its chemical stability, whilst extent of its surface hydration determines mechanical stability. Fatty acid levels – including volatile fatty acids (VFA) – can give some indication of the chemical stability of NRL, but are seldom reflected in its MST, and VFA number at a Lot's initial certification will almost certainly change between then and its delivery. Mechanical stability times of NRL can be artificially increased or decreased without changing its chemical stability, but changing the latter wil alter its MST, by affecting the negative charge that maintains surface hydration of the particles. From viscosity increase observed in the zinc oxide thickening test, it is reasonable to conclude that release of zinc ions (Zn^{++}) in NR latex (i) reduces the particles' chemical stability, and (ii) the resulting particle agglomeratior increases its viscosity but also causes proportionate and measurable reduction of latex' mechanical stability.

Using that principle, I devised a rapid, numerically-quantifiable method to measure chemical stabilit differences in NRL. The method involves a small, measured addition of weak (0.025M) zinc acetate solutio to a latex sample prepared, proportional to its total solids content (Table 1), as for the same Lot's MST test. In the latex, the zinc acetate rapidly disassociates to form ammonium acetate and release of a finite quantity c free, divalent Zn^{++} ions. The Zn^{++} ions are rapidly adsorbed onto the rubber particles' surface, reducing th chemical stability by an amount that reflects the level of the particles' original charge (its chemical stability which can then be measured by running an "'MST" test on the treated sample. Time taken in that – which term Chemical Stability Time (CST) – can then be compared with the Lot's original MST, and expressed as percentage of the latter.

Examples at bottom of Table 1 show that an NRL Lot with an original VFA of 0.022 and 1030 seconds MS gave a CST of 560 seconds, expressed as 0.543 of the original MST. Another with VFA of 0.032 and 107 seconds MST had a CST of 686 seconds, expressed as 0.641 of MST. In dipped manufacture of NR medical gloves, latex Lots with "CST" values between 0.450 and 0.550 (identically compounde prevulcanised and used under the same conditions) produced significantly less product quality problems tha those with values significantly above 0.550.

I recommend manufacturers of "straight dipped" or coagulant-dipped, thin wall NR goods to try this test ar note the range of raw latex CST values most suited to their current formulation, rather than judging Lot quali by MST alone. And, if the only available latex yields a higher than desirable CST value, consider reductior a formulation's added chemical stabiliser or a marginal, circa 0.10 pph/DRC increase in its zinc oxide conter The test is equally applicable to Low- or High-ammonia NR latices

METHOD

For the Control, weigh 100 gms of NR latex concentrate and add to it the amount of pure water needed reduce its solids content to 55% (see Table 1, below). Take a further 100 gms sample from the same lat and add to it a combination of pure water and zinc acetate solution of 0.025 Molarity (M) to similarly reduce solids to 55% (see Table 1 below). Place each sample's container in a water bath of 60^0 Celcius temperatu and gently stir to bring the contents to 37^{0}C, and maintain Control and treated samples at 37^{0}C for 15 minut to allow equilibrium in the latter's Zn^{++} ions release. After 15 minutes, filter 80 gms of each sample through an inert, fine-mesh filter (such as Terylene voile) into separate Klaxon machine test pots, and conduct mechanical stability time tests on each, at the specified speed. Compare treated sample's result (CST) with that from the control (MST) and express the former as a percentage of the latter.

Total Solids Content (%)	100 gms MST Control (a) Water addition (mls)	100 gms CST sample (b)		
		Water add. Mls	+	0.025M Zinc Acetate, mls.
60. 0	9. 1	Nil		9.1
60. 5	10. 0	0. 8	+	9. 2
61. 0	10. 9	1. 6	+	9. 3
61.5	11. 8	2. 4	+	9. 4
62. 0	12. 7	3. 2	+	9. 5
62. 5	13. 6	4. 0	+	9. 6
63. 0	14. 5	4. 8	+	9. 7
63. 5	15. 4	5. 6	+	9. 8

Latex Lot.	Mechanical Stability Time (MST)	Chemical Stability Time (CST)	$\frac{CST}{MST}$
LOT 1 – 61.8 % t/s	1030 seconds	560 seconds	0. 543
LOT 2 - 62.5% t/s	1070 seconds	686 seconds	0. 641

Table 1. Volumes of (a) water for MST sample, and (b) water plus 0.025M zinc acetate solution for CST sample, for a range of total solids content NRL concentrate. Also, examples of MST and CST results from two NRL Lots, Lot 1 of 61. 8% & 0.022 VFA content, and Lot 2 of 62.5% total solids and 0.032 VFA..

COMPOUNDING

An important aspect of compounding natural and synthetic latices is to ensure that pH of all aqueous dispersions and solutions is – at point of compounding – at or slightly above that of the latex. Also, dispersions of insoluble solids – sulphur, zinc oxide, accelerator(s), pigments and antioxidants – should be diluted with ammoniated, de-ionised water, from Stockbin concentration to 10% by weight (or the lowest practicable level) before addition to the latex. This particularly applies to ZnO dispersions, because of its destabilising potential. Dispersions at higher concentration attract stabiliser from the rubber particles, – particularly if pH of the aqueous part is significantly below that of the latex – and cause loose but irreversible agglomeration around the relatively larger chemical particles.

That may not initially be noticeable, but can lower stability in a latex compound as its prevulcanisation increases, and form small rubber particle agglomerates in the dipping tanks. Aqueous solutions of significantly lower pH similarly destabilise NRL but stable, water-based oil or wax emulsions seldom a. problem, as those have reasonably high pH via an emulsifier, to which rubber particles are not attracted An effective concentration of ammoniated water is one gram of 0.880 ammonium hydroxide solution per five litres of deionised water. In choosing compounding ingredients for goods intended for skin contact, prime consideration should be to reduce potentially allergenic accelerator(s) to a minimum. The Medical Device Agency have recommended that butylated accelerators – such as zinc dibutyl dithiocarbamate (ZDBC) are preferable to ethylated types (such as ZDEC) and that the potentially mutagenic methylated (ZMDC) or more allergenic thiuram (TMTD) accelerators should be avoided wherever possible.

The quantity of accelerator used should be the minimum required, commensurate with the formulation and time available for its final vulcanisation, but some manufacturers attempt to shorten established production cycles by increasing compounds' accelerator content and vulcanisation temperature; this usually results in products with unacceptably higher accelerator residue and shorter shelf life **(See Figure 1, Vulcanisation Chapter)**. But, dithiocarbamate accelerators can in be boosted by synergistic action of a small (one-tenth of main accelerator content) amount of a mercaptobenzthiazole, such as Zn salt of 2-mercaptobenzthiazole, offering a route to reduce the main accelerator. Analysis of the residual accelerator content of skin contac products should regularly be made, and levels reduced wherever possible.

If optimum particle size (circa 3 to 6 micron) can be achieved, that may also assist reduction in the amount of accelerators used: at optimum size, these chemicals have maximum activity and less prone to loss through fall-out in latex compound Reserves or dipping tanks..

PREVULCANISATION

The basic methods of prevulcanisation are, (a) storing compounded latex for one or more days at room temperature, or (b) heating it as high as 70°C for hours rather than days, then rapidly cooling it when sufficient cross-linking has occurred. The Swelling Index (S.I.) test - measurement of the extent of swell of a thin, dried but unheated latex test piece placed in toluene – can rapidly but quantitatively assess extent of that cross-linkage. It may, however, be of interest that the S.I. test can be similarly used to assess the self-vulcanisation level of acrylonitrile-butadiene ('nitile') latex compounds, using 2-butanol instead of the toluene.

In room temperature prevulcanisation, NRL compounds can be prepared each day and used after 24 to 72-hours storage, dependent on formulation. If use is delayed through breakdown of a dipping line, causing its prevulcanisation level to go beyond optimum, it is usually possible to adjust its S.I. by blending into it some less prevulcanised compound, taken from a 'younger' batch intended for a subsequent days' production.

An alternative method involves use of large particle size sulphur and accelerator, in quantities adjusted to present an equivalent particle surface area to that of 'normal' (circa 3 – 6 micron) dispersions. The NRL compound is placed in a stirred, cylindrical vessel which has a conical base that contains a discharge valve, and is slowly heated to and maintained at 70°C until it reaches a desired level of prevulcanisation. Stirring and heating then ceases, allowing the latex to deposit most of its sulphur and accelerator residue into the vessel's conical section as it cools, subsequently removed by discharging to waste a few litres of chemically-rich latex via the valve in the cone's base. This type of low-sulphur, prevulcanised latex is sometimes further refined by centrifuge.

Antioxidant and other ingredients are then added, and the resulting compound has a very slow rate of further prevulcanisation. It is particularly suitable for processes that have small material throughput, and proprietary compounds of this type (and of various modulus) commercially available. Manufacture of dipped goods made from it is less critical than with conventional NRL compounds, and its optimum physical strength can be gained at relatively low vulcanisation temperature.

DIPPED PRODUCT MANUFACTURE

Again, latex technologists will be fully acquainted with the two basic methods – the 'batch' and the continuous line system. Each has advantage and disadvantage; the batch system allows variations in a cycle, but less consistent production, whilst the continuous process usually has higher output but its fixed parameters can rapidly result in large numbers of defective products if the coagulant or latex compound deteriorates or a mechanical malfunction occurs.

In manufacture of dipped, thin-wall NRL goods, it is important to maintain correct wall thickness and thickness distribution, for reasons of product quality and material cost. In Batch dipping, it is possible to vary not only coagulant strength and latex compound' viscosity but also the product moulds' rates of immersion, "dwell" time and withdrawal from the latex, to gain or reduce the products' wall thickness.

Moulds on the majority of continuous dipping production lines have fixed rates of immersion, dwell time and withdrawal from the latex but, for short-dwell dipped goods (e.g. medical gloves) it is possible to devise a screw-driven, movable mould withdrawal section that permits hour-to-hour manual variation in dwell time, if the line speed is not too fast. The movable section, when moved toward direction of the production cycle, effects increase in the moulds' latex immersion time and – conversely – a reduction by movement in opposite direction. However, at a line speed of 10 metres/minute and 12 seconds full immersion time of the moulds, a dipping tank would need to be seven metres in length to allow ± 3 seconds on that dwell time.

In manufacture of dipped NRL gloves, a common problem is formation of thin, fluid latex films between the moulds' fingers at point of withdrawal from the latex. This is termed "long webs" and – if webs do not break until the mould fingertips leave the latex – can cause entrapped bubbles in still-fluid latex within the moulds' finger-clefts. When the rubber gel is dried, the entrapped bubbles become either holes or, at the least, weak areas in the gloves. Some manufacturers use silicone defoaming agents to reduce incidence (or, at least, length) of webs but risk contamination of the moulds. There are, however, effective, vegetable-based proprietary defoamers, primarily developed for the British textile industry, which work equally well in latex dipping compounds and do not contaminate moulds. A well-known latex defoamer of this type is available from a company in Beverley, Yorkshire.

A factor with substantial influence on dipped product quality is the latex compound's prevulcansiation level: If too advanced, through unexpected production delay, it is advisable to modify that by blending in less-prevulcanised compound until samples indicates its Swelling Index as near to normal Without that, product shrinkage will be greater and – in production of thin medical gloves – mechanically rolled cuffs will tend to become uneven and develop a defect termed 'creased Beads'. If moulds carry a pattern, excess shrinkage whilst leaching in hot water, or during vulcanisation, can result in its 'double-image' on the finished products.

As previously mentioned, excessive chemical stability of latex compound can adversely affect product quality, by causing the surface of a thin latex coating to dry before its underlayer. Then, when areas of retained moisture eventually dry, uneven stresses are set up in the rubber gel, and the surface above those develops fissures which deepen during heat vulcanisation. In relatively thicker, coagulant-dipped products, the gel's syneresis normally prevents that but retained moisture may still cause blisters in gloves' rolled cuffs during vulcanisation. A 'first aid' measure is to slightly raise the dipping tank's zinc oxide content but, a a small reduction of a formulation's supplementary chemical stabiliser is better longer term action.

VULCANISATION

This critical stage of dipped product manufacture requires optimum balance of time and temperature. When established, any departure from that can adversely affect product quality, its performance in use and its potential shelf life. But, technologists are regularly under pressure to increase continuous cycle machine output by increasing the line speed, which shortens the vulcanisation period. In modern, relatively short, production cycles, that reduction cannot be adequately compensated by increase in vulcanisation temperatures, and is invariably detrimental to the finished products' properties.

Heat vulcanisation progressively increases the rubber's cross-linkage, to bring to optimum that which commenced in the compound's prevulcanisation. During heating, rubber's tensile strength increases toward a theoretical 'peak', and the optimum is to end the vulcanisation stage with its strength somewhere 10% to 15% before that peak. The rubber's strength will continue to slowly increase over following months, reaching that peak and then reducing down a very shallow 'slope' during storage. If, however, vulcanisation heat is excessive (or its period too long), its strength reaches and passes that peak, commencing the downward slope before end of the process. During subsequent natural or artificial ageing, excessively heated products' strength will decline more rapidly than those of optimum cure, and result in shorter shelf life.

Figure 1 (below) illustrates that a rubber product ("B") subjected to excess heat at vulcanisation may have an initial tensile strength (or test pieces' Break Strength) similar to one at optimum heat ("A"), but the strengths lay on opposite sides of the tensile 'peak'. When both samples are subsequently subjected to artificial (heat) ageing (168 hours at 70^{0}C) "A" loses less strength than "B" because it continues to rise toward and slightly over that peak, whilst "B" has passed it and already on the way down ! . An interesting further aspect is that initial elongations at break of products at optimum cure usually increase during ageing, whilst those of excessively vulcanised products show substantial loss. The illustrated results were obtained from different production Lots from a medical glove manufacturing company during 2003, using the specified 3mm-neck dumb-bell test pieces and test method (EN 455:2 - 2000 - Standard for Medical Gloves for Single Use)

<u>**Manufacturer "A"**</u>	<u>**Manufacturer "B"**</u>.
Uses heat gradient of 90^0 ->110^0 -> ->115^0 ->110^0 –> 90^0 C over ten minutes to vulcanise natural latex rubber Examination gloves.	Uses heat gradient of 90^0 –> 115^0 –> 120^0 – >115^0 –> 90^0C over 8..5 minutes to vulcanise identical NRL Examination glove s..
Achieves an initial tensile strength of **23.5 MPa** & **770%** Elongation at Break, 92% toward a theoretical Tensile Strength "peak" of 26 MPa.	Achieves a similar, circa **24 MPa** initial tensile strength & **780%** E.b.,, but at a point 8% beyond its **26 MPa** Tensile strength "peak" .
During 168 hrs heat 'ageing' at 70^0 C, the material's tensile strength rises, passes its peak & decreases to **22.5 MPa**, little changed from its Initial Strength. And, its Elongation at break <u>rises</u> to **840%**.	During identical heat ageingthe material strength of "B" falls to **18 MPa**, a substantially greater loss than with "A"; and its Elongation <u>falls</u> to **700%**.

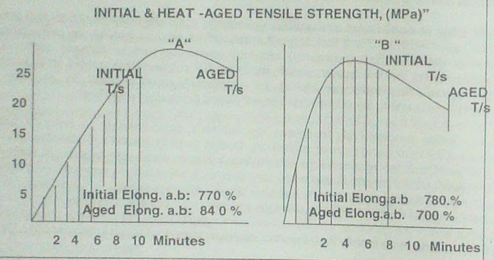

INITIAL & HEAT -AGED TENSILE STRENGTH, (MPa)"

Fig. 1 The graph "B" illustrates adverse effect of excess heat on the potential shelf-life of dipped NRL Examination gloves, where a combination of increased machine speed & vulcanisation temperature was used to increase output. This contrasts with "A", vulcanised at lower temperature for optimum period . .

GLOVE PROCESSING

Final processing determines important features of medical gloves. Not least is, how easy is it to put the gloves on but, of equal importance, is that the process should also reduce the allergenic potential of NRL (and synthetic rubber) gloves to a minimum.

There are two types of allergenic contact reaction to rubber gloves. The most publicised is Type I, contac urticaria (CU), often termed "immediate" because it usually occurs within minutes rather than hours of donnin gloves, and disappears almost as rapidly after taking the gloves off. This reaction is to allergenic fractions o natural protein in NRL and, whilst it usually causes only temporary discomfort, in fortunately rare cases it ca lead to life-threatening anaphylactic shock, similar to that experienced by people who have extreme sensitivi to peanuts. Fortunately, as in treatment for the 'peanut reaction', it can be rapidly remedied by administerin a suitable adrenaline compound,.

CU occurs in people who either develop or have inherent sensitivity to one or more of the NRL protein fractions; several people with that sensitivity also experience intolerance to some fruits (Kiwi fruit, Avocados etc.,) or to contact with animal fur, thought due to similar proteins present in those. Of note to the rubber industry is that inhalation of powder from medical gloves has been identified as a route of individual sensitisation, due to NRL proteins adsorbed onto glove starch particles that subsequently become airborne.

The other allergy associated with NRL and synthetic rubber gloves alike is termed a Type IV, delayed allergic contact (DAC) reaction to residual accelerator in the rubber. In essence, a medical worker may wear NRL or other rubber gloves for months or years without problem, until their skin's 'defence mechanism' no longer accepts contact with the potential allergen, triggering a biological sequence that – on subsequent contact – causes release of histamine from the skin's mast cells at point of contact with the rubber, and a consequent erythema. If daily contact with the allergenic product continues, painful skin eruption can develop and an affected person will eventually have to avoid further contact with it. It is said that, whilst DAC reaction to rubber never killed anyone, it has ended the professional careers of sensitised hospital Theatre staff whose work automatically requires them to wear rubber gloves. Those on Ward duties can, however, usually change to virtually non-allergenic vinyl gloves, whilst sensitised Surgeons are sometimes provided with (expensive) gloves made from a styrene copolymer that does not require chemical acceleration...

Fortunately, some process methods can significantly reduce both categories of allergen in NRL gloves Most effective is chlorination, in which freshly-made gloves are subjected to concentrations of chlorine gas in water; this not only modifies the rubber's surface and enables easier donning of gloves, but is also an effective extractant that can reduce residual NRL protein to below 50 micrograms per gram of rubber (50mcg/g). It can also reduce accelerator residues to below 0.15% w/w and, at that level, many sensitised people find the gloves do not provoke a skin reaction.

Synthetic coatings, such as polyurethane (PU), have been developed and applied to inner or both surfaces of medical gloves, as an alternative to assist glove donning. Measurement of coated gloves' residual protein (by the modified Lowry method) has shown levels apparently below fifty micrograms per gram of rubber (50 mcg/g) but – so far – it is not known if coatings consistently act as a barrier to allergens during glove use or, merely restrict protein extraction from the relatively unflexed gloves during that test.

Some manufacturers rely on extended, water leaching of NRL gloves to reduce residual protein, and levels as low as 70 mcg/g have been obtained. But, it is necessary to achieve well below 50 mcg/g before the gloves' allergenic potential is significantly reduced, and leaching in water does not reduce accelerator residues. Leaching gloves in ammoniated water has been tried but has disadvantage of reducing the antioxidant, shortening the gloves' potential shelf life.

Whatever process methods are used, reduction of allergen content is of major importance in products intended for skin contact. In recent years, successful Civil actions against hospitals (and other employers) were brought by staff who either experienced an anaphylactic contact reaction, or had to give up work due to allergic contact reaction to medical rubber gloves

STATISTICAL PROCESS CONTROL

The low price obtained for mass-produced dipped goods, such as NRL medical examination gloves, makes air-inflation testing each glove uneconomic. Instead, rapid visual inspection is usually made whilst manually packing the gloves. But, the gloves must meet EN 455 (Standard for Single-use Medical Gloves) which – amongst other aspects – specifies an Acceptable Quality Level (AQL) of 1.5 at G.I Sampling Level for freedom from holes. So, statistical control of all relevant factors needs to be applied throughout glove production, from compounding of latex through to final processing, if that quality level is to be achieved.

Statistical process control (SPC) commences by setting process parameters and optimum quality levels for every aspect of manufacture, with considerably 'tighter' in-house AQLs than those required by any product's external Standard. Where EN 455 specifies AQL 1.5 for freedom from holes, but gloves are not individually air-tested, a reasonable in-house quality target would be AQL 0.65 with an upper limit at AQL 1.0

SPC requires continuous product sampling and testing at every stage in manufacture, not only at end of a production line but from latex compounding onward. When product quality deviates to the extent that it approaches the AQL above it (not the final, outgoing AQL), SPC must be able to trigger a pre-agreed course of action and monitor its effect by enhanced product and process testing until quality returns to optimum.

Good glove manufacturing companies employ staff to continually sample and test gloves at point of removal from the ceramic moulds. The sampled gloves are rapidly dried (unless already dry) and visually inspected under air inflation, measured (and usually weighed), and relevant data and any defects recorded; this is normally followed by water-testing the sample, using the method specified in EN 455. At the same time, all relevant plant conditions (in-process material properties and temperatures) similarly recorded by those in charge of production lines. Each test must be devised to give rapid results, communicated with equal rapidity to those who can to use the information to correct a process or material deviation.

Analysis of test data and its comparison with outgoing quality assessments will, over a relatively short period, establish material and manufacturing conditions that produce gloves of optimum quality. From that, it is a relatively short step to implement a programme that automatically initiates corrective action directly test results shows a deviation near a pre-established quality limit..

In SPC, outgoing Lot inspection has to not only confirm gloves' compliance with the product Standard but also reconcile its results with defect levels found at earlier stages of inspection. If, when sampled at or prior to packing stage, a Lot's defects are found to not meet an agreed, tighter in-house AQL 1.0, the glove Lot ishould then be individually, 100% air-tested for holes and other defects prior to packing, and still subjected to a further, outgoing quality inspection. The constant objective should be to achieve product quality that meets 'tighter' AQLs ; if AQL 1.5 is the officially-specified. EN 455 standard for freedom from holes, the manufacturer's objective should be to (i) consistently achieve glove Lots of AQL 0.40, with (ii) an overall, monthly mean within AQL 0.65 and no Lots above AQL 1.0

The speed of modern production lines is such that, if defects are not detected and corrected in the shortest possible time, a large number of gloves will have to be scrapped or – worse – pass through the system and potentially result in serous complaints from hospitals or others that receive them. ! In these days of increasing litigation, product quality must be paramount.

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[1] "Mechanical stability of natural rubber latex", Blackley D.C., Loha S., & Twaits R. International Polymer Conference, London 1978

[2] "Plastics & Rubber : Materials and Applications" Calvert, K.O., 1977, 2: p.59

GRINDING IN AGITATOR BEAD MILLS – TECHNOLOGY AND APPLICATIONS

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BIOGRAPHICAL NOTE

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ABSTRACT

Unlike the chemical "bottom-up" process of the gas or liquid phase, wet fine grinding on agitator mills is a process from top to bottom. Starting from a size of some microns, suspended particles can be ground even to finenesses of 40 – 100 nm.

The main demands on a modern agitator bead mill for a grinding task – even down to the nanometer range – are the effective transfer of the kinetic energy to the grinding media in order to achieve the necessary stress intensity. A further requirement is the continuous separation of smallest grinding beads, that are kept inside the grinding chamber, from the product flow at the outlet of the mill.

In this article we introduce to you the working principle of agitator bead mills. The high-speed NETZSCH ZETA™ circulation mills are designed for the use of micro beads to achieve particle sizes in the range of 40 to 100 nm. Besides the machine, a variety of application examples will also be presented.

Process technology of agitator mills - General description

Agitator mills are composed of a vertical or horizontal (see figure 1) mostly cylindrical tank filled up to 70 – 90 % with grinding media. For the most part, grinding media is of steel, glass or wear-resistant ceramic materials. An agitator with suitable agitating elements, pegs, disks or a smooth body causes an intensive movement of the grinding media. The product suspension is continuously pumped through the grinding chamber, the suspended solid materials are crushed or dispersed between the grinding beads by shear and collision forces. At the outlet of the mill, the separation of grinding media and product to be ground is done via a separating gap, separating sieve or a centrifugal separation system.

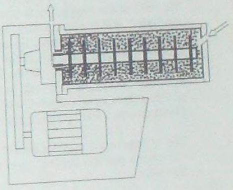

Figure 1: Principle of an agitator mill

The development of fine grinding

Since the introduction of the attrition mill in the fifties, wet grinding on agitator mills has been continuously developed (see figure 2). Two important targets were to leave the batch process, as practised on ball mills or on attrition mills, and to achieve a continuous flow through the systems.

This is synonymous with a reduction of grinding chamber volumes and an increase of volumetric energy inputs at the same time.

A further target was and still is to improve the finenesses achieved. At the beginning, finenesses of 20 µm were sufficient for paints and printing inks whereas these days finenesses below 1 µm are requested for high-quality products.

This progress is achieved by using smaller grinding media and by making the necessary modifications of the machine and its handling, activation and separation.

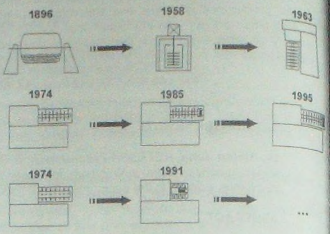

Figure 2: Development of NETZSCH Agitator Mills

Theoretical basis

The theoretical basis of grinding techniques on agitator mills were worked out at the University of Braunschweig[1]. It was found that the transferred grinding energy E_{SP} (Eq. 3), which is necessary for the grinding process, is proportional to two basic values namely the number of loads BZ (Eq. 2) and the load energy BI (Eq. 1).

$$\boxed{BI \propto BI_{MK} = d_{MK}^3 \cdot \rho_{MK} \cdot v_t^2 \left[-\right]} \qquad (1)$$

$$\boxed{BZ \propto BZ_r = n \cdot t \cdot \left(\frac{x}{d_{MK}}\right)^2 \left[-\right]} \qquad (2)$$

$$\boxed{E_{Sp} \propto BI \cdot BZ} \qquad (3)$$

The load number increases by a quadratic factor with the ratio of the initial particle size to the grinding media diameter. If the particle size X of the product to be ground decreases, it can be compensated by using smaller grinding media in order to get a load number which is high enough. At the same time, the load intensity decreases in a ratio to the bead mass if they collide against each other. Up to a limited degree, this effect can be balanced by higher load speeds.

The conclusion is that the limit of the finenesses which can be achieved is set by the necessary load energy - to cause particle breaks - and a high enough load number which mainly depends on the grinding media diameter.

Grinding media

Values gained from experience for the ratio between grinding media size and product particle size are between 10 and 10^4 for dispersions or disagglomerations and between 10^2 and 10^3 for the real comminution. These values show which finenesses are generally possible to achieve (see figure 3). For real comminution, average finenesses of approx. 100 nm are possible whereas 40 nm can be achieved when dispersing. The necessary grinding media size is Ø 0,1 – 0,5 mm.

It is important to see during grinding that the product to be ground is not contaminated. Therefore, suitable materials of low wear rates and whose abrasion will not influence the product quality required have to be used (see figure 4). Generally materials as sand, glass, ceramics, plastics or even steel are possible and available in all sizes required.

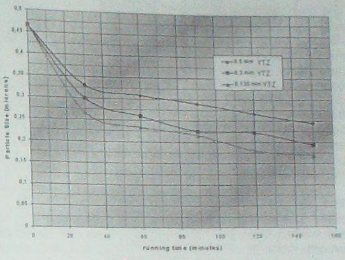

Figure 3: Fineness in dependence on the grinding media size and running time

Grinding Beads	Density [kg/dm³]	ϕ_{min} [mm]	Judgement regarding wear
Plastic	0,9 - 2,1	0,15	+
Quartz sand	2,65	0,1	o-
Ottawa sand	2,65	0,2	+o
Glass	2,5	0,1	o
Al_2O_3 (99,9%)	4,05	1,0	++
Al_2O_3 / ZrO_2	4,1	0,6	+
Zirconium silica	3,7 - 3,8	0,2	o
ZrO_2 / MgO - stabilised	5,5	0,4	-
ZrO_2 / CeO - stabilised	6,1 - 6,2	0,4	+
ZrO_2 / Y_2O_3 - stabilised	6,0	0,1	++
Steel Shot	7,0	0,1	o
Steel	7,75	1,0	o

Decrease of quality

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++ + o - --

Figure 4: Judgement of different grinding media types regarding

Modern agitator mills

The main demands on a modern agitator mill for grinding to the nano range are the effective transfer of the kinetic energy to the grinding media in order to achieve the necessary load intensity and the continuous separation of the smallest grinding beads from the product flow at the outlet of the mill. Peg agitators (see figure 5) with agitator pegs on the rotor or on the chamber are best suited for high power densities and viscosity-independent transfers of energy.

The capacity brought to the product is almost completely converted into heat and the product must be therefore cooled in order to keep the temperature limit set for the suspension. As for the grinding media, an optimal choice regarding the grinding chamber material must be made to avoid contamination of the product.

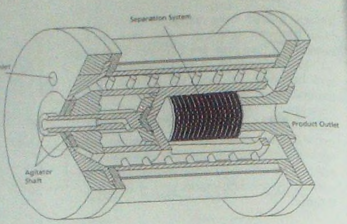

Figure 5: Circulation grinding system "ZETA™"

Most important for the continuous operation of an agitator mill is the trouble-free function of the separating system. Static separation systems as simple flat or inserted sieves cannot be used for small grinding media as they quickly "block". Annular gap separation must be excluded because of the necessary small gap widths.
For this reason, only centrifugal separating systems come into question where centrifugal forces counteract the flow forces of the product suspension.

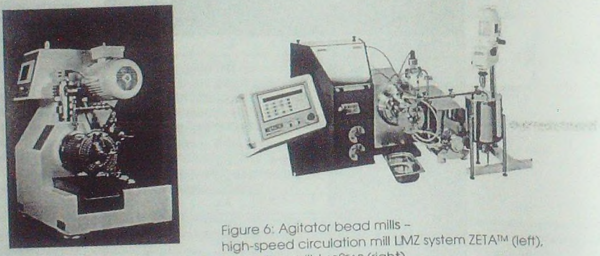

Figure 6: Agitator bead mills –
high-speed circulation mill LMZ system ZETA™ (left),
laboratory mill *LabStar* (right)

Process types

In general there are three process types for continuously working agitator mills. Simpler products are ground in one passage (see figure 7) if possible. However, when grinding in to the nano range, a very high specific energy input is expected for which one passage would not be sufficient. In this case multi-passage grinding in pendular (see figure 8) or circulation operation (see figure 9) will be applied.

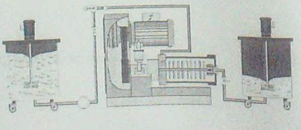

Figure 7: "Single-passage" operation

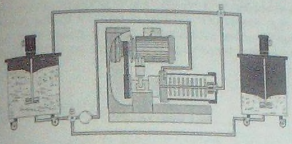

Figure 8: "Pendular" operation

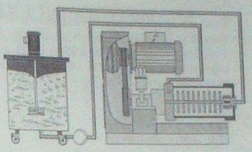

Figure 9: "Circular" operation

Applications

Continuously working agitator bead mills from laboratory to production size are used for a variety of applications, like for example for chemical products, inks and paints, pigments, inorganic materials/minerals, sealants and adhesives, ceramics as well as in life science for pharmaceutical, food or biotechnological applications.

Grinding in to the nano range on agitator mills was first employed in the paint and printing ink industry. One of the most difficult requests is to produce jet black automotive paints. The carbon black particle agglomerates are of primary particle sizes between 13 – 20 nm. They have to be dispersed and stabilized in a formulation to achieve the black depths requested.

For quite a long time it had been supposed that the so-called chips quality of packaging printing inks could not be reached by grinding techniques. Only grinding processes in to the nano range have replaced the original manufacturing techniques.

In the meantime, applications considerably exceed the original range and especially for life science the possibilities are diverse for nano-grinding.

The pharmaceutical industry has developed new insoluble active substances. To enable the body to absorb these active substances (see figure 10), they have to be ground considerably finer than they used to be. Optimal absorb rates are achieved if the crystals (see figure 11) are ground to a fineness below 400 nm.[2]

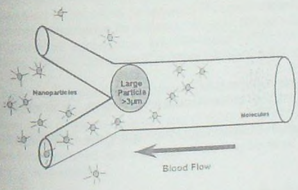

Figure 10: Depiction of absorbing active substances

Figure 11: REM-absorption of pharmaceutical crystals

Processing pigments often demands a very fine preparation. One example is phthalocyanine blue. Salt grinding, a frequently used process type, has a high energy demand and is harmful to the environment. Grinding on an agitator mill by using suitable surface-active substances makes it possible to bring raw pigments (see figure 12) environmentally friendly and at a low energy requirement up to the final quality requested (see figure 13).

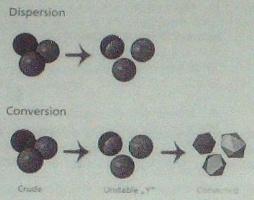

Figure 12: Depiction of dispersing and converting phthalocyanine blue

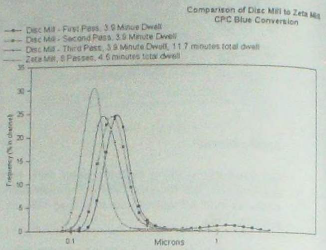

Figure 13: Grinding process of phthalocyanine blue

Summary

Suspensions of particle sizes below 100 nm can be prepared on modern agitator mills. However it has to be distinguished between real comminution of primary parts and the dispersion of agglomerates. An essential point when grinding nano products is stabilizing the particles of the suspension which has not been described in detail. There is an extensive range of applications for nano grindings in various areas and a further increase can be expected in the next few years.

Important developments can also be expected for the grinding technique both for the materials of mills and grinding media and for grinding and separating systems.

Literature

[1] Course and colloquium Grinding and Dispersing on Agitator Mills
Research and Development; 11 September 1999, Institute for Mechanical Engineering, TU Braunschweig

[2] NanoCrystal, Technology for Poorly Soluble Drugs, Publication, Elan Pharmace utical Technologies

MODERN SYNTHETIC LATEX PRODUCTION

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BIOGRAPHICAL NOTE

Dr. Volker Erb, Ph.D. studied Chemistry and Polymer Science at the University of Mainz, Germany and the University of Massachusetts, Amherst until 1993. He completed his masters' degree and his Ph.D. at the Max-Planck Institute for Polymer Research at Mainz in the field of surface and bulk phenomena of ultra thin films.

After his Ph.D. in 1997, he joined the 3M Laboratories (Europe), where he was responsible for solvent based and hotmelt adhesive developments in Europe. Since 2000 he works for PolymerLatex in Dormagen, Germany for the Paper and Specialty Business Unit.

ABSTRACT

The presentation will give you a insight view into a modern latex production site and an idea how polymer ad colloid chemistry is converted into industrial processes. General figures are presented and different techniques are discussed.

The art of latex production lies in allowing the latex particles to grow while preventing the protective shell on the expanding particle surface area from breaking down. At the same time, by the end of the process the correct number of particles per unit volume must have been produced in the correct size. The inside of the particle must also be adjusted to the intended application by appropriate means, without adversely affecting either of the two points mentioned above.

Mastering this delicate balance, choosing all the parameters in such a way that the latex possesses the best possible properties for a given application, and eliminating any influences that could harm the intended smooth particle growth process; this is the skills base of the experts at PolymerLatex. The variety of parameters that can be adjusted to obtain new and better products represents a fascinating challenge in this work.

INTRODUCTION

The interior of a latex particle consists of what is known as a polymer, i.e. a plastic, whose properties can nowadays be modified as required. This means that the interaction of the latex particles with different surfaces, and hence its adhesive strength, can be adjusted by means of the chemical and physical properties of the polymer. This interaction can be fine-tuned by increasing or reducing the level of cross-linking of the chain-shaped polymer molecule within a particle.

The softening point of the polymer, known as the glass transition temperature, determines the hardness and flexibility of the polymer as well as its ability to form a transparent, continuous film as the latex dries. The outer skin of the particle consists of substances that prevent the particles from moving too closely to one another and melting together (coagulating). These substances are molecules that have been absorbed or are firmly bonded to the particle. They may be either electro statically charged or long-chained, uncharged and water-soluble.

If the substances are charged, the surface of the particle carries an overall electrical charge. If two particles move too close together, they repel each other because of their like electrical charge, just like the positive poles of two magnets. On the surface of uncharged particles there are uncharged water-soluble molecular chains that prevent the particles from coagulating because they cannot move close enough to one another. For the same reason it is almost impossible for the particle to sink to the bottom and settle. If this protective shell breaks down, however, lumps tend to form even as the latex is being produced because the particles coagulate so if that happens, the product cannot be used.

The art of latex production therefore lies in allowing the particles to grow while preventing the protective shell on the expanding particle surface area from breaking down. At the same time, by the end of the process the correct number of particles per unit volume must have been produced in the correct size. The inside of the particle must also be adjusted to the intended application by appropriate means, without adversely affecting either of the two points mentioned above.

Latex

"Latex" comes from the Latin word for liquid or milk. In everyday life latex is understood as natural rubber latex, the dispersion of natural rubber in water, which comes from the milk of tropical trees.
Indeed this is only partly correct:

Latex contains caoutchouc, not rubber and it can also come from other plants. Not all milks from plants contain caoutchouc and latex is not only a natural product, but is also produced synthetically in a broad variety of different types. eg NBR,SBR.
Latex is a colloidal dispersion of polymer particles in water.

There are three principle ways to produce latex:

a) through plants (hevea brasiliensis),
b) through emulsion polymerization,
c) through conversion of dissolved polymers (secondary emulsions).

In the following sections I will describe the development from theory to bulk production of synthetic latex through emulsion polymerization.

Synthetic Latex

Basics of the Emulsion Polymerization

The emulsion polymerization is a heterogeneous reaction and in the beginning an aqueous and an oily phase exist side by side. During the reaction the liquid system transfers into a 2-phase system, one phase is the dispersed solid polymer phase and the other the continuos water phase.

First the oily phase is divided to many small droplets by intensive agitation and the size of the droplets can be influenced dramatically by the usage of an emulsifier.

Initiator radicals, usually of a hydrophilic type, typically are generated in the aqueous phase at a temperature between 10°C and 90°C.

At the end of the reaction the emulsified monomers are converted into a polymer dispersion, where solid polymer particles are dispersed in water.

The emulsion polymerization process has some significant advantages against conventional methods like solvent based polymerization and bulk polymerization:

- Primarily because of the large amount of water in the system, the removal of the excess heat of reaction is very easy

- Secondly the viscosity of latex is several magnitudes lower than polymer solutions with the same solid content, especially if the particles are not too small.

The kinetics and mechanism of the emulsion polymerization is described in details in textbooks[1]. The following section gives a general idea how the polymerization is divided into certain stages and describes the main processes which take place during the reaction.

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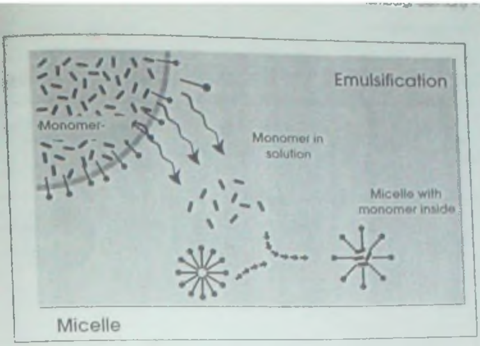
[1] P. J. Flory, *Principles of Polymer Chemistry* (London: Cornell University Press, 1971).
P.C. Hiemenz, "Polymer Chemistry, The Basic Concepts", Marcel Dekker, Inc., 1984
G. Odian, "Principles of Polymerization," third edition,
Wiley NY, 1991.



Emulsifier-Monomer equilibrium in aqueous phase

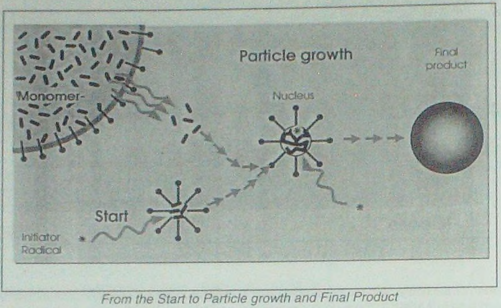
The agitation of a mixture of monomers, emulsifier and water forms an emulsion with monomer droplets which have a size of about 0, 5 µm up to several micrometers, besides them, so called micelles exist. They are formed by organized emulsifier molecules in the way that the hydrophilic part of the molecules reach into the water phase and the hydrophobic part is in contact with the oil phase, in which some of the monomers are dissolved.

In the water phase are the initiator molecules (like $S_2O_8^{2-}$ ions), some dissolved monomers (solubility of styrene in water is about 0.04%) and emulsifier molecules. There is an equilibrium between the emulsifier molecules in the aqueous phase, in the micelles and at the monomer droplets.

Depending on the chosen temperature in the reactor, the initiator starts to decompose and radicals are then forming and the polymerization starts.
In the beginning the reaction takes place in the aqueous phase, where the initiator radicals and the monomers form monomer radicals and oligomer radicals. These diffuse into the micelles which are swollen by the monomers and start the polymerization within the micelles.

As soon as the micelles contain polymerizing molecules they are transformed into latex particles.

The emulsion polymerization can be divided into three steps.



From the Start to Particle growth and Final Product

In step one as described above, the particles are forming and the phase is finished when no more micelles are available.

In step two the particles are growing and here the latex particles are gaining volume and surface area. During the growth monomer molecules are diffusing from the monomer droplets through the aqueous phase into the latex particles, in that way a constant concentration of monomers build up in the particles. This concentration is dependent from the chemistry of the monomers and the polymer and because the concentration of the monomers is constant in this step the speed of reaction is also constant.

In step three the reservoir of the monomers in the droplets are used up and all the droplets are emptied, also the speed of reaction reduces because of the reduction of the monomer concentration in the latex particles.

Emulsion Polymerization Technology

Introduction

The production of synthetic latex through emulsion polymerization is done technically by three different methods:

- Batch Process
- Feeding Process
- Continuous Process

The choice for the right process is done by leverage of the following aspects:

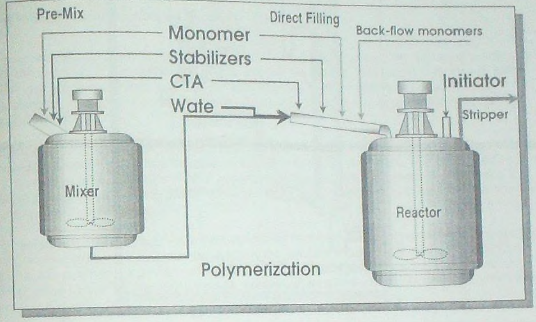
- Heat transfer
- Flexibility
- Volume-Time-Yield
- Profitability
- Safety

Batch-Process

In a batch process all the ingredients are brought into the reactor one afteranother at the beginning of the batch. The temperature is regulated through the vessel jacket and the reaction runs until the all monomers are used up.

At the beginning of the polymerization the conversion increases constantly as well as the polymerization speed. In this first phase the latex particles are formed and with the growing number of reactive sites (particles) the speed of reaction increases. As soon as the particle formation is finished the conversion is proportional with time and the speed stays constant. This is the second phase of the emulsion polymerization and in the third phase the speed decreases because of the disappearing monomer droplets. The latex particles are no longer swollen by unreacted monomers and the conversion is usually between 60 and 98%.

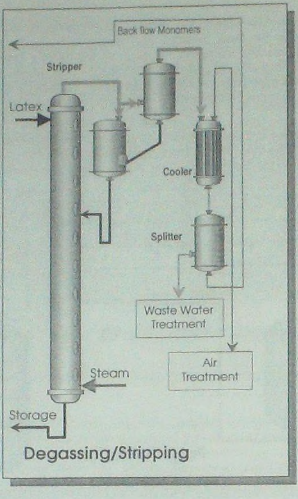
The only way the reaction can be influenced once it is started is by changing the temperature of the vessel jacket. The properties of the latex are tuned by the selection of the monomer composition, the activator concentration and through the type and quantity of emulsifier which is used.



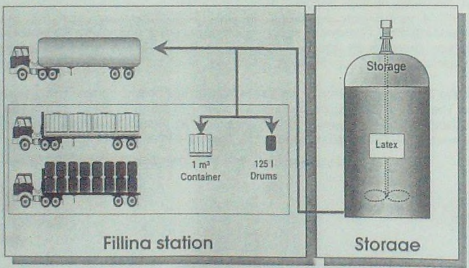
After the polymerization the monomers which have not reacted and other volatile organic compounds (VOC's) have to be removed from the latex and this is done because of environmental and safety aspects of modern industrial production practice. This process is done in a separate vessel which has a steam inlet and the residual monomers removal is usually done in two steps:

1. **Degassing Step**. Removal of highly volatile gases (lower boiling), eg like butadiene under a vacuum. Therefore the latex is pumped into an evacuated large vessel where the gases are completely removed from the latex. Monomers, which can be removed in this way, are recycled.

2. **Steam Stripping.** Removal of the less volatile (higher boiling) components, like styrene, acrylonitrile etc. The latex in the evacuated vessel is treated with steam so the whole procedure is a large steam distillation where the steam is condensed after it has passed through the latex. After condensing the vapour the resultant distillate needs to be separated from the water phase before recycling.



After the steam stripping process, the latex is cooled down and the solid content and pH are brought into the specific range. Afterwards the latex is filtered and the other properties of the product are measured. If the latex is within all specification limits, it is pumped into the storage facilities for sale.



The batch process requires technically seen a simple equipment and results in a simple procedure.
If more than one monomer is used, the polymer resulting from the batch process is mainly a mixture of several co-polymers. The reason for that is a drift in the composition as a function from the conversion due to the different co-polymerization parameters. The degree of internal cross linking is relatively low because of the high supply of monomers most of the time during the reaction. Therefore these polymers are needed wherever the application demands a low degree of internal cross linking like foam and dipping applications.

One disadvantage to the other methods is the lower densities of the monomers in regard to the polymers so that means that the reactor is never as full in the end as it was at the beginning.

The profitability of the batch dispersions is a direct function of the volume of one batch and the batch size is limited by the heat transfer from the reactor once the reaction has started. The reaction speed has also an influence on the evolved heat per time. If the heat cannot be removed, the increasing temperature accelerates the activation and the speed of polymerization increases, too. This results in an exponential increasing heat development which can cause a major incidence. Therefore the batch process is always problematic because in the beginning a big volume of highly reactive substances are present. This requires a safety system which has a very efficient radical killer/short stopper or a large blow down system. This is a larger empty vessel in which an uncontrollable/runaway batch is transferred to expand and cool down it may also contain some short stopper.

Feeding Process (Semi-continuous Process)

In this polymerization process the particle formation step and the particle growth step is separated into two parts. In the first step, the so called seed phase, a part of the water is filled into the reactor with some emulsifier and some monomers (5-20% of the total volume). Then the initiator is added and the polymerization is started with increasing the temperature so particles are formed which have typical diameters from 20-100 nm.

After this particle formation step the other monomers and the rest of the aqueous solution from emulsifier and initiator are feed in with a time program in dependent upon the conversion. The main objective is that there is no new particle generation. With a constant number of particles the particles are growing to a calculated size and due to the constantly growing surface area, emulsifier has to be added continuously to ensure the stability of the dispersion.

During the feeding step the structure of the latex can be modified by changing monomer ratios or special polymerization conditions at a certain stage, that is the clear advantage of this method. As with the batch procedure, the polymer composition can be customized at any point of the feeding step and specific monomer ratios can be built into the polymers. So one can actively work against ratio drifts which are always present in the standard batch process, by using so called 'starving conditions'.

The degassing and finishing is done in the same way as the batch process.

The equipment used with the feeding process is more technically advanced than for the batch process in addition the procedure needs more attention and knowledge.

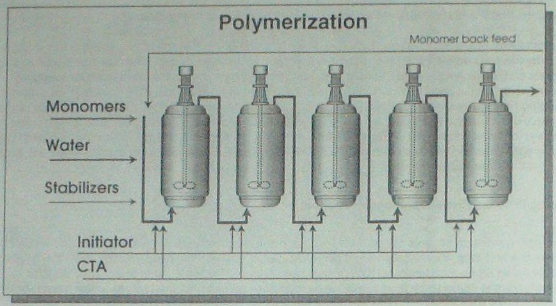
The flexibility of that method is tremendous. With one specific overall monomer ratio a large variety of particle structures can be achieved, depending on the final demanded properties of the latex in its application.

Due to a lower monomer concentration, which results in a lower reaction speed leads to a lower profitability as with the batch process. This can be compensated through a higher temperature.

Continuous Process

In contradiction to the former processes with the continuous process all the ingredients, like monomers, emulsifier and initiators are fed in continuously and the latex is removed continuously at the end.

This leads to some characteristic differences between the continuous process and the batch and feeding process.



In batch and feeding process's the particle generation is finished after a relatively short time while with the continuous process particles are generated during the whole time. In the batch and feeding process the dwell time of all particles is about the same, but the particles in the continuous process have a very broad dwell time distribution. This is due to the different time scales certain volume segments stay in the different reactors. The distribution becomes narrower when more reactors are included in the cascade. With an infinite number of reactors the theoretical dwell time distribution of the cascade is about the same as the one of a batch reactor again. In practice with 6-10 reactors in series the difference to a batch reactor is no more detectable.

The same effect can be observed with the particle size distribution. The more heterogeneous the dwell time of the particles is in the reactors the more heterogeneous is the particle size distribution. This can be reduced by a larger cascade of reactors if a new particle generation, due to too much emulsifier, is to be avoided.

Similar to the feeding process the polymer composition and other polymer parameters can be adjusted by the dosage of monomers and initiators as well as by tuning the reaction parameters. Theoretically the conditions are comparable to the conditions of the feeding process if the cascade has 6-10 reactors.
In principle in every reactor a batch process is running. Because the volume is transferred continuously from one reactor to the next, through addition of the contents in each reactor of the cascade the properties of the latex can be adjusted stepwise.

The advantages of the continuous process are

- Highly consistent quality
- Highest profitability (no filling and emptying time of the reactors)
- High flexibility concerning product properties
- Efficient heat transfer (can also be used for polymerizations with high reaction heat and speed)

These advantages are paid with low flexibility in regards to switch from one product to the other. It takes about 5 times the average dwell time to switch over.

Also the costs and complexity of the equipment is much higher as the equipments used with the batch and feeding process. The procedure and control of the process is also very complex.

Summary

There are a number of polymerization parameters which are influencing the emulsion polymerization. About twenty of them can be adjusted by the different types of industrial production processes presented in this paper. All three processes have their specific advantages and disadvantages, so that all of them have their application fields and are used widely in the chemical industry.

In this short report only general sketches could be given. All plant managers handling these processes can add many more details to every step and aspect.

The following table summarizes the main differences of the three processes in regards of latex structure and process properties.

	Process			
	Batch	**Feeding**	**1 Reactor Continuous**	**Multiple Reactor Continuous**
Particle size distribution	narrow	narrow	broad	narrow
Chemical Structure	irregular	adjustable	irregular	adjustable
Morphology	less controllable	controllable	less controllable	controllable
Heat Transfer	problematic	easy	easy	
Volume-Time Yield	medium	acceptable	high	
Safety	demanding	high	medium	
Flexibility	medium	high	low	
Investment Costs	low	medium	high	

Acknowledgements

The author would like to thank Sören Butz, Gunther Müller, Dieter Rahlwes, Graham Reed, Hubert Scheuermann, Hans Vogt and Jens Wieboldt for their contribution to this presentation.

QUALITY ASPECTS OF CONDOM MANUFACTURING IN THE 21ST CENTURY

David Hill,
SSL International, UK

BIOGRAPHICAL NOTE

A polymer chemist by training, David Hill joined the Research and Development department of LRC Products (as SSL International was then known) in 1981, and worked with both natural and synthetic latices on a wide range of glove and condom projects. As well as laboratory based R&D, he worked on the installation and commissioning of glove and condom manufacturing plants in the USA, Malaysia, Spain, Thailand and Italy. In his current position as Group Process Development Manager, based at SSL's Cambridge R&D facility he works closely with the manufacturing sites as well as on more fundamental research projects.

ABSTRACT

This paper will review the requirements for the successful manufacturing of natural rubber condoms to meet current regulatory needs and customer expectations against a background of growth in sexually transmitted infections. The importance of correct raw material selection, formulation and compounding are discussed and typical manufacturing processes described. Some problems which can impact on quality are reviewed, together with their causes. The importance of selecting and running the correct quality systems at the different stages of the production will be emphasized, together with the way in which experience in manufacturing can be coupled with feedback from the consumer to identify programmes for continuous improvement.

INTRODUCTION

The subject of this paper is condom manufacture (fig. 1) – specifically natural rubber condoms – with an emphasis on what is required to make high quality condoms which comply with regulatory requirements and meet customer needs in today's world. It will describe briefly the manufacturing of condoms, the problems which are met and how to deal with them, and speculate on what the future holds.

Not very many years ago the subject of condoms would not have been deemed suitable for a scientific conference other than a small medical gathering, and yet now the condom is an acceptable topic for discussion in society at large. Why? Partly because of the more open nature of today's society, but also because of a general awareness in the growth in various types of sexually transmitted infections. Over the last decade or so, the growth of sexually transmitted infections (STIs) and HIV/AIDS has been explosive (fig. 2). In the UK, chlamydia and gonorrhoea have doubled in the last five years, and syphilis, although the numbers are small compared to gonorrhoea and chlamydia, has increased by almost 150%. (1)
It is no surprise therefore that the condom is classified as a medical device, that is to say, in the EU it is regulated by the Medical Device Directive (MDD, fig. 3). The MDD classifies medical devices from I to III based upon the potential risk to the user. A condom is classified as a Class IIb device.

The changing status of the condom over the years is reflected in the way the international standards have changed (figs 4, 5).

The first condom standard, in 1964 required an acceptable quality limit (AQL) of 1.33% for freedom from holes on a 1% sample size with a limited burst strength requirement of 3 litres of water (2 litres aged). The 1989 standard is much more rigorous, with a tighter requirement for freedom from holes of 0.4% AQL and an emphasis on the tensile properties of the condom film. The 1993 European standard is still stricter on holes, with the AQL moving from 0.4% to 0.25% and the introduction of burst volume and pressure requirements, whilst the current BS EN ISO 4074 has dropped tensile requirements for standard condoms and uses burst properties to demonstrate good film strength.

In principle, a condom is simple to make, just a shaped tube dipped into latex and dried. The requirement, however, in today's market of 8-10 billion (2) annually is to make not one, but millions, consistently, reliably and of a high standard. And this is where the challenge is. The technology appears to be simple but closer inspection reveals many knowledge gaps, especially in the area of sulphur prevulcanization and predicting the processability of latex compounds. An intact condom provides an excellent, flexible barrier, sometimes as thin as 50 µm., which nevertheless provides a strong and secure shield against sperm and infection, even to the organism causing HIV at some 0.1 µm in diameter. The barrier properties of condoms have been challenged in the past (3), but numerous studies (4 - 11), including clinical studies, have proved that good quality condoms are an effective barrier.

The only way to ensure that quality is maintained during mass production is to pay attention to the details and make full use of manufacturing history and experience.

The critical manufacturing steps in condom production are listed in fig 6, and shown as a flow diagram in fig. 7. The first critical parameter is the selection of raw materials.

RAW MATERIALS

The latex is probably the most important. It is to the credit of the latex suppliers that a natural material can be supplied to such a high standard of quality and reliability. A list of some of the latex properties which can be measured is given in fig. 8, but not one of them will predict how the latex will dip on plant. There have been many attempts over the years to find a test that predicts the performance of latex on the manufacturing plant, but still the only test is the empirical one – run it and see. So what can be done about this? The use of experience and a solid historical database will help, as will buying from a reliable material source. Of course, there is a price to pay for this. Latex is cheaper on the spot market, but to ensure the consistency and performance of this critical raw material it is better to remain with a reliable supplier. The cost of the latex in a finished condom is a very few percent, so paying a relatively high price for good and consistent material has little impact on the finished cost: buying cheap is taking a risk, and can have a disastrous impact on quality and reputation, especially in today's critical and regulated environment. By working with one or two reputable suppliers, who are aware of the relevant quality requirements and are familiar with the end use, one potential source of problem will be reduced, if not eliminated. A reputable latex supplier will use dedicated transport containers, not ones that have been used for other materials as well, which can contaminate the latex and give considerable manufacturing problems.

Turning to the other materials needed in a latex formulation, solid materials such as curatives and antioxidants can be bought-in ready milled as high quality dispersions, or can be made on-site using one or more of the several different milling or grinding machines on the market. Buying-in is the easiest way to obtain small particle size dispersions, but is generally more expensive, and some aspects of the formulation may not be disclosed. If you need to have control of the ingredients, make the dispersions in-house. It is generally recognized that the particle size of the dispersions must be small – the smaller the better, no greater than 5 µm. and preferably smaller. This small particle size is not needed to facilitate the chemical reactions - work has shown (12) that the rate of the vulcanization reaction is not greatly affected by particle size. It is not even necessary to add the ingredients into the mix – heating the latex in vessels coated with sulphur and accelerator will vulcanize the latex (13). What is important about particle size is the effect of residual particles as impurities in the film. A 70 µm. thick condom film, in the burst test, will be approximately 3 µm. thick at the 18 dm^3 specification limit. Any large rigid particles in the film will very soon act as defects to prompt breakage. Furthermore, large particles sediment much more quickly in the dispersion and latex. Fig. 9 shows a particle of approximately 40 µm. diameter. Such particles can readily be removed by filtration.

The selection of active materials will be influenced by safety as well as by effectiveness. For example, recent studies (14) have shown that, of the commonly encountered dithiocarbamates, using zinc dibutyl dithiocarbamate (ZDBC) would reduce or remove the health concerns arising from accelerator residues. These active ingredients also differ in the ease with which they can be prepared and milled. The difficulties in milling sulphur are well known to anyone who has tried it, and some of the antioxidants used in latex formulations can similarly pose problems in getting a small particle size dispersion within a reasonable timescale. Note however that zinc oxide generally comes with an adequately small particle size, and sulphur is available as a fine "colloidal" grade. However the science and technology of preparing small particle-size dispersions is a large and complex area, and well outside the scope of this paper. It is enough to recognize that dispersions of solid ingredients should have a small particle size to avoid creating potential weak points in the film and to help stay dispersed. A small particle size means a large surface area, and the surfactant system should be good enough to prevent re-aggregation. The pH of the dispersion should be similar to that of the latex, and similarly solutions and emulsions should be compatible ionically with the latex, as far a possible, to prevent ionic shock. It is common to prepare several of the ingredients, for example accelerator, antioxidant and activator, together in one dispersion. This will facilitate compounding and reduce the possibility of error, but it is necessary to recognize that the different materials will show different characteristics during milling. It is best to mill, at least to some extent, separately and combine at a later stage.

COMPOUNDING (fig. 10)

It is often said that quality is made in the compounding. It is possible to dip bad condoms from a good latex compound, but very much more difficult to dip good condoms from a bad compound. One of the key factors is to keep the formulation consistent; simple and not variable. The fewer changes the better. The basic rules of compounding are well known. The stabilizers – soaps, alkalis etc – should be added before the potentially destabilizing zinc salts. Water acts as a stabilizer, so add as much water as possible early in the sequence, saving only enough to rinse out any containers and make the final viscosity adjustments. It is best to filter all dispersions before adding – remember the importance of small particle size – and additions should be made slowly and steadily. The pH of the dispersions and solutions should be as close to the latex as possible, to avoid rapid changes of pH and electrolyte concentration which can result in latex instability and coagulum. Most latices used in the manufacture of condoms are prevulcanized to some extent, and the rate of heating and cooling must be appropriate – heating or cooling too quickly can cause stability problems. Latex can be prevulcanized at surprisingly high temperatures – 80° C is possible with care – but lower temperatures will give better control and properties. When filling the container with latex, and adding the other ingredients, try to avoid splashing. This not only loses volatile alkalis such as ammonia, but it also creates foam which will dry and leave solid particles in the latex. Stirring speeds should not be too vigorous, and agitation can often be enhanced by the use of baffles. After natural rubber latex has been prevulcanized, it is normal to allow several days for maturation. The reasons for this are complex, and not well understood, but the consistency of the latex and quality of the finished product are always improved.

DIPPING (fig. 11)

A flow diagram for a typical condom dipping plant is shown in fig. 12.

The first consideration in dipping is the former. The former is the template upon which the condom is made, and clean, undamaged formers are essential. The usual former material is glass, but any material with a suitably high energy surface in the required shape can be used. Any flaws on the formers will be replicated on the condom, so the formers must be well maintained and replaced if there is any damage. With a film that could be as thin as 0.050 mm, any damage on the former should be treated with suspicion. Examples of formers which have been damaged by mechanical contact with parts of the plant through misalignment are shown in figs. 13 and 14.

Many of the solutions encountered on a condom dipping plant are alkaline, and can etch soda glass and other alkali-sensitive materials. Fig. 15 shows a soda-glass former after some time on a dipping plant, and the boundary between the dipped part and the undipped part of the former is clearly seen. Although more expensive, borosilicate glass is much more resistant to alkalis, as well as being lighter. It also has a lower coefficient of thermal expansion, which can simplify mounting the formers onto the machine. Formers need to be able to be wet by the latex easily and rapidly. The speed of wetting of clean glass formers can be calculated, for example by work done on the coating of magnetic tape media (15). Using equations derived in this work the critical entry speed for air entrainment can be calculated. If the former enters the latex faster than this speed there will be air pulled into the latex. Note that if the formers are rotated on entry the speed of the former surface relative to the latex is increased.

Dipping of NR latex – especially straight dipping, as used for condoms – necessitates many compromises. The key to successful dipping is a carefully controlled balance of stability. Too stable a latex will give a poor pick-up and flow. Too unstable a latex will give coagulum. The use of a fugitive alkali, such as ammonia, to help stability will improve pick-up of the latex, with the viscosity of the film increasing rapidly on exit from the dipper as the ammonia flashes off. Excessive flow will give an uneven film, which will crack as the latex dries (fig. 16). The thinner part of the film will dry faster than the thicker; and as it dries it both shrinks and builds strength. As NR latex is film-forming, the strength is built faster than the stress caused by shrinkage, but if the drying film is next to a wetter, and weaker, area the drying film will pull away to leave a crack. Agitation in the dip tank is important, to prevent curatives and other components settling out, to prevent creaming and skinning and to ensure temperature equilibrium. However, agitation is most effective in a circular tank, and at it's most inefficient in a long thin tank: most latex dippers tend to be long and thin. Efficient agitation is also better if the material is not shear-sensitive. Compounded NR latex, adjusted to give the optimum balance of stability, is very shear-sensitive. The consequence is that efficient agitation in a latex dip tank is difficult. The formers passing through the latex make very effective paddles, and contribute greatly to the agitation, but in doing so create turbulence, which will affect the evenness of pick-up. Turbulence can be reduced, but not eliminated, by having a separate return channel for the latex., so the latex circulation does not take it back past the formers. Using a small dip tank, minimizing "dead space" and giving a rapid turnover of latex is good practice, but a small tank, with minimal clearance between the formers and the tank wall, gives increased turbulence, necessitating further compromises. The maximum entry speed is governed by the speed of wetting, but this is not usually a problem in practice. The exit speed, coupled with the latex viscosity, dictates latex pick-up and hence film thickness. A rapid exit promises to give a more even film (and a faster production rate), with less time for flow of latex down the condom, but less flow means a thicker condom, unless the viscosity or solids content of the latex is reduced. Lower solids means lower viscosity, hence more flow and more water to dry off in subsequent operations, which in turn places constraints on production rate and available drying capacity.

The shape of condom formers also leads to problems. All formers, whether plain- or teat-ended have curvature at the end of the former. As the former leaves the latex this curvature means that, although the linear withdrawal rate is the same, the effective withdrawal rate, that is the rate at which the former surface leaves the latex, increases (fig. 17). This results in a greater pick-up of latex, thickness variation, and an increased risk of cracking. The solution to this problem is not easy. Inversion and rotation of the former can help, as can focussing heat onto the teat to help set and dry the film, but even so, cracking on the teat of condoms, especially plain-end condoms can be a serious concern. In a broader sense, it pays to control the level and temperature of the dip tank closely, as latex viscosity, and hence flow, is temperature dependent. A clean and dust-free environment goes without saying, and enclosed dip tanks will help keep out flies as well as dust. The smell of ammonia, a component of rotting meat, will draw flies to a dipper like iron filings to a magnet. Automatic level controls to regulate the addition of latex are useful, although any turbulence caused by the formers going through the latex can make sensing the correct level difficult. It is better to keep the former loading full if possible, to ensure that the displacement of latex caused by the formers in the dip tanks remains constant. After the dip comes the drying, and circulation of hot air will give rapid and effective drying, but there is also a place for radiant heat, which can be directed onto thicker areas of the film to dry them more rapidly and help prevent cracking. Temperature monitoring by infra-red sensors, which measure the temperature of the film, rather than the surrounding air, is a valuable aid to help maintain consistency. Where there is another dip after a drying stage it is necessary to ensure that the former is not too hot when entering the latex. Too hot a former can cause rapid creaming and skinning, instability and, in extreme cases, bubbles; especially as the generally poor agitation means that the latex temperature control may not respond rapidly. The requirement to moderate the surface temperature of the former imposes constraints on the maximum oven temperature which can be applied, which in turn limits the latex pick up which can be achieved in the preceding dipper. The extent of drying is important if more than one dip is being applied. If the first dip is too dry, interlaminar adhesion will not be good, and the two films may delaminate. If the underlying film is too wet, cracking and wrinkling can occur. Drying is also important at beading, where the film is rolled down to form a ring at the open end of the condom. If the film is too dry it will not release from the glass properly, and the bead will tear. If the film is too wet the bead will not adhere properly, and can roll back leaving a damaged area adjacent to the bead, as can be seen in fig, 18. After drying and vulcanizing the condom, it will usually be leached. Leaching is carried out by soaking in hot water, possibly with some alkali and/or surfactant added. Its purpose is to remove water-soluble impurities and it can also be used to loosen the film from the glass to ease stripping. Leaching can also help to reduce extractable latex proteins.

FINISHING (fig. 19)

The fresh natural rubber surface is very tacky, and some anti-tack treatment is needed. This can be applied on- or off-line, but either way it is critical to subsequent operations, and can in itself be a major cause of quality problems. Powders are frequently used to remove tack, and many powders have been used for this purpose. Some of these are shown in fig. 20. No material can be used on a condom in amounts that are harmful, and many of these powders, such as talc and lycopodium, are now actively discouraged because of health-related concerns.

ELECTRONIC TESTING (fig. 21)

Virtually all condoms are electronically tested. In its simplest form, the condom is pulled over a metal mandrel and a voltage is applied. If a current passes through the condom, it is assumed that the condom is holed and it is rejected. If no current passes it is assumed that the condom is intact, and it is accepted. The electronic test (ET) is often regarded as a quality test – it is not. The selectivity of the test can be altered by changing the conditions – voltage, duration of test, size of mandrel etc. The ET is a production screen, to remove defective condoms and ensure that only product likely to meet the stringent release specifications progresses through. This is one of the areas where the anti-tack treatment is important, slippery enough to allow the condom to be pulled onto the mandrel without damage, yet not so slippery that it slides off too easily. In particular any damage after ET – your production screen - must be avoided. ET is one area where the quality of the condoms can be quantified – the number of "good" and "bad" condoms under the conditions of the ET is easily measured, but it is important to have more than this. The quality of condoms after the ET, when tested by one of the standard methods – a water test or the electrical test – can be compared with the results obtained for that lot of condoms after dipping. The ratio of these figures gives a very good measure of how the ET is performing. It is assumed that the level of holes after ET will be well within the standard limit of 0.25% AQL, but a well set up ET will screen out satisfactorily a incoming level of holes many times greater. On the other hand, the handling and manipulation of the condom which takes place during ET can damage the condoms, and so a low incoming level of holes can actually be increased at ET, and yet still meet the standard. A knowledge of ET performance is essential to optimizing quality in the factory.

FOILING (fig. 22)

Foiling – putting a rolled condom into the familiar foil pack – is another critical manufacturing operation. This, and subsequent operations are after the screen of ET, and any defects introduced here will not be automatically detected before release to the consumer. In addition, the value of the work content of the condom is high, and any scrap at this stage is expensive. For this reason, foiling must be carried out carefully and with attention to detail. It is another area where the tack/lubricity of the condom is important. Condoms which are too tacky do not slide easily through the machine and can get trapped in the sealing, whilst condoms which are too slippery can also fail to be correctly positioned in the foil.

TESTING

As can be seen by this brief review of the manufacturing process, there are several critical operations within the manufacturing process where the quality can be made or broken, and monitoring of the key parameters is central to obtaining good and consistent product, as well as building the quality history that allows deviations to be quickly identified and corrected. Only key parameters need to be monitored. Measuring everything that can be measured rapidly leads to data overload and the important messages will be diluted. The condom gains value through the manufacturing process, and any quality programme must identify problems early in the process to minimize loss and apply corrective action. This starts with compounding, where process and material history is important. With an established latex supply from an established supplier one possible problem is minimized. An established, and preferably simple formulation is also essential. There are advocates of a "flexible" formulation, which is varied according to certain criteria, whether it be summer or winter, or some parameter of the incoming latex, but this is not the way to achieve the quality today's market demands. A proven formulation, using materials from a proven supplier and compounded using a proven and well-controlled process is the best way of achieving a high and consistent level of quality. With this level of attention to detail, testing is carried out to confirm quality rather than to discover it. The testing therefore needs to be appropriate rather than extensive, and typical properties measured will be stability, state of cure, pH, viscosity and alkalinity. On the dipping plant again attention to detail and a proven process are key. Dipping plants are highly mechanical creatures, and are susceptible to mechanical problems. A well thought out preventative maintenance programme will help keep problems at bay, and a regular monitoring of plant conditions should be carried out to identify problems such as touching formers, dead heating elements, non-spinning formers, broken formers etc. A quality assessment, such as holes and visible defects, carried out as soon as possible after dipping, on a statistically significant sample, will confirm if the production is good. Furthermore, a detailed assessment of any defects can give information to feed back to the production. The cause of many defects can be identified by a careful examination of the defective condom, and this can help with rectification and identify problems before they become major. For example the production on one day can have as few holes as on the previous day, but if the cause of those holes has changed – for example today the defects are mainly bubbles, whereas yesterday the defects were a mixture of many different causes – then it is possible that the plant is giving early warning of problems in the making, and should not be ignored. It is better to use a statistically valid sampling plan, which has sufficient power to detect problems whilst minimizing work to make the best use of the available resources. Similarly a system that allows switching to a smaller sample size if the product is consistently good (and conversely increasing the sample size to maintain efficiency if there are problems) will give a better return for work investigated. Such sampling plans are readily available in the literature. Involving the plant operators in the quality by training them to carry out many of these tests will also pay dividends. As in so many other areas good communication is important, and these relevant quality results should be recorded and communicated, both to show the current situation and also to build historic data for the future.

CUSTOMER FEEDBACK

Another source of valuable data is feedback from customers. Properly treated, customer feedback can be a valuable part of a continuous improvement programme. These data can be evaluated and characterized; and when assessed in relation to the manufacturing process, customer feedback can highlight aspects of the product whose significance may have been underestimated. As has been stated earlier, an attitude to quality which embraces the whole of the manufacturing process, from selection of raw materials to feedback from the end user, is essential if product performance is to meet and surpass consumer expectations.

THE FUTURE (Fig. 23)

Predicting the future is difficult, but some things can be confidently anticipated: for example the regulatory environment in which we work will not get easier. The use of condoms as contraceptives has been under threat by other, mainly hormonal, methods for many years, but a good quality condom, properly used, is still the only form of prophylaxis against STIs. With the rapid growth of STIs and HIV/AIDS in many developing countries the need for condoms and good education in their use is likely to persist for many decades to come. At the present the vast majority of condoms are made from natural rubber, with a small minority made, for example, from polyurethane. When one looks at the requirements of the ideal condom material – tough, strong, able to form an intact barrier, highly elastic to ensure a good fit, safe on exposure to mucous membranes, cheap enough to be sold into the third world and yet able to be manufactured to the stringent quality controls mentioned in this review – there are currently few candidate materials which are likely to be successfully researched. There are now synthetic latices on the market which approach the physical strength of natural rubber latex, and are free from natural rubber latex proteins. The cost, however, is relatively high and condoms from such materials are not yet in commercial production. It appears that the outlook for natural rubber condoms is safe for the foreseeable future, but only if the manufacture of these products is technically competent and quality driven. Our users and our regulators are becoming more demanding and more aware. There is no room for complacency, only for a relentless attention to the details.

ACKNOWLEDGEMENTS.

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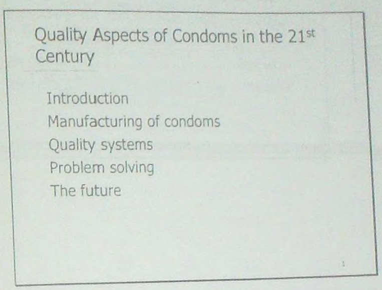
Figure 1

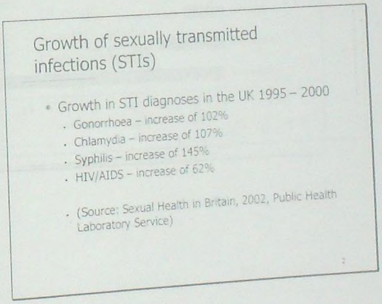


Quality Aspects of Condoms in the 21st Century

Introduction
Manufacturing of condoms
Quality systems
Problem solving
The future

1

Figure 2



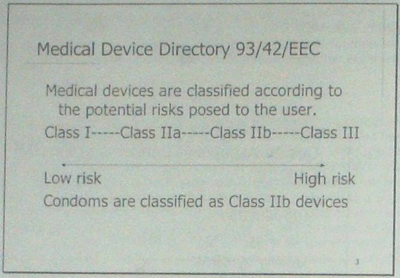
Growth of sexually transmitted infections (STIs)

- Growth in STI diagnoses in the UK 1995 – 2000
  - Gonorrhoea – increase of 102%
  - Chlamydia – increase of 107%
  - Syphilis – increase of 145%
  - HIV/AIDS – increase of 62%

  - (Source: Sexual Health in Britain, 2002, Public Health Laboratory Service)

2

Figure 3



Medical Device Directory 93/42/EEC

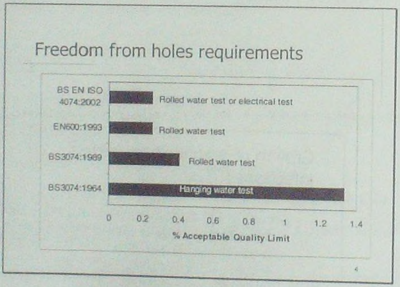
Medical devices are classified according to the potential risks posed to the user.

Class I-----Class IIa-----Class IIb-----Class III

Low risk ↔ High risk

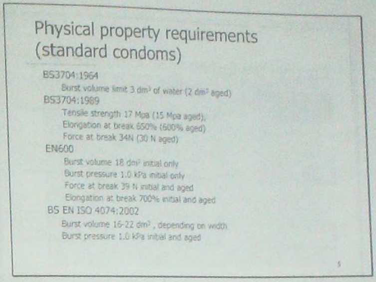
Condoms are classified as Class IIb devices

Figure 4



Freedom from holes requirements

Figure 5



Physical property requirements (standard condoms)

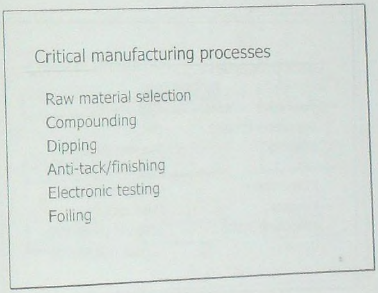
BS3704:1964
- Burst volume limit 3 dm^3 of water (2 dm^3 aged)

BS3704:1989
- Tensile strength 17 Mpa (15 Mpa aged),
- Elongation at break 650% (600% aged)
- Force at break 34N (30 N aged)

EN600
- Burst volume 18 dm^3 initial only
- Burst pressure 1.0 kPa initial only
- Force at break 39 N initial and aged
- Elongation at break 700% initial and aged

BS EN ISO 4074:2002
- Burst volume 16-22 dm^3 , depending on width
- Burst pressure 1.0 kPa initial and aged

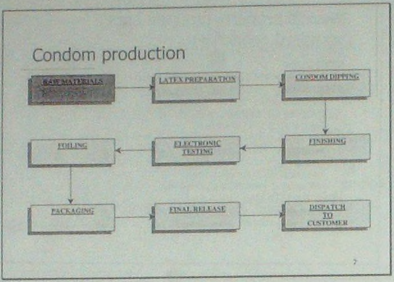
Figure 6



Critical manufacturing processes

- Raw material selection
- Compounding
- Dipping
- Anti-tack/finishing
- Electronic testing
- Foiling

Figure 7



Condom production

RAW MATERIALS

LATEX PREPARATION

CONDOM DIPPING

FINISHING

ELECTRONIC TESTING

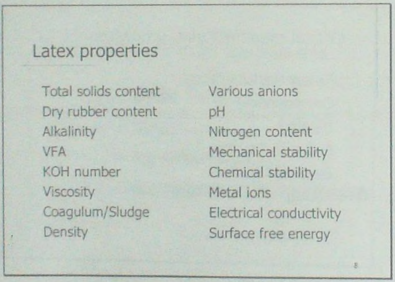
FOILING

PACKAGING

FINAL RELEASE

DISPATCH TO CUSTOMER

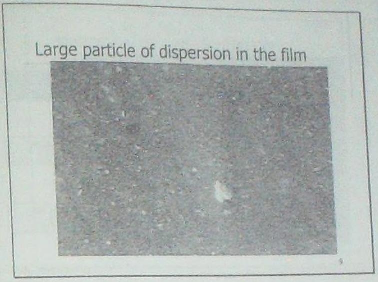
Figure 8



Latex properties

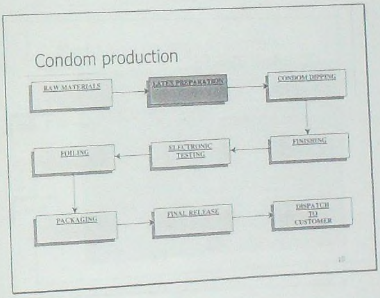
Total solids content	Various anions
Dry rubber content	pH
Alkalinity	Nitrogen content
VFA	Mechanical stability
KOH number	Chemical stability
Viscosity	Metal ions
Coagulum/Sludge	Electrical conductivity
Density	Surface free energy

Figure 9



Large particle of dispersion in the film

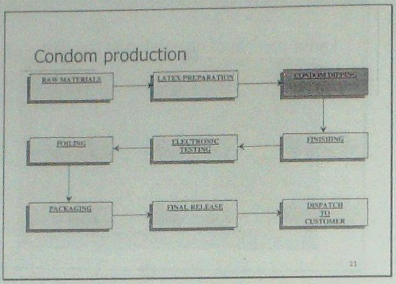
Figure 10



Condom production

RAW MATERIALS
LATEX PREPARATION
CONDOM DIPPING
FOILING
ELECTRONIC TESTING
FINISHING
PACKAGING
FINAL RELEASE
DISPATCH TO CUSTOMER

Figure 11



Condom production

RAW MATERIALS

LATEX PREPARATION

CONDOM DIPPING

FINISHING

ELECTRONIC TESTING

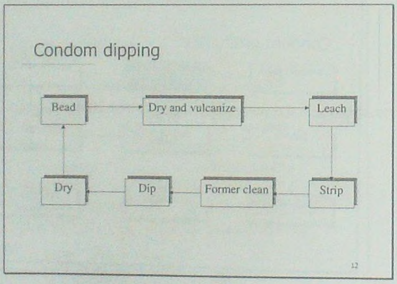
FOILING

PACKAGING

FINAL RELEASE

DISPATCH TO CUSTOMER

Figure 12



Condom dipping

Bead

Dry and vulcanize

Leach

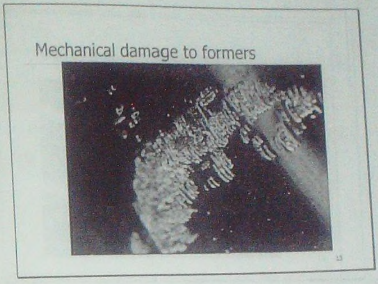
Strip

Former clean

Dip

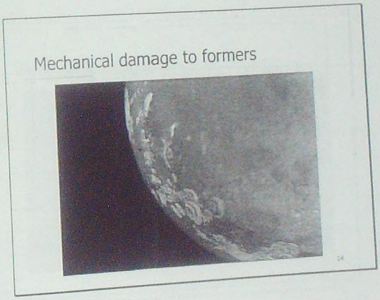
Dry

Figure 13



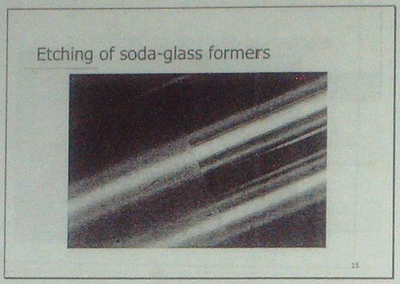
Mechanical damage to formers

Figure 14



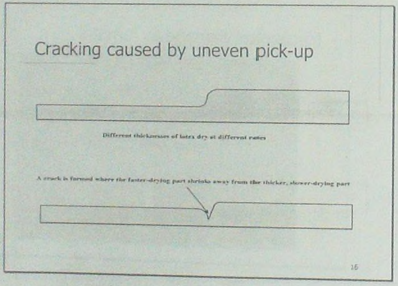
Mechanical damage to formers

Figure 15



Etching of soda-glass formers

Figure 16

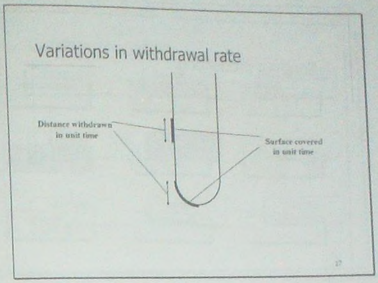


Cracking caused by uneven pick-up

Different thicknesses of latex dry at different rates

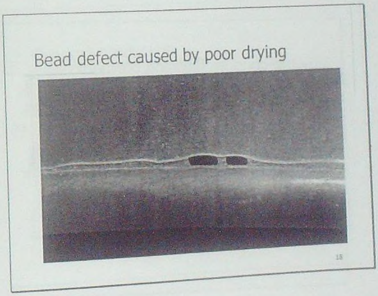
A crack is formed where the faster-drying part shrinks away from the thicker, slower-drying part

Figure 17



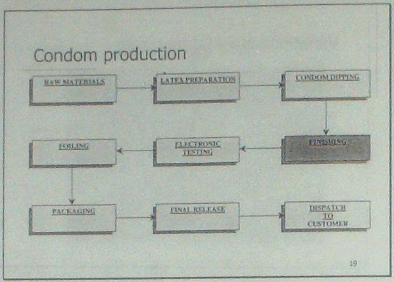
Variations in withdrawal rate

Figure 18



Bead defect caused by poor drying

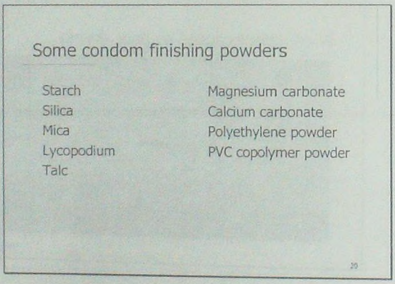
Figure 19



Condom production

RAW MATERIALS → LATEX PREPARATION → CONDOM DIPPING → FINISHING → ELECTRONIC TESTING → FOILING → PACKAGING → FINAL RELEASE → DISPATCH TO CUSTOMER

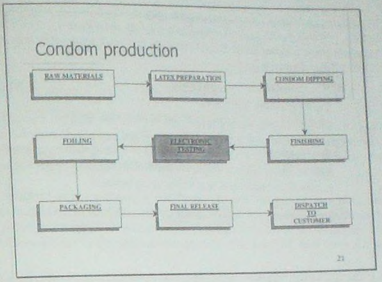
Figure 20



Some condom finishing powders

- Starch
- Silica
- Mica
- Lycopodium
- Talc
- Magnesium carbonate
- Calcium carbonate
- Polyethylene powder
- PVC copolymer powder

Figure 21



Condom production

RAW MATERIALS
LATEX PREPARATION
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FINAL RELEASE
DISPATCH TO CUSTOMER

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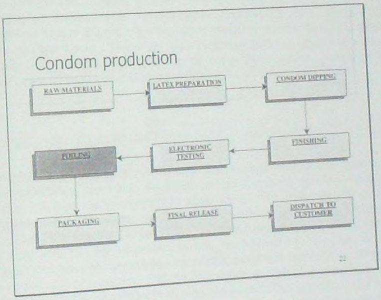
Figure 22



Condom production

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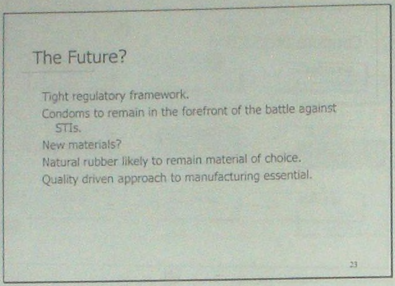
Figure 23



The Future?

Tight regulatory framework.

Condoms to remain in the forefront of the battle against STIs.

New materials?

Natural rubber likely to remain material of choice.

Quality driven approach to manufacturing essential.

RECENT TECHNICAL SURVEILLANCE ON EXTRACTABLE PROTEIN CONTENT OF LATEX CONDOMS

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BIOGRAPHICAL NOTE

Dr Ong Eng Long obtained his BSc (Hons) from the University of Malaya in 1969 and PhD in 1973 from the Queen Mary College, London. He joined the Rubber Research Institute of Malaysia in 1973, and retired as the Deputy Director General in charge of R & D in May 2001. He then joined the Malaysian Rubber Product Export Promotion Council as its Deputy CEO in June 2001.

Dr Ong's pioneered research is in the rheology and friction of raw natural rubber. His research activities later included latex protein sensitivity in latex dipped products. When the protein allergy issue threatens the survival of the latex glove industry, Dr Ong is involved in the promotion of the Standard Malaysian Glove scheme to instill confidence back to the users and to promote the positive attributes of Malaysian quality rubber gloves.

ABSTRACT

Consumers rely on condoms for protection from HIV (AIDS) and other sexually transmitted diseases (STDs), as well as for contraception. The natural rubber latex condoms have been shown to provide superior barrier protection against viral transmission. However, since the onset of latex protein sensitisation relating to the use of natural rubber latex products, especially gloves, the extractable protein content has become a very important parameter to users of latex products including condoms. A surveillance study of the extractable protein and antigen contents of condoms was therefore carried out using ASTM D 5712-99 and ASTM D 6499-00 respectively. The protein contents of latex condoms were found to be low with about 70% of samples tested having protein content below the detectable level of 23.5 µg/g. About 75% of the samples showed low antigen values below 5 µg/g. In this study there is also a good correlation between the extractable protein and antigen levels. The study also indicated that the use of low protein latex and/or improved processing technology had further reduced the extractable protein content of condoms. Latex condom is also environmental friendly and is biodegradable.

INTRODUCTION

The need for latex condoms is growing as HIV/AIDS and other sexually transmitted infections spread. It has been estimated (1) that worldwide, more than 40 million people are living with HIV or AIDS, almost half of whom are women and a full third are young people aged 15-24. The vast majority of HIV infections are sexual and they are preventable. Condoms can be effective both at preventing pregnancy and sexually transmitted infections. The FDA and the Center of the Disease Control (CDC) of US also recommend the latex condom as the most effective barrier protection and the hallmark form of protection recommended (2,3). Laboratory studies (4-6) have shown that the intact natural rubber latex film is effective as a barrier to spermatozoa which is of the size of 3 microns and the HIV which is about 0.1 micron in diameter and other infectious agents responsible for the transmission of sexually transmitted infections (STIs). These findings have prompted governments in many countries and voluntary agencies to distribute condoms in social marketing programmes to prevent the spread of AIDS. To ensure that the quality of condoms is reliable, condoms are manufactured and tested in accordance with established standards (7) for size, resistance to breakage, freedom from holes and packaging and labelling to assure high quality.

In spite of the importance of latex condoms in preventing the spread of HIV and AIDS, there are some quarters advocating that latex condoms should not be used because of the latex protein sensitization issue. To suggest banning the use of latex condom is really uncalled for. A document (8) from the World Health Organisation (WHO) states that latex allergies are very rare among the general population. While 1-2 billion condoms are used per year in the USA, the FDA only received 44 reports of allergic reactions associated with condom use between October 1988 and end of 1991. A toxicologist at the FDA also considered that the problem of latex allergy with condoms is "really minimal" compared to gloves as the protein content of condom is very low. The Centres for Disease Control, Atlanta, USA estimate that the population risk of an allergic reaction to latex is 0.08% and the nature of the reaction tends to be very mild. A study was also conducted in Germany (9) to assess the prevalence of sensitization to latex in a group of women with a high risk for atopy and to determine whether the use of condoms is a relevant risk factor. The conclusion from the study was that condoms are not a risk factor for sensitisation to latex. Prior use of condoms does not appear to be a specific risk factor for sensitization to latex in postpartum women at high risk for atopy.

There are two types of allergic responses related to latex allergy: the 'immediate-type' responses (Type I associated with the production of specific IgE antibodies, and 'delayed-type' hypersensitivity responses (Type IV) which are caused by certain types of chemicals used in compounding of rubber including both natural and synthetic rubber. Type IV allergy has a longer latency of about 12-36 hours and is not associated with 1gE antibodies.

The Type I allergenicity of gloves is usually assumed to relate to the total extractable protein. The older generation of latex gloves could have extractable protein level as high as 1000 µg/g of glove. However, with the awareness of the problems, glove manufacturers have improved their processing technology resulting in a reduction of protein level to as low as 50 µg/g of glove, even for powdered gloves.

Much of the protein measurements have been carried out with latex gloves rather than condoms. This paper attempts to survey the latex protein contents of condoms produced in Malaysia and to ascertain i improvement in processing technology causes a reduction in protein level. Two surveys were conducted, one in 2001 and the other in 2003. In both surveys, determinations of extractable protein contents and antigenic protein contents of condoms were carried out using the relevant ASTM standards.

MATERIALS AND METHODS

CONDOM SAMPLES

All the manufacturers of condoms in this country were approached to send in samples for testing. 10 condom manufacturers participated in the 2001 survey. 8 out of the 10 manufacturers also participated in the 2003 survey. The batches of condoms submitted for evaluation varied from one to six production lots. About 40 % of the manufacturers participated in the survey used HA latex as the starting material whereas the rest reported using Pre-Vul Latex. Almost all used nonoxynol-9 as the spermicide for their condoms.

TOTAL EXTRACTABLE PROTEIN DETERMINATIONS

The whole condom was cut open and extracted with 25 mM Phosphate Saline (5ml/g) at room temperature for 2 hours. The extractable protein (EP) content of the condom extract was determined following the protocol drafted in the ASTM D5712-99 (10). The process involved sample preparation, protein extraction from the test samples, precipitation of proteins in the extracts, solubilising the precipitated proteins in sodium hydroxide, complexing the proteins with copper reagent and measuring the absorbance of reduced Folin at 750 nm. The amount of the total EP was extrapolated from the standard curve.

ANTIGENIC PROTEIN DETERMINATION

The extraction of condom with 25 mM Phosphate Saline was carried out in the same manner. The antigenic protein content in the condom extract was then determined using the ASTM D6499-00 (11), which is a standard test method for the immunological measurement of antigenic protein in natural rubber and its products. The standard antigen and the primary antisera were the Industry Reference Materials obtained from Guthrie Research Institute, US. A recommended AP limit of 10 µg/dm^2 and a EP value of 200 µg/dm^2 have been introduced in the standard specification for rubber examination gloves (12). These two levels are also adopted in the present study.

RESULTS AND DISCUSSION

For the condom samples surveyed in 2001, the measured EP and AP values are given in Table 1. It was observed that the EP value ranged from very low value below the detection limit of 23.5 µg/g to moderate value of 223 µg/g. There is only one factory having EP value exceeding 200 µg/g. The corresponding range of AP level covers from 0.8 to 73.7 µg/g.

Table1: Extractable protein and antigenic protein contents of condoms (2001 Survey)

	Sample Reference/ Description	Extractable Protein (EP) Content µg/g	Antigenic Protein (AP) Content µg/g
A	Packed	40	0.8
B	Unpacked	35	4.0
C	Unpacked	44	4.4
D	Packed	46	0.9
E	Packed	78	39.4
F	Packed	56	11
	Unpacked	63	8
G	Packed	72	18
	Unpacked	88	25
H	Packed	<23.5* (15)	1
I	Packed	197	34
J	Packed	223	73.7

* The limit of detection of ASTM D5712-99 is 23.5 µg/g

Compared to the natural rubber latex glove manufacturing process, the condom has undergone a more extensive leaching treatment. The EP level for condoms is therefore generally expected to be lower than that for latex gloves. Although about 50% of the condom samples tested gave EP values below 50 µg/g an AP level below the recommended value of 10 µg/g, the other condom samples show surprising high EP an AP values. Technical consultancy team from the Rubber Research Institute of Malaysia was asked to visit the manufacturers to provide suggestions such as flow rate of leaching water, adjusting of line speed etc. in order to reduce the EP and AP level. The high values of EP and AP obtained form factories I and J could b due to interference of chemicals in the analysis. No attempts were made to do the interference correction.

In the survey carried out two years later in 2003, there is a vast improvement in the values of EP and AP values, being very much lower compared to the survey conducted in 2001 (Table 2). The EP ranged from 23.5 µg/g which is the detection limit to 174 with more than 75 % of the manufacturers having EP below 50 µg/g. (Table 3) Included in Table 2 are the data reported by S W Tan who carried out an evaluation of EP and AP values of commercial condoms in 2002 (13).

Table 4 shows the distribution in AP values for condoms. It is seen that in 2001, about 50% of the manufacturers produced condoms with AP below 5µg/g whereas in 2003, this has increased to 62.5% representing an improvement in the capability of manufacturers in producing condoms with lower AP value

COMPARISON BETWEEN EP AND AP VALUES

TABLE 2: EXTRACTABLE PROTEIN AND ANTIGENIC PROTEIN CONTENTS OF CONDOMS (2003 SURVEY

	Extractable Protein (EP) Content µg/g	Antigenic Protein (AP) Content µg/g
A1	<23.5	0.5
A2	<23.5	0.3
B1	<23.5	3.9
B2	<23.5	2.8
B3	<23.5	1.9
B4	<23.5	2.3
B5	<23.5	2.4
B6	<23.5	3.0
E1	<23.5	1.9
E2	26	4.6
F1	<23.5	2.8
F2	<23.5	3.9
F3	<23.5	4.2
G1	75	13.2
G2	50	7.9
H1	27	0.8
H2	<23.5	0.7
H3	<23.5	0.6
H4	<23.5	0.5
I1	174	29.2
I2	117	23.9
K1	44	13.9
K2	30	9.4

TABLE 3: DISTRIBUTION OF EP VALUES FOR CONDOMS

Year of survey	EP < 50 µg/g	50 to 100 µg/g	101 to 200 µg/g	> 200 µg/g
2001	50%	30%	10%	10%
2002 (13)	83%	17%	0%	0%
2003	75%	12.5%	12.5%	0%

TABLE 4: DISTRIBUTION OF AP VALUES FOR CONDOMS

Year of survey	AP < 2.5 µg/g	2.6 to 5µg/g	5.1 to 7.5 µg/g	7.6 to 10 µg/g	> 10 µg/g
2001	30%	20%	0%	10%	40%
2002 (13)	50%	17%	0%	0%	33%
2003	25%	37.5%	0%	0%	37.5%

Taking the full range of EP and AP values for condoms surveyed, it is seen that there is a good correlation between the two sets of values with $r^2 = 0.884$. This also means that if it is recommended that the AP level to be below 10 µg/g of condom, the corresponding value of EP cannot be 200 µg/g as suggested for examination gloves (12). For the recommended AP value set at 10 µg/g, the corresponding value of EP should be around 65 µg/g. For condoms having AP values 3 µg/g or below, the corresponding EP values obtained will be below the detectable limit of 23.5 µg/g. The results obtained from this study agree well with that reported for latex examination gloves. Hasma et al (14) had reported that for the AP value of 10 µg/dm^2 of latex examination gloves, the corresponding value of EP is 60 µg/dm^2 and for EP values exceeding 200 µg/dm^2 the corresponding AP values will exceed the recommended value of 10 µg/dm^2. Latex examination gloves having AP value of 3 µg/g correspond to a low allergen level (15).

LUBRICANTS

A comparison was made on the effect of lubricants on the EP and AP levels of condoms. Preliminary results showed that the lubricated condoms showed a lower values, by about 10%, compared with the control.

LOW PROTEIN LATEX

Previously, it has been shown that the total extractable protein values of latex products such as gloves can be reduced if low protein latex is used as the starting material (14, 16). Since 1996, Ansell France (Cergy-Pontoise, France) has marketed a deproteinised latex condom (Manix Crystal), which is prepared from low protein latex, in France and other European countries. It was reported that the total protein content of the conventional latex condom was 38 µg/g condom, whereas the total protein content and the latex antigen content of the Manix Crystal condom were below the level of detection. Manix Crystal condoms were purchased and the extractable protein and antigenic protein contents were measured and compared with those from condoms samples prepared from low protein latex from Malaysia. The results given in Table 5 show that generally using the low protein latex reduces the EP and AP content of latex condoms. However, these levels of EP and AP can also be achieved using the normal latex but with extensive leaching process (Table 2).

TABLE 5: EP AND AP CONTENTS OF CONDOM PRODUCED FROM LOW PROTEIN LATEX

	Sample Reference/ Description	Extractable Protein µg/g	Antigenic Protein (AP) µg/g
Normal condom	Normal latex	44	6.0
Commercial Deproteinised condom	Using low protein latex	24	2.1
Factory scale (13)	Using low protein latex	12	0.5

Ansell France also conducted studies (17) by providing Manix Crystal condoms to nineteen adults (14 women, including 13 healthcare professionals, and five men, including two healthcare workers) with documented latex allergy who were unable to use classic latex condoms because they had previously had one or more allergic reactions when using them. Each patient used 12 Manix Crystal condoms provided over a period of 6 weeks. At the end of the study, none of the 19 patients had an allergic reaction or any other adverse event on or after contact with these condoms. The studies demonstrated that even latex allergic patients can continue to use latex condoms without local and/or systemic symptoms or signs of an immediate hypersensitivity reaction provided the condoms have very low or undetectable level of extractable protein or antigenic protein levels.

monstratedthatevenlatex

POLYURETHANE CONDOMS

For persons with latex sensitivity, polyurethane condoms provide a good alternative. However, users of polyurethane condoms must be aware of the fact that polyurethane condoms are not as effective as latex in preventing pregnancy and also in preventing HIV/AIDS. A study (18) involving 900 healthy couples from 10 US cites, showed that the probability of pregnancy occurring in six months of typical use was 9.0 percent for polyurethane condoms and 5.4 percent for latex condoms. Polyurethane condoms were more likely to break (3.8 compared with 1.2 percent) or slip (4.9 compared with 2.0 percent) compared with latex condoms.

From an environmental viewpoint, natural rubber latex condoms are biodegradable (19) and they are environmental friendly, being produced from a renewable resource, the rubber tree. After 12 months of soil burial, the mass loss for NR condoms was about 58%, whereas over the same period, the PU condom was not readily biodegradable with 97% of initial weight remaining (19).

CONCLUSION

This paper reports the results of two surveys on the EP and AP contents of condoms manufactured in Malaysia. For the two surveys conducted in 2001 and 2003, it is seen that there is a reduction in the EP and AP contents of natural rubber condoms manufactured in Malaysia. The share of condoms belonging to the worst category having AP level exceeding 10 µg/g has decreased from 50% to 30%. About 75% of the samples showed low antigen values below 5 µg/g. More than 50% of the condoms produced in Malaysia have EP values below the limit of detection and AP values below 3 µg/g corresponding to low allergen level. The reduction of EP and AP contents stems from the government's effort in bringing the awareness to the manufacturers of the need to reduce the latex protein content in order to prevent sensitisation of users of condoms. The technological advancement also plays a significant role and in this area and the importance of R & D cannot be ignored.

The use of low protein latex can further reduce the extractable protein and antigenic protein content of condoms. Manufacturers are informed that technology is now available to produce condoms having EP level below the detectable limit and AP level below 3 µg/g and many of them have achieved this level of competency. Even latex sensitised people can use low protein latex condoms without adverse consequences. Some latex sensitive people may prefer to use polyurethane condoms. They must be aware of the fact that the performance of polyurethane condoms is not as efficient as that of natural rubber latex. The latex condom is also more environmental friendly.

It is also scientifically proven that the transmission of HIV during sexual intercourse can be prevented when latex condoms are used correctly and consistently. Concerns about latex allergies should not inhibit people from using latex condoms. It must be made clear that millions of people use latex condoms with no ill affect at all.

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NEW FUNDAMENTAL RESEARCH WITH NATURAL RUBBER LATEX

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BIOGRAPHICAL NOTE

Gunther Lottmann obtained his degree in chemistry from Universidad Del Valle in Guatemala and starts his work with Natural Rubber Technology Training in 1981 with plantation agencies and the RRIM. After 23 years in the industry he has carried out many jobs. He is currently Manager at Pica De Hule Natural. He has published and presented many works in central and south America, at the IRC in Kuala Lumpur in 1997, and in Hannover in 2000

ABSTRACT

Development work in Guatemala has been able to show that natural rubber latex concentrate with a new chemical, develops faster than the normally produced control.

This result is very interesting because it allows producers to prepare natural latex concentrate in a shorter time. MST can develop quickly with a smaller addition of ammonium laureate. This reduces the dependence on soap addition to develop stability, and thus may help consumers that might be vulnerable to webbing originated from the soap. Being that the chemical used is marketed as an antioxidant it is not surprising that compound films produced from the newly treated concentrate, show better aging resistance. We conclude that the new latex concentrate treatment shows clear antioxidant behaviour.

Allthough laboratory tests have been very successful continued research is recommended on the consumer side to show there is no interference with the traditional dipping or extruding technologies.

Our recent research is showing the influence of this product on single clonal latex. As expected some clones develop mst better than others. All clones tested react positively to the new treatment.

INTRODUCTION

Natural Rubber latex concentrate processing has had no significant changes in many years. Being a very complex system there has been little encouragement to change what is basically a very successful product. On one hand consumers do not welcome changes, because these may affect their already sensitive procedures. On the other hand, the producers correctly recognize that the main factor that determines the Natural Rubber latex concentrate properties is the clonal identity of the plantations. Clonal identity of the plantations comes from investment decisions made by planters that are more worried by production than the properties of the future production. So we end up with a system that is difficult to change.

Recent challenges to the industry have forced some changes. The search for latex with no nitrosamines to help meet very strict regulations has motivated us to develop a TMTD free latex concentrate. The protein allergy has also motivated a lot of experimental work.

This time we present the results from new research with the preparation of Natural Rubber latex concentrate. It is well known that after collection in the field, latex is rushed to a processing centre for centrifuging. In this phase the main concern is the protection of latex from the development of bacteria, and is almost universally achieved by preservation with ammonia and secondary preservatives.

After centrifuging, latex concentrate must spend some time in storage to develop and stabilize specification properties. During this time attention is paid mainly to the development of the MST, VFA and KOH values. Experience has shown that the stabilization of these values needs around two months time. As we have mentioned above the "natural" properties for one particular latex concentrate are heavily influenced by its clonal identity. Clones develop properties differently. So the producer ends up with a blend of clones he will try to regulate into an acceptable concentrate. Traditionally ammonium laureate (or sometimes other soaps) are added to develop a MST time that suits the needs of consumers. The amount of the soap addition is dependent on many factors, but basically the intention is to regulate the final MST. Unfortunately the addition of ammonium laureate in larger amounts conflicts with the interest of dipping technology consumers (mainly for thin articles), because excess ammonium laureate (or other soaps) may produce "webbing" or many other problems. This is a big disadvantage.

The treatment of our Natural Rubber latex concentrate described in this work has shown that the development of properties changes dramatically, reducing the need to use larger amounts of ammonium laureate.

EXPERIMENTAL

The latex concentrates we have used were all produced at the processing factory of Pica de Hule Natural in the southern plains of Guatemala. Latex for this experiment has come from the end of the rainy season, which is the time of maximum production. Having basically no rain during mornings, the best production season is while trees enjoy lots of water coming from almost daily rain.

The preservative chemicals used in this work were tetra methyl thiuram disulphide (TMTD) and zinc oxide (ZnO), both in form of aqueous dispersions, to obtain basic latex concentrates. Both chemicals were used in well known and popular concentrations.

Since the basic idea is to compare MST, all latex was treated with no addition of ammonium laureate.
Latex concentrate was treated with 0.4 phr Struktol LA352 leaving half of the same lot as control without.
Film results were obtained by independent laboratory testing and are not presented at this time.

RESULTS

The tables below show the results of research.

Latex properties development:

VFA:
TMTD / ZnO Latex developed VFA from original values of 0.01 to 0.02 in 60 days. This is normal for latex produced at this facility. We conclude the treatment has no effect on VFA of latex concentrate. VFA was tested 12 times during this period and no difference could be established.

KOH:
The development of KOH number is presented in Table 1. We see a faster development of the KOH number in the treated sample. This shows faster development of latex properties.

MST:
MST values of latex (treated and untreated) are shown in Table 2. MST development follows observation of KOH number. % change in the MST difference reduces slowly.

Table 1: KOH development in Natural Rubber latex concentrate

Time in days	Control	LA 352 (0.4 phr)	% change
7	0.37	0.37	0%
9	0.45	0.42	-7%
16	0.50	0.51	2%
23	0.50	0.51	2%
30	0.52	0.55	6%
37	0.52	0.58	12%
44	0.52	0.58	12%
55	0.52	0.58	12%

Table 2: MST development in Natural Rubber latex concentrate

Time in days	Control	LA 352 (0.4 phr)	% change
7	25	25	0%
9	50	100	100%
14	80	135	69%
17	100	155	55%
24	125	200	60%
28	150	220	47%
31	170	230	35%
35	170	240	41%
38	170	245	44%
42	180	250	39%
49	210	285	36%
55	250	330	32%

Behavior of latex after 3 months:

Ageing of latex treated and untreated for three months allows easy adjustment to MST value of 1000 sec by minimal addition of ammonium laureate.

SUMMARY

It has been demonstrated that Natural Rubber latex concentrate treated with 0.4 phr Struktol LA 352 develops and matures faster than the untreated control. This allows for stabilizing using les ammonium laureate. Consumers certainly welcome this development.

Consumers testing the latex were not able to note differences in normal dipping process. This is very reasonable because Struktol LA 352 is an antioxidant and thus part of their normal formulation. These results come from a laboratory test. We have agreed to make industrial tests as soon as possible. No problems are expected at this stage.

At this stage we are carrying out experiments to show the influence of the treatment on individual clone latex concentrate. All clones react positively. At this stage we find that some clones react better.

HSI:

HST development in lots of different climes,
(5-days & 3 days)

1) Structural LA 352 (Instrument)

② Koli development

③ [illegible] data development

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EXTRACTABLE PROTEIN LEVELS OF LATEX GLOVES DO NOT RELATE TO ALLERGEN LEVELS FOUND IN POWDER ON GLOVES

Dan Olson
Charter Pipeline, USA

BIOGRAPHICAL NOTE

Dan Olson - A latex manufacturing consultant with an educational background in nursing and medicine, located in Iron Mountain Mi, USA. Provides regulatory and technical services to companies involved in the manufacturer and distribution of medical gloves.

Organized and coordinated the latex allergy conference in San Francisco in 2000 which focused on issues of latex and latex allergy. Has been involved in numerous research projects and co-authored numerous industry articles and scientific papers concerning latex gloves glove donning lubricants. Has also been involved in work with glove protein testing and standards and FDA compliance activities for medical and food grade gloves

ABSTRACT

Introduction:
Current perception is that gloves produced with low total extractable protein (EP) will also have low allergenic EP associated with the powder. The current review of data shows that powdered latex gloves with low levels of extractable protein in the rubber will still have significant amounts of allergenic EP associated with the powder.

Methods:
A study focusing on EP levels at various process points on glove manufacturing lines, including the slurry tanks, performed over a period of 30 days was conducted using RIA (Rast Inhibition Assay) to measure latex allergen. The purpose was to locate contributing sources of EP and develop new methods to reduce the allergen content of gloves.

Discussion:
The study demonstrates diffusion of EP from gloves being dipped into the slurry tank is continual, and the EP level of the slurry water can rise to levels which can cause powder, which is prone to attach to protein, highly allergenic. The study clearly indicated that a low EP glove can contain high levels of allergenic EP in the glove powder, and that the level of allergenic EP in the powder could be due to many different variables.

Conclusion:
The factors affecting protein diffusion in the slurry tank, likely are a combination of ionic strength, starch type used, and the extractable protein content of the glove. USP cornstarch was seen to have a strong affinity to attach to the allergenic protein acting like an exchange media and increasing the amount of allergen bound powder.

Given it is the glove powder and not the glove rubber which is considered to be the primary route of latex sensitization, the same efforts to reduce EP levels in the glove rubber should also be made in reducing the EP level in the glove powder. Guidelines from powder suppliers on slurry tank management are also strongly encouraged.

Introduction:

Studies show that powdered latex gloves with low levels of extractable protein in the rubber will still have significant amounts of allergenic EP associated with the powder.[i, ii]

This study followed two latex glove manufacturing lines run in similar methods with the exception of the donning lubricant. One line used Absorbable Dusting Powder USP (ADP) the other used oatstarch (OS).

The latex glove manufacturing lines, in this study, run on a continuous chain system. For the purpose of this discussion the "beginning point" will be after the finished glove is stripped from the former.

The formers are porcelain molds attached to the continuous chain. The formers are cleaned in a tank system, using a combination of mechanical brushes, acid and alkaline baths, followed by clean water rinsing to remove debris from the last cycle.

The formers are then passed through an oven for drying, then onto the coagulant tank. (Sample Point 1) The coagulant tank contains powders that have two purposes. Calcium nitrate is used to hold the liquid latex to the former. Calcium carbonate is used to allow the finished gloves to be released from the formers upon completion of the manufacturing process.

The formers then again travel through an oven to dry the coagulant and correct the former temperature for dipping into the compounded latex.

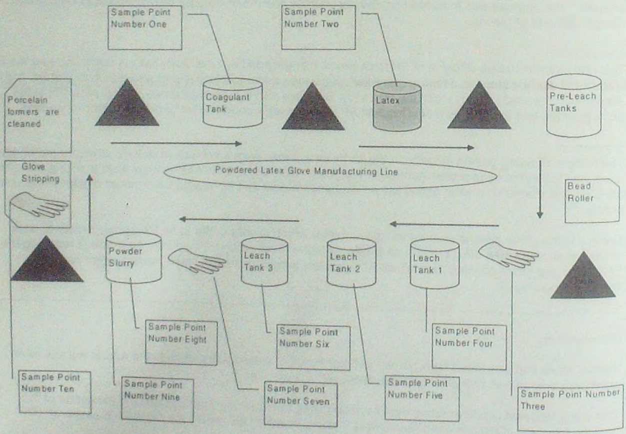
The formers then travel through a bath of compounded latex. (Sample Point 2) This forms a smooth and even distribution of latex over the former. The formers then travel through another oven to gel the latex.

The formers are then processed through a series of "pre leach tanks". These tanks are designed to remove gross chemical, and water-soluble proteins from the gloves prior to vulcanization. The gloves in this study had rolled cuffs, so the formers passed through a bead roller mechanically forming this feature.

The formers then pass through the vulcanizing ovens.

Following vulcanization (Sample Point 3) the formers pass through a series of three leach tanks. (Sample Points 4, 5, 6) These tanks are continuously fed with fresh water at a controlled rate. The leach tanks are designed to rinse water-soluble proteins from the finished glove. (Sample Point 7)

The formers then go through the powder slurry tanks. (Sample Point 8, 9) In this tank the latex glove picks up the chosen donning lubricant from a suspension. The residual heat over the distance covered while moving to the stripping station removes excess moisture, and the gloves are then stripped from the formers completing the manufacturing process. (Sample Point 10)



Methods:

A laboratory reference standard extract of powdered latex gloves (Bodyguards^{TM} T.K. Glove Products Co., Ltd., Huntington Beach, Ca) was prepared as a 1:5 w/v extract in Dulbecco's phosphate-buffered saline (0.0027 M KCL, 0.0015 M KH_2PO_4, 0.008M Na_2HPO_4, 0.14 M NaCL, pH 7.5) (PBS). The extract was centrifuged 15,000 X g for 20 minutes. The supernatant was then ultra-filtered and concentrated 20 times through a YM2 (1000 MW cut-off) Amicon Diaflo® membrane (Amicon Division of W.R. Grace & Company, Danvers MA) at 45 psi of pressure. This concentrate was then assayed for protein content by bicinchoninic acid method and assigned a protein concentration of 7 mg/ml.

When natural rubber allergens were extracted from manufacturing samples, they were extracted 1:5 w/v in 0.1 M phosphate buffer containing 0.2% bovine serum albumin, 1% Tween 20 and 0.01% NaN_3.

Latex allergens were quantified by an inhibition immunoassay using latex specific human IgE. Extracts of the manufacturing samples or the reference standard glove extract compete with the immobilized reference latex allergens for specific IgE antibodies obtained from five latex sensitized health care workers. Affinity-purified rabbit ant IgE-^{125}I-radiolabeled antibody detects the latex allergens in a relationship inversely proportional to the bound counts. Briefly, Immulon IV microtiter plates (Dynex Technologies, Inc., Chantilly, VA) were adsorbed with 1µg of latex glove protein. Latex glove reference standards (7mg/ml) or manufacturing samples were delivered (50 µl) in the well along with human sera (50 µl) containing IgE antibodies to latex allergens. The results were calculated from the latex glove extract standard curve plotted by logistic regression and expressed as protein mass per gram or ml.

The samples were quantified for natural rubber allergen content by competitive immunoassay using human IgE and labeled antihuman IgE detection. Range and mean values follow.

Results:

Data: Range and Mean Values

Location	Cornstarch Line	Oatstarch line
Coagulant Tank	49-143; 100	82-194; 133*
Latex Compounding	891-304; 191	164-227; 192*
Pre-Leach Glove	216-400; 116	267-118; 71
Leach Tank 1	ND-42; 8	ND-0.2; 0.2*
Leach Tank 2	ND-25; 5	ND-24; 0.5*
Leach Tank 3	ND-3; 0.9	ND-2; 0.3*
Post Leach Glove	16-38; 27	18-34; 28
Slurry/Powder	29-146; 99	8-79; 29
Slurry/Water	0.5-23; 9	6-34; 18*
Finished Glove	36-87; 51	29-92; 51

Results: **- values are µg/ml; otherwise µg/gram; ND- non detected; (<0.1 µg/ml; <0.5 µg/gram)*

The EP level of the gloves from both the ADP manufacturing line and the OS manufacturing line were consistent with each other. The normal Lowry proteins levels for these gloves were ~200µg/gm when done by the manufacturer during the study period.

The leach tanks during the study maintained low levels of protein, but the slurry tank protein levels increased very rapidly on the very first day of production regardless of donning powder used. The slurry tank is a closed system, unlike leach tanks where there are large volumes of fresh water flushed through the tank daily. The glove manufacturer reported that a leach tank will have a flow of about 12 liters of water per minute. The slurry tanks are not designed with a flow system. The only fresh water added is what is required to replace the slurry mix taken from the tank by the gloves during the dipping process. Because of this fact, protein build-up in the slurry tank is inevitable.

These data demonstrate that protein from post leached gloves continue to leach into the slurry tank and accumulate in the slurry. The study demonstrates diffusion of EP from gloves being dipped into the slurry tank is continual, and the EP level of the slurry water continues to rise. The protein then becomes available to be picked up by the powder.

Discussion:

Currently most manufacturers change the slurry tanks about once every 20 - 30 days on average. One of the ADP manufacturers has recommended to the FDA that when using ADP, glove manufacturers should change the slurry tanks every day or twice per week to address this problem.[iii] Glove powder manufacturers do not provide labeling or manufacturing guidelines regarding frequency of change to the glove manufacturers.

Therefore, it is important that a standardized test be developed that determines not only the allergen content of gloves, but similarly the allergen content of the glove powder.

Based on 1,000 liters of slurry in a closed system (a typical sized slurry tank), the build up of allergen to high levels is unavoidable, even in a very low allergen glove (i.e.<10ug/gm).

For example, consider 100,000 eight gm gloves with an average allergen content of 27 ug/gm passing through 1,000,000 cc of slurry. The potential maximum leachable protein could be as high as 21.6 ug/ml per day. The leached protein levels of the lines studied is shown in Graph 1.

The factors affecting protein diffusion in the slurry tank, likely are a combination of ionic strength, starch type used, and the extractable protein content of the glove. Temperature and pH have little effect.[iv] USP cornstarch has a strong affinity to attach to the allergenic protein acting like an exchange media and increasing the amount of allergen bound powder. Striking, is the separation of the slurry components.

The water fraction of the slurry is represented in Graph 2. Rapid increase of allergen is noted in the OS slurry water as compared to the ADP. But, in contrast, Graph 3 represents the comparison of allergen found on the powder taken from slurry tanks on consecutive days of production.

Notable differences, were observed between the starch types, with ADP binding considerable amounts of allergen very early in the production cycle, leaving the water almost absent of significant levels of allergen.

Because the slurry components acted notably different in similar conditions, this further supports that the allergenic EP level of the associated powder has little to do with the EP level of the glove.

Graphs 4 and 5 show the contribution of allergen found in the glove powder as a percentage of the total glove allergen. One gram of the glove product is used in the comparison. Graph 4 is a moderate allergen glove powdered with ADP, where Graph 5 is a moderate allergen glove powdered with OS.

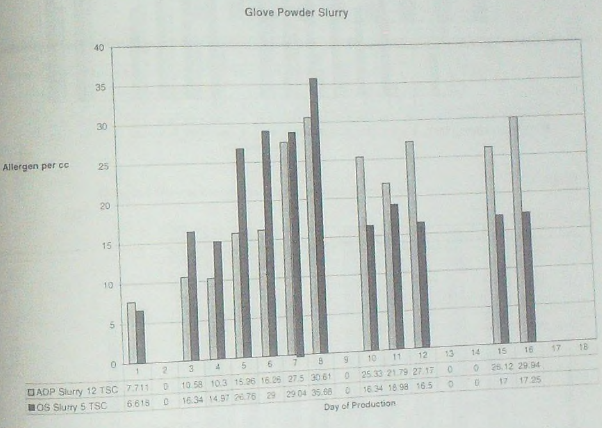
The data represented in Graphs 4 and 5 shows that the allergenic EP levels of the OS powder was significantly lower than that of the ADP powder in spite of the fact that the gloves were consistent in EP levels.

The FDA, NIOSH and many other medical and industry experts recognize protein bound to the glove powder, can cause reactions in sensitized individuals, and may be a contributing factor in latex sensitization.[v, vi] In a study released by NIOSH it states that healthy, intact skin allows the penetration of only a small percentage protein into the body. Glove powders can bind and aerosolize these latex proteins.[vii, viii] This latent powder bound protein can linger in the environment until physically removed.

Based on all available data, a low EP glove can still contain high levels of allergenic protein. Manufacturers of gloves, and those who distribute them, should be aware that there is no data which shows that a reduction in extractable protein in the glove will result in a lower allergenic EP level in the powder. If ADP is used in the glove manufacturing process, guidelines on how to safely use the product by the ADP manufacturers should be made available. The recommendations could include minimum recommendations on how often the slurry tanks should be changed and how allergenic EP levels should be measured and monitored.

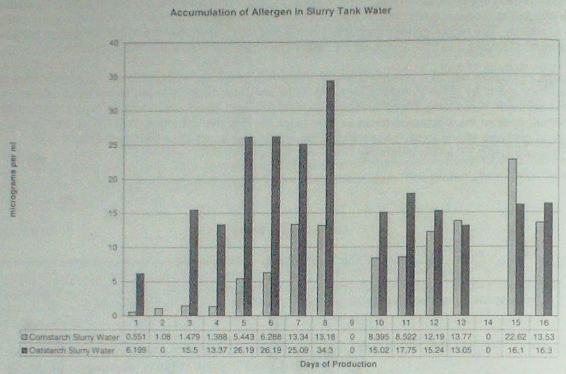
Given that glove powder can be a potent vehicle of allergen to sensitized individuals, it should important that the same efforts made by glove manufacturers and distributors to reduce EP levels in the glove rubber should also be made in reducing the EP level in the glove powder. The development of guidelines from the ADP and other powder manufacturers could be very helpful in this effort. Further the FDA as well as the ASTM should continue efforts to set measurement standards that would allow the quantification and monitoring of allergenic EP levels in powder.[ix]

Graph 1



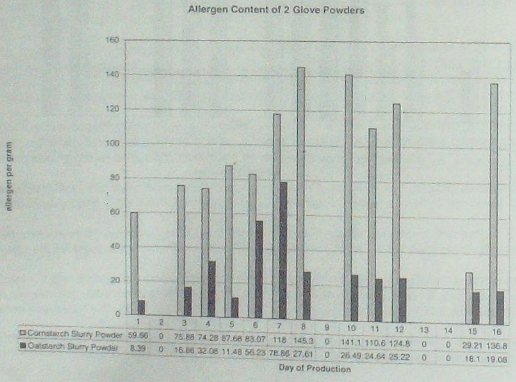
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
☐ ADP Slurry 12 TSC	7.711	0	10.58	10.3	15.96	16.28	27.5	30.61	0	25.33	21.79	27.17	0	0	26.12	29.94		
■ OS Slurry 5 TSC	6.618	0	16.34	14.97	26.76	29	29.04	35.68	0	16.34	18.98	16.5	0	0	17	17.25		

Graph 2



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
☐ Cornstarch Slurry Water	0.551	1.08	1.479	1.388	5.443	6.288	13.34	13.18	0	8.395	8.522	12.19	13.77	0	22.62	13.53
■ Oatstarch Slurry Water	6.199	0	15.5	13.37	26.19	26.19	25.09	34.3	0	15.02	17.75	15.24	13.05	0	16.1	16.3

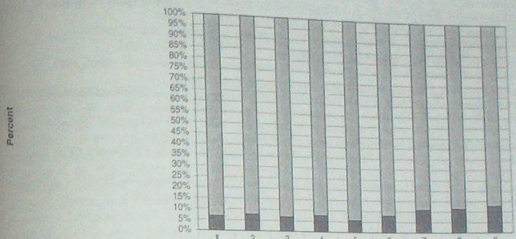
Graph 3



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
☐ Cornstarch Slurry Powder	59.66	0	75.88	74.28	87.68	83.07	118	145.3	0	141.1	110.6	124.8	0	0	29.21	136.8
■ Oatstarch Slurry Powder	8.39	0	16.86	32.08	11.48	56.23	78.86	27.61	0	26.49	24.64	25.22	0	0	18.1	19.08

Graph 4

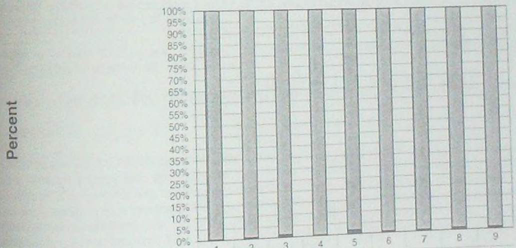
Calculated Alleregen Contribution from Glove and Absorbable Dusting Powder USP (Keoflo)



	1	2	3	4	5	6	7	8	9
☐ Glove w/ Evaporated Slurry Tank Water	23796	26040	29461	29744	39564	38720	34121	24483	24146
■ 200 mgs powder divided by 7 gm glove	1705	2168	2122	2505	2374	3372	4150	3159	3567

Graph 5

Calculated Alleregen Contribution from Glove and Oat Starch (Ostar)



	1	2	3	4	5	6	7	8	9
☐ Glove w/ Evaporated Slurry Tank Water	22888	29146	25344	34820	38884	42733	38541	23301	26463
■ 50 mgs powder divided by 7 gram glove	74	148	281	101	691	242	232	216	221

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[viii] **Factors Affecting Binding of Natural Rubber Latex (NRL) Proteins to Glove Powder**
V.J.Tomazic-Jezic, A.D.Lucas, B.A.Sanchez, Center for Devices and Radiological Heath, Food & Drug Administration, Rockville, MD, USA http://www.cfsan.fda.gov/~frf/forum03/abs03ct.html

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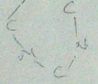
Anne D. Lucas, Liliana Krasteva-Sedmakova, and Vesna J. Tomazic-Jezic, CDRH, FDA, Rockville MD 20852

For better adhesion:

3wt % TCI/EA

Trichloroisocyanuric acid:

1,3,5 -trichloro-1,3,5 triazin-2,3,6-trione



① MEK wiping of [illegible]

SURFACE TREATMENTS TO IMPROVE VULCANISED LATEX ADHESION: CURRENT STATE OF THE ART

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BIOGRAPHICAL NOTE

José Miguel Martín-Martínez is currently Full Professor and head of the Adhesion and Adhesives Laboratory of the University of Alicante (Spain). He graduated in Chemistry in 1978 and obtained the PhD degree in Sciences in 1981 at the University of Granada (Spain) both with high honour distinction. Visiting Professor at the Centre de Microcalorimetrie et Thermochimie of CNRS (Marseille, France), The Pennsylvania State University (State College, PA, USA), University of Amsterdam (The Netherlands), and Virginia Polytechnic Institute and State University (Blacksburg, VA, USA). Currently, he is a member of the Advisory Editorial Board of *The Journal of Adhesion, International Journal of Adhesion and Adhesives, Journal of Adhesion Science and Technology*, and *Rubber Chemistry and Technology*.

1997-date : Honorary Member of the Advisory Council of the International Biographical Centre (Cambridge, UK). 2003-date : Honorary Member of the Research Council of the International Biographical Centre (Cambridge, UK).

1997-2002 : International Coordinator of CYTED network VIII.D.

2000-date : Spanish representative in COST action 527 of the European Commission. Coordinator of working group B in COST action 527.

2003-date : President of the Spanish Adhesion and Adhesives Society.

Several citations in biographical books : *Who's who in the world, Who's who in Science and Engineering, 2000 Intelectuals of the 21st Century, ...*

Authors of over 180 papers, 13 books, 150 presentations at International Conferences, and several key invited lectures at International Conferences.

Several prizes (EUROCOAT98, EUROCOAT02) and recognitions have been awarded.

ABSTRACT

Latex materials (in this study latex soles for footwear) are relatively difficult to join with adhesives due to its low surface energy and the existence of additives in formulation able to migrate to the surface. Surface treatments are mandatory to achieve reasonable adhesion, the most common is halogenation. Although this surface treatments is generally effective, organic solvents are required and new more environmental friendly alternative treatments are currently under development. Halogenation of latex successfully removes antiadherent moieties from the surface, and also chemical moieties are produced; creation of roughness also increases the mechanical interlocking with the adhesive.

In this contribution two different issues will be addressed : *i)*. The effects produced by treatment of different latex soles with a chlorinating solution whose are responsible for their improved adhesion to polyurethane adhesives; *ii)*. New recent results on the UV radiation treatment of different latex soles will be also described.

INTRODUCTION

As for any adhesive joint, the adhesion between the upper, the adhesive and the sole surfaces in footwear manufacturing must be properly optimised to produce adequate joints. Therefore, the adhesion in shoe bonding can be increased by surface modification of the upper and/or sole materials (by application of adequate surface treatments and/or primers), by modifying the adhesive formulation (incorporation of adhesion promoter), or both. Considering that most of the upper materials are porous and the adhesives used in shoe bonding (polyurethane and polychloroprene adhesives) are applied as liquids, an acceptable penetration of the adhesive into the upper is expected and then the mechanical adhesion is generally favoured. However, because the different sole materials are non porous and have in general a relatively low surface energy, both mechanical (for example, roughening) and chemical (for example, halogenation) surface preparations are necessary and enhanced chemical adhesion is required. Furthermore, in the bonding of some rubber soles (such as for latex soles) the weak boundary layers produced by surface contaminants and/or by migration of antiadherent moieties to the interface must be removed before joint formation.

Latex soles are currently used in footwear industry due to their comfort and excellent properties. However, due to the low surface energy of latex and the migration of additives in its formulation, a surface treatment is mandatory. In general, several surface treatments have been proposed to enhance rubber adhesion, including mechanical (i.e. roughening), chemical (i.e. halogenation with organic solvent solutions of trichloroisocyanuric acid – TCI), or physical (i.e. corona discharge, low pressure gas plasma, UV radiation).

Few literature on the surface modification of latex materials to enhance adhesion has been published. Surface treatments have been used to modify adhesion and friction of surgical globes [1]. It has been established that factors of importance in the reduction of dry friction were an increased surface roughness and hardness. Under slightly wet or damp conditions, friction can increase above the dry value. Furthermore, the surface of medical goods (e.g. catheter) made from natural rubbers treated with a solution of vinyl silicone rubber in a benzene solvent impart smoothness and biocompatibility [2].

To our knowledge, only three papers dealing with the improved adhesion of natural rubber has been published [3-5]. Oldfield and Symes [3] demonstrated the effectiveness of the treatment of natural rubber with sodium hypochlorite solutions which is due to the creation of carbon-chlorine moieties and roughness. Lawson *et al* [5] manufactured natural rubber thermoplastic elastomers by dynamic vulcanization of natural rubber during its mixing with polypropylene and they were subjected to various halogenation surface treatments. Marked reduction in the coefficient of friction was obtained. As a result of halogenation there is an increase in the micro roughness and hardness of the natural rubber surface. Another consequence of halogenation was the increase in the surface energy of natural rubber which in turn promotes adhesion to various polar substrates. Indeed it was determined that halogenation of natural rubber is an effective way of priming the surface of these materials for adhesion to acrylic and other substrates. Ellul and Hazelton [5] showed that the reaction of trichloroisocyanuric acid with natural rubber (NR) was produced by substitution reactions, but a minor amount of addition was also produced. Furthermore, isocyanuric acid or other nitrogenous residues were present on treated surfaces before washing with ethanol solutions in water.

In this study different surface treatment were applied to two difficult to bond vulcanised latex soles commonly used in footwear industry. Due to the limitations of halogenation as surface treatment, some preliminary results of the use of UV radiation to increase the adhesion of latex soles to polyurethane adhesives will be given.

EXPERIMENTAL

Materials

Two commercial vulcanized latex soles (whose formulations are unknown) were used in this study. The materials were provided by Cauchos Arnedo (Arnedo, Spain). These soles were chosen due to their different adhesion performance.

To determine the adhesion properties of the vulcanised lateces, latex/polyurethane adhesive/leather joints were prepared. A chromium-tanned bovine leather (Tensile strength = 13 MPa; Elongation-at-break = 60 %; Ash content (950°C) < 5 wt%) was used. The polyurethane adhesive solution (PU) was prepared by dissolving 17 wt% Desmocoll 540 pellets (Bayer, Leverkusen, Germany) and 10wt% fumed silica (Aerosil 200, Degussa) in an acetone/toluene (80:20, w:w) mixture. To facilitate the dispersion of the fumed silica in the polyurethane and avoid further settling, the adhesive was prepared in two consecutive steps: i) The fumed silica was mixed with a small amount of the solvent mixture at 2500 rpm for 15 min in a laboratory mixer to facilitate the dispersion; ii) The polyurethane pellets were added to the solvent fumed silica mixture, simultaneously adding all the solvent; the mixture was stirred in the laboratory mixer at 2000 rpm for 2.5 h, until a homogeneous solution was obtained. The viscosity of the solution obtained in a rotational rheometer

(*Rheolab MC 100* supplied by *Raar Physica*, Germany) was 2.5 Pa.s at 25 s^{-1}. Just before adhesive application, 5 wt% polyisocyanate (Desmodur RFE from Bayer, Leverkusen, Germany) was added and mixed for one minute in a mechanical stirrer to produce an homogeneous solution.

Several surface treatments were applied to the vulcanised lateces. *i). Solvent wiping.* Lateces were wiped with a tissue impregnated with MEK. After wiping, 30 minutes were allow for solvent evaporation before the adhesive solution was applied on the latex surface. *ii). Halogenation treatment.* The chlorinating agent used in this study was a solution of 3 wt% trichloroisocyanuric acid (TCI) in ethyl acetate (EA). The solution was brushed onto the latex surface. Surface modifications were always monitored 1 hour after applying the chlorinating solution on the latex surface. Similarly, adhesive joints were produced one hour after halogenation of latex was carried out. *iii). UV radiation treatment.* The UV treatment was carried out in a barrel type reactor equipped with an O-ring sealable door at one end and O-ring sealable gas inlets at the other. Gases can be introduced into the reactor through appropriate inlets and also a thermocouple can be placed to monitor the temperature inside the reactor. The interior of the reactor was provided with a mercury vapour grid lamp (*BHK Inc.*). The lamp was made of pure, clear fused silica, able to transmit all mercury UV emissions, including the two strong UV lines at 184.9 and 253.7 nm. The intensity of the UV radiation was 12-15 mW/cm^2 at a distance of 2.54 cm. The gas supplied to the interior of the reactor was extra-dry compressed air (dew point=-65°C), at a flow rate of 1000 ml/min measured using an *MKS* mass-flow controller. UV treatment of vulcanised lateces were carried out at different distances from the lamp (5 and 15 cm) and for different times (2 and 5 minutes).

Experimental techniques

The surface treated vulcanized lateces were characterized by different experimental techniques.

Contact angle measurements. The surface-treated latex pieces were placed into the thermostated chamber of a *Ramé Hart 100* goniometer. The chamber was previously saturated with the vapour of the test liquid at 25 °C (bidistilled and deionised water) for at least 10 minutes before placing a drop of the test liquid on the latex surface. The contact angles on the surface-treated lateces were measured immediately and 10 minutes after placing 4μL drops of bidistilled deionized water on the sample. The experimental error was ±2 degrees.

Attenuated Total Multiple Reflection-Fourier Transform Infrared Spectroscopy (ATR-IR spectroscopy). The use of attenuated total reflectance technique of IR examination (ATR-IR spectroscopy) allows the surface of a rubber to be examine by clamping a specimen to a prism from which the IR radiation is reflected. The reflected radiation shows a spectrum similar to the transmission spectrum of the rubber but corresponding to that of a very thin surface layer (2 to 5 μm depth, depending on prism nature and experimental conditions). The infra-red spectra of the treated samples were obtained using a Nicolet 205 spectrometer. To avoid deep penetration of the IR radiation into the sample, the attenuated total multiple reflection method was employed (ATR-IR spectroscopy) and a SeZn crystal was used. The ATR-IR spectroscopy allows to analyse about 5 μm of the treated latex surface. 100 scans were collected and averaged at a resolution of 4 cm^{-1}.

SEM. Scanning Electron Microscopy (SEM): The morphological modifications produced on the treated latex surfaces were analysed using a *JEOL JSM-840 SEM* system. The latex samples were gold-coated before analysis and the energy of the electron beam was 20 kV.

T-peel strength measurements. T-peel strength measurements were carried out for adhesive joints produced with latex rubber and leather strip test specimens (150 mm × 30 mm). The polyurethane adhesive solution was applied to each test specimen (treated latex and leather) using a brush. After allowing the solvent to evaporate for 20 min, the dried polyurethane adhesive films on the surface-treated R2 specimens and on the leather were melted for 10 seconds at 100°C using infrared radiation. These specimens were then placed in contact and a pressure of 0.8 MPa was applied for 10 s to achieve a suitable joint. The T-peel strength was measured using a *Shimadzu* universal test instrument (peel rate = 0.1m/min). The values obtained were the average of three experimental replicate determinations (standard deviation was less than 10%). The adhesive joints were kept at 25°C and 50% relative humidity before undergoing the T-peel test. The evolution in T-peel strength values was measured 24h after joint formation. After the T-peel test was carried out, the failed surfaces were analysed using ATR-IR spectroscopy, to more precisely assess the loci of failure of the joints.

RESULTS AND DISCUSSION

As-received vulcanised lateces

Two different commercial vulcanised lateces formulations were used in this study.

Latex 1 contains silica (broad Si-O band at 1098 cm^{-1}) and calcium carbonate (bands at 836 and 1460 cm^{-1}) as fillers – Figure 1 - and noticeable amounts of antiozonant microcrystalline paraffin wax (CH$_2$ bands at 72 2852 and 2914 cm^{-1}). On the other hand, the typical C=O band at 1541 cm^{-1} due to zinc stearate can be distinguished in the ATR-IR spectrum of Figure 1. The typical band of latex at 907 cm^{-1} is present, although its relative intensity is quite low. Considering the low relative intensities of the latex and silica bands in the ATR-IR spectrum, it can be concluded that paraffin wax and zinc stearate migrate to the latex 1 surface, imparting antiadherent properties because the creation of a weak boundary layer. In fact, the water contact angle value (25°C) on the as-received latex 1 is quite high (107 degrees), indicating a poor wettability. Figure 2 shows the SEM micrograph of latex 1 surface. The surface is quite heterogeneous and is covered by a layer of wax. Finally, the peel strength value of as-received latex 1/PU adhesive + 5 wt% polyisocyanate/leather is 0.8 kN/m (an adhesion failure is obtained). Therefore, the poor adhesion of latex 1 is due to the existence of a weak layer of paraffin wax and zinc stearate.

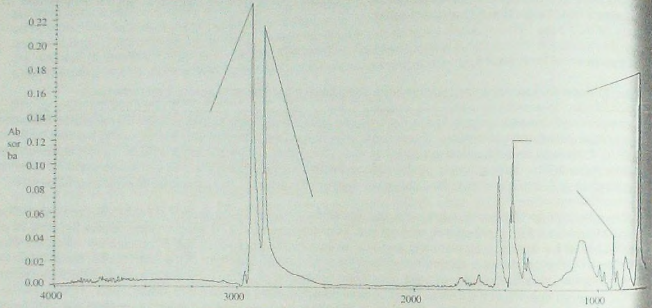


Figure 1. ATR-IR spectrum of vulcanised latex 1.

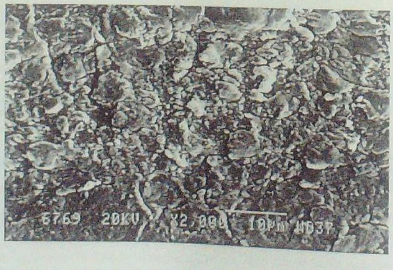


Figure 2. SEM micrograph of as-received vulcanised latex 1.

Latex 2 contains calcium carbonate (bands at 836 and 1460 cm^{-1}) as filler – Figure 3 – and noticeable amounts of zinc stearate (C=O band at 1541 cm^{-1} and CH_2 bands at 2852 and 2914 cm^{-1}). Furthermore some bands due to C=S moieties (1012 and 1093 cm^{-1}) of the vulcanising system are also noticed. The presence of zinc stearate on the latex 2 surface allows poor wettability (water contact angle = 98 degrees) and the SEM micrograph (Figure 4) shows the existence of a weak layer on the surface. As a consequence, the adhesion to polyurethane adhesive is quite poor (peel strength value of as-received latex 2/PU adhesive + 5 wt% polyisocyanate/leather is 1.1 kN/m) and an adhesion failure is obtained.

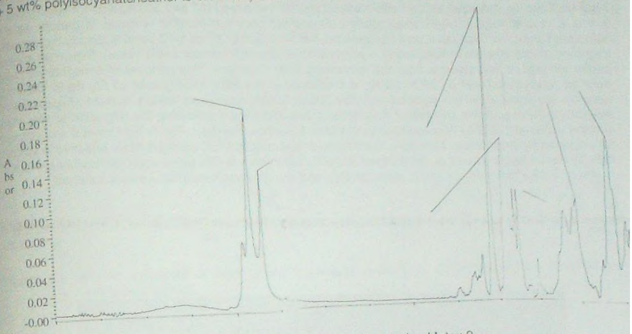


Figure 3. ATR-IR spectrum of vulcanised latex 2.

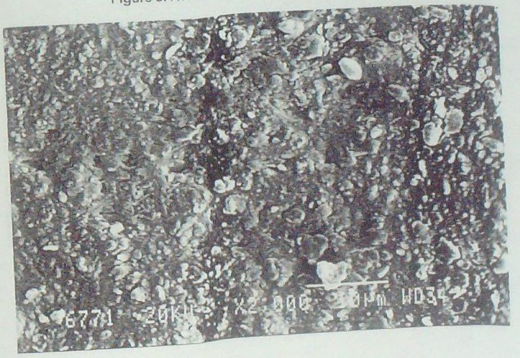


Figure 4. SEM micrograph of as-received vulcanised latex 2.

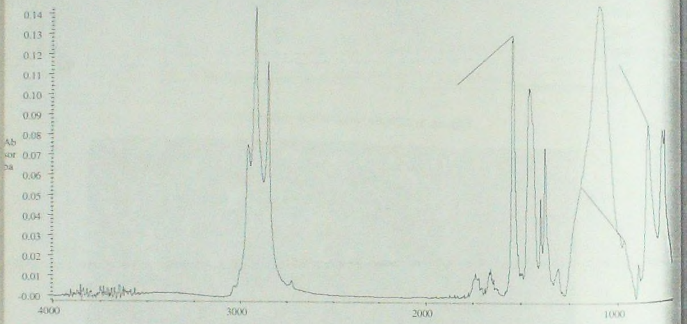
Solvent wiping of vulcanised lateces

In general, rubber soles tend to swell by application of solvents and the mechanical interlocking o
adhesive is favoured. The best performance is obtained with polyurethane adhesives and only in

circumstances it is possible to use polychloroprene adhesives. The solvent can be applied on the rubber surface by wiping, spray or immersion, in or out an ultrasonic bath. Toluene and ketones are the most used solvents. The treatment with solvent is effective in the removal of processing oils and plasticizers in SBR rubber soles, but zinc stearate is not completely removed and antiozonant wax gradually migrates to the rubber/polyurethane adhesive interface [6].

Solvent wiping with MEK was carried out to remove surface contaminants on vulcanised lateces surfaces. After MEK wiping, the water contact angle values slightly decrease (101 and 98 degrees for vulcanised latex 1 and 2, respectively). ATR-IR spectroscopy (Figure 5a) shows noticeable removal of paraffin wax from vulcanised latex 1 surface (as a consequence the relative intensity of the Si-O band is greatly increased), but migration of zinc stearate is favoured (it is responsible of the high contact angle value). Figure 5b shows the partial removal of zinc stearate from the vulcanised latex 2 surface. The removal of antiadherent moieties from the lateces surfaces by MEK wiping is evidenced in the SEM micrographs of Figure 6. MEK wiping removes the weak layer but rounded particles bloom to the vulcanised latex 1 surface (Figure 6a). EDX analysis of these particles shows that they contain zinc and silicon, indicating the migration of zinc stearate and the exposition of silica filler particles to the latex 2 surface. However, Figure 6b shows a smooth surface fully covered by small holes. Therefore, the degree of cleaning by MEK wiping is more effective in vulcanised latex 2. Peel strength values of MEK wiped latex/PU adhesive + 5 wt% polyisocyanate/leather joints are low (1.4 and 1.8 kN/m for latex 1 and 2, respectively), and always an adhesion failure was obtained.

a.



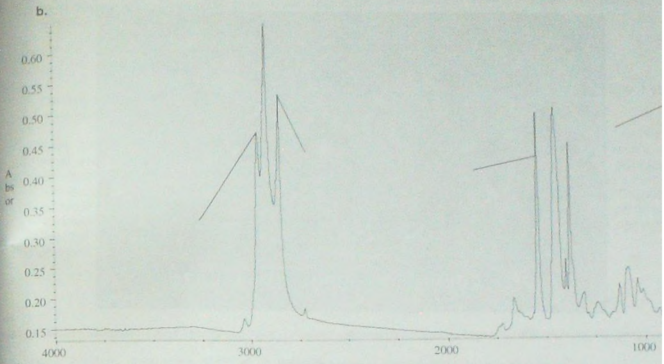
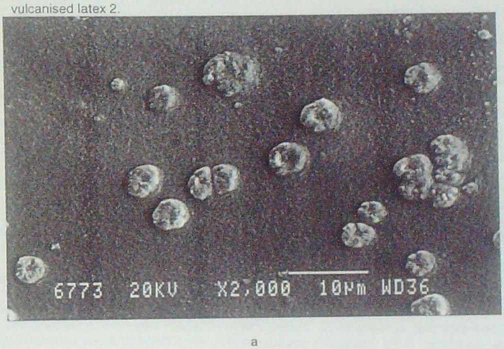


Figure 5.a. ATR-IR spectrum of MEK wiped vulcanised latex 1. **b.** ATR-IR spectrum of MEK w vulcanised latex 2.



a

b

Figure 6.a. SEM micrograph of MEK wiped vulcanised latex 1. **b.** SEM micrograph of MEK wiped vulcanised latex 2.

Treatment of vulcanised lateces with ethyl acetate solutions of 3 wt% TCI

The use of chlorination in shoe industry is due to its high effectiveness in improving the adhesion of several type and formulations of rubbers, it is cheap and easy to apply. Furthermore, chlorination makes the rubber surface compatible with many adhesives (epoxy, polyurethane, acrylic); removes contaminants and antiadherent moieties from the surface avoiding their migration to the rubber/adhesive interface; improved durability and ageing resistance are imparted to the joints; and the treated surfaces remain reactive with the adhesive for at least three months after surface preparation [7]. Chlorination of rubber soles also shows some limitations : *i)*. Poor stability of the solutions (chlorine evolution with time is produced); *ii)*. Organic solvents are necessary to react with the chlorinating agent and to facilitate the wetting of the rubber surfaces; *iii)*. Polychloroprene adhesives are incompatible with the chlorinated rubber surfaces producing low peel strength values; *iv)*. Treatment is not restricted to the outermost surface but penetrate into the rubber decreasing its mechanical properties. The extent of penetration of the chlorinating agent into the rubber depends on its concentration and rubber formulation. Oldfield and Symes [3] show that a depth between 1 and 5 µm is reached by treatment of different rubbers with acidified sodium hypochlorite aqueous solution.

Several chlorinating agents have been used in shoe industry for rubber soles bonding. In the 70s, aqueous solutions of chlorine were successfully used. Later acidified sodium hypochlorite aqueous solutions were also used to improve the adhesion of rubber soles. Although successful, neutralization with ammonium hydroxide and extensive washing of the treated rubber sole with water are necessary, followed by drying; furthermore, the stability of the chlorinating solutions is relatively poor [8]. The mechanism of rubber chlorination with acidified sodium hypochlorite aqueous solutions has been established [8-12]. The dominant electrophile species depends on the pH of the solutions. Thus, between pH 10 and 11 the weakly electrophilic hypoclorous acid dominates.

$$NaClO + H_2O \leftrightarrow HClO + NaOH$$

By decreasing the pH (HCl addition) the electrophile H_2ClO^+ is formed and finally the actual chlorinating spec (chlorine) is produced.

$$HClO + H^+ \leftrightarrow H_2ClO^+$$
$$4\ HClO \rightarrow 2\ Cl_2 + 2\ H_2O + O_2$$

Chlorine is added to double C=C bond in the rubber producing chlorinated hydrocarbon moieties and sc crosslinking [12].

Early 70's SATRA proposes the use of an organic chlorine donor for treatment of rubbers [13] to avoid rapid evolution of chlorine produced with the inorganic chlorinating agents. The most commonly u chlorinating agent in rubber sole bonding is an organic solvent (ketone or ester) solution trichloroisocyanuric acid (TCI) - 1,3,5-trichloro-1,3,5-triazin-2,4,6-trione - (Figure 7) which is very cheap common (it is generally used as chlorinating agent in swimming pools). The organic solvent in TCI solu determines the degree of rubber wetting and furthermore, the actual chlorinating species are produce reaction of TCI with the organic solvent. Thus, the chlorinating species in TCI/MEK solutions are α-cl ketones, whereas acid chlorides are formed in TCI/ethyl acetate solutions [14].

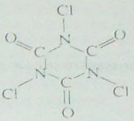


Figure 7. Chemical structure of trichloroisocyanuric acid (TCI) - 1,3,5-trichloro-1,3,5-triazin-2,4,6-trior

Figure 8. Photograph showing the cohesive failure in 3 wt% TCI-EA treated latex 2/PU adhesive + polyisocyanate/leather joints.

Halogenation of vulcanised lateces results in a noticeable increase in peel strength values of 3 wt% treated latex/PU adhesive + 5 wt% polyisocyanate/leather joints (6.5 and 5.3 kN/m for latex 1 respectively), and a cohesive failure in the vulcanised latex was obtained (Figure 8).

$O_2 + h\nu$ (185 nm) → O_2
$O_3 + h\nu$ (254 nm) → $O_2 + O$

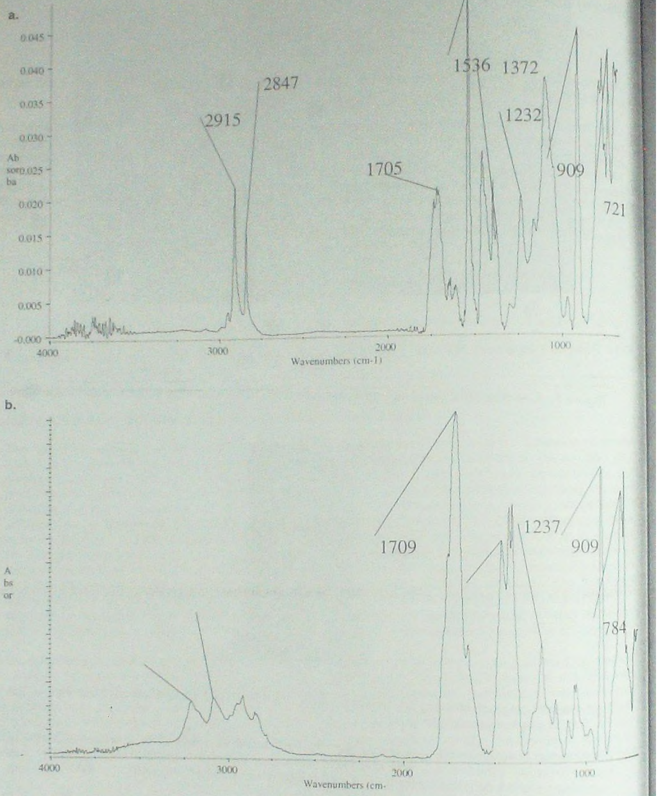


Figure 9.a. ATR-IR spectrum of 3 wt% TCI/EA treated vulcanised latex 1. **b.** ATR-IR spectrum of 3 wt% TCI/EA treated vulcanised latex 2.

The improved adhesion of vulcanised lateces after halogenation can be ascribed to the improvement several mechanisms of adhesion :

1. Thermodynamical adhesion. Treatment with TCl solution decreases the water contact angle v on vulcanised lateces (from 107 and 98 degrees on the as-received to 90 and 67 degrees on surface chlorinated lateces 1 and 2, respectively), i.e. improved wettability is obtained. This decre is more marked for vulcanised latex 2 due to the absence of paraffin wax on its surface. decrease in contact angle values can be ascribed to the creation of surface chemistry roughness on vulcanised lateces surfaces. In fact, an earlier study [5] shows that a consequenc halogenation of natural rubber is the increase in its surface energy which in turn promotes adhe to various polar substrates.

2. Chemical adhesion. The chemical modifications on vulcanised lateces produced by chlorination evidenced by ATR-IR spectroscopy. Similar chemical modifications are produced in both vulcan lateces, but in a greater extent in latex 2 (this one without paraffin wax on its surface). Chlorinatic produced in the C=C bonds of isoprene creating chlorinated hydrocarbon – 1232 and 1372 cm^{-1} - C-Cl – 784 and 909 cm^{-1} - moieties. C=O groups - 1705 cm^{-1} - are created due to oxidation reac and deposition of TCl reaction by-products (mainly isocyanuric acid) (Figures 9a and 9b). Furtherm paraffin wax (bands at 726, 2851 and 2920 cm^{-1}) are removed (only in vulcanised latex 1). Chlorina also produces the formation of C-N moieties (1709 and 3214 cm^{-1}) due to the formation of reactior products (mainly isocyanuric acid). Furthermore, the increase in the relative intensity of the silica C=S bands is an indication of the removal of antiadherent moieties from the vulcanised lateces surf by chlorination. Zinc stearate is not removed by chlorination of vulcanised latex 1 (Figure 9a) adequate adhesion is obtained. Therefore, the lack of adhesion of vulcanised latex 1 can be m ascribed to the existence of a weak layer of paraffin wax.

3. Mechanical adhesion. Although chlorination with ethyl acetate solutions of TCl removes the w boundary layer on both vulcanised lateces, noticeable differences in surface morphology produced. For the surface chlorinated latex 1 (Figure 10), some holes and unreacted TCl parti can be noticed on the surface; furthermore, silica particles arise to the surface as a consequenc the treatment. For the surface chlorinated latex 2 (Figures 11a and 11b) smaller and more nume TCl particles and deep cracks appear, and surface is more highly degraded as a consequence o chlorination treatment. Therefore, the mechanical adhesion is favoured in chlorinated vulcan latex 2.

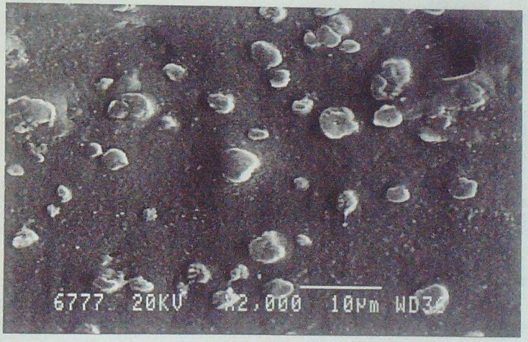
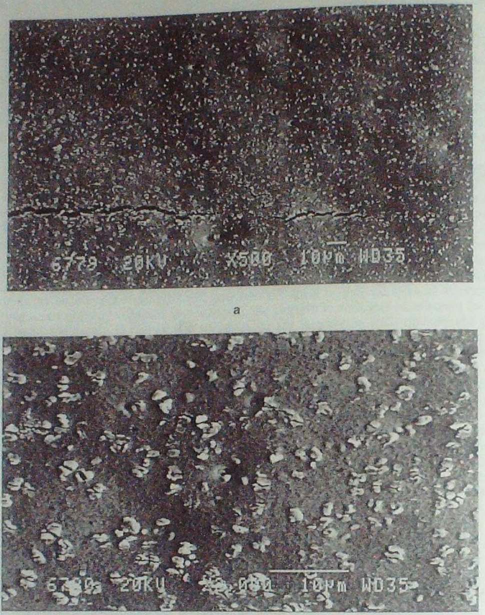


Figure 10. SEM micrograph of 3 wt% TCl/EA treated vulcanised latex 1.



a

b

Figure 11. SEM micrograph of 3 wt% TCI/EA treated vulcanised latex 1. **a.** X 500. **b.** X 2000.

The improved adhesion between the surface chlorinated layer and the urethane adhesive has been ascribec the creation of hydrogen bonds between the urethane group and the chlorine [15]. An alternative rec explanation [16] suggests that residual unreacted chlorinating agent on the rubber surface reacts with polyurethane producing chlorinated moieties at the interface.

Treatment of vulcanised lateces with UV radiation

Several environmental-friendly surface preparation involving the treatment of sole materials with radiatic have been recently studied. These treatments are clean (no chemicals or reactions by-products produced) and fast, and furthermore on-line bonding at shoe factory can be produced, so the future trenc surface modification of substrates in shoe industry will be likely directed to the industrial application of the treatments. Corona discharge, low-pressure RF gas plasma and UV treatments have been successfully us at laboratory scale to improve the adhesion of several sole materials in shoe industry [17-19]. Corc discharge is not sufficiently effective to improve the adhesion of vulcanized rubber [18]. Oxygen plasr however, is very effective in improving the adhesion of different rubbers to polyurethane adhesives [1

However, from a technical point of view, the use of oxygen plasma requires that the treatment takes place in a vacuum, which is a serious limitation for some rubber applications.

UV treatment is economical and environmentally friendly. It is also easily applicable to the surface modification of three-dimensional objects and can be carried out at atmospheric pressure without the nee for chemical agents. UV treatment has been used for a long time as a method of cleaning and purifyin water supplies, and in the last few years it has been used as a surface treatment to clean and modif polymer surfaces, including rubbers [20].

Several types of UV sources have been investigated and described in previous literature. Low pressur mercury lamps are commonly used to produce UV radiation. In this case, the arc is formed in mercur vapour at pressures of the order of 10^{-3} Torr. The resultant radiation is composed mainly of two narro intense lines at 185 and 254 nm. The UV radiation produced at 185 nm generates ozone and ground stat oxygen atoms O (^{3}P) from oxygen in the air. By irradiating materials with UV it is possible to break molecul bonds because the energy produced can be as high as 155 kcal/mol, which is sufficient to break the typic bonds in polymers: H_3C-H 102 kcal/mol, CH_2=CH-H 105 kcal/mol, H_2C-H 86 kcal/mol and CH_3-CH_3 8 kcal/mol [21].

The UV radiation produced at the wavelength of 254 nm is absorbed by the ozone molecule causing it photodecompose to molecular oxygen and O (^{1}D). This O(^{1}D) species is a very reactive form of atom oxygen. It is able to oxidize the molecules creating polar moieties such as hydroxyl and carboxylic group which increase the wettability of the polymer surface. The O (^{1}D) may also react with contaminants on t polymer surface, so cleaning is also a result of treatment with the UV radiation [21]. The following reactio have been proposed [21] for the photo-oxidation of polymers at 254 nm by atomic oxygen:

$$
\begin{aligned}
O_3\,(^1A) + h\nu\,(254\ nm) &\rightarrow O_2\,(^1\Delta_g \text{ or } {}^1\Sigma^+_g) + O\,(^1D) \\
P\text{-}H + O\,(^1D) &\rightarrow P^{\cdot} + {}^{\cdot}OH \\
P^{\cdot} + O_3\,(^1A) &\rightarrow PO^{\cdot} + O_2\,(^1\Delta_g \text{ or } {}^1\Sigma^+_g) \\
P + O\,(^1D) &\rightarrow PO^{\cdot}
\end{aligned}
$$

Two different UV treatments of the vulcanized lateces were carried out : one "mild" treatment at a distance 15 cm for 2 minutes; other "aggressive" treatment at a distance of 5 cm for 5 min. Immediately after treatment, the water contact angles on the treated vulcanized lateces surfaces were measured. UV-15 cm min treatment does not noticeably decrease the contact angle values of vulcanized lateces (mainly for la 2) and thus wettability is not increased (Table 1). However, the UV-5 cm-5 min treatment strongly increas the wettability of both vulcanized lateces.

Table 1. Water contact angle values (25°C) on UV treated vulcanized lateces.

Vulcanised latex	Treatment	Contact angle (degrees)
Latex 1	As-received	107
	UV-15 cm-2 min	86
	UV-5 cm-5 min	50
Latex 2	As-received	93
	UV-15 cm-2 min	91
	UV-5 cm-5 min	49

The UV-5 cm-5 min treatment of vulcanised lateces creates O-H bonds (wide band at 3328 cm^{-1} due to stretching) – Figures 12 and 13. A band at 1650 cm^{-1} which can be ascribed to either C=C stretching i C=C or C=N stretching in O-C=N groups (produced by incorporation of nitrogen from air after treatmen also produced. A broader band at 1708-1713 cm^{-1} is seen, arising from the C=O stretching in a numbe functional groups (ketones, acids, etc.) in the isoprene. A band at 1079 cm^{-1} is created due to an aliphati O-C group (C-O-C stretching). Furthermore, a decrease in the intensity of the bands due to CH_2 and groups at 2914 and 2852 cm^{-1}, the formation of a small band at 826 cm^{-1} (=CH bending out of plane in C C=O groups), and the decrease in the intensity of the band at 3006 cm^{-1} are also produced.

effectiveness of the UV-15 cm-2 min treatment is much less important, and the chemical modifications produced by UV treatment are more marked for vulcanized latex 2. Zinc stearate (band at 1536 cm^{-1}) and paraffin wax on the vulcanised lateces surfaces are not fully removed by UV treatment.

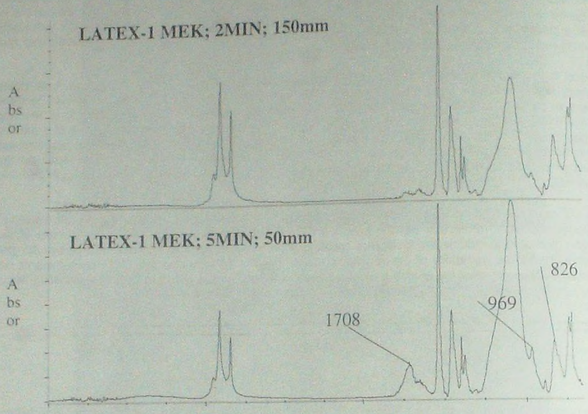


Figure 12. ATR-IR spectra of UV treated vulcanised latex 1.

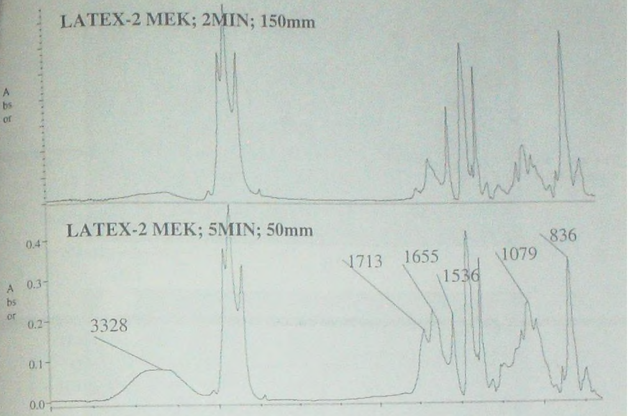
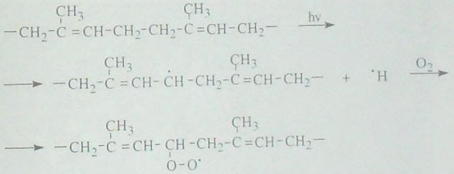


Figure 13. ATR-IR spectra of UV treated vulcanised latex 2.

As the chemical changes in the vulcanised lateces surfaces produced by UV treatment can be followe using ATR-IR spectroscopy, the treatment must penetrate into the surface on the order of approximately µm (the estimated depth of IR radiation penetration allowed by the ZnSe crystal under the experiment conditions used in this study).

The mechanism of the photo-oxidation reaction of *cis*-1,4-polyisoprene [21] can be used to understand t effects of UV radiation on the vulcanised lateces:

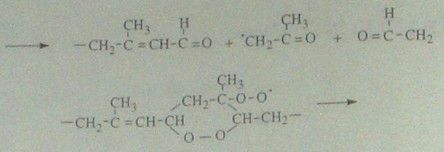


$$-CH_2-\overset{CH_3}{C}=CH-CH_2-CH_2-\overset{CH_3}{C}=CH-CH_2- \xrightarrow{h\nu}$$

$$\longrightarrow -CH_2-\overset{CH_3}{C}=CH-\dot{C}H-CH_2-\overset{CH_3}{C}=CH-CH_2- \quad + \quad {}^{\cdot}H \xrightarrow{O_2}$$

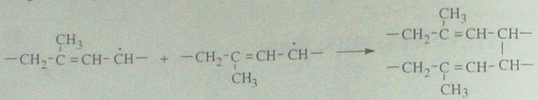
$$\longrightarrow -CH_2-\overset{CH_3}{C}=CH-\underset{O-O^{\cdot}}{CH}-CH_2-\overset{CH_3}{C}=CH-CH_2-$$

The peroxy radicals may react intramolecularly with a double C=C bond to form a cyclic peroxide which m react with another oxygen molecule to form a peroxy radical. This radical is destroyed by UV radiation:

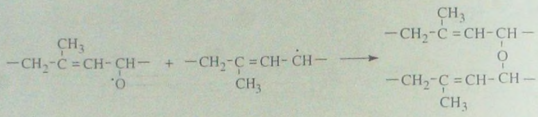


$$\longrightarrow -CH_2-\overset{CH_3}{C}=CH-\overset{H}{C}=O + \dot{C}H_2-\overset{CH_3}{C}=O + O=\overset{H}{C}-CH_2$$

The alkyl, alkoxy and peroxy radicals produced by UV radiation may react with each other to produce crosslinking of the polymer at the surface:



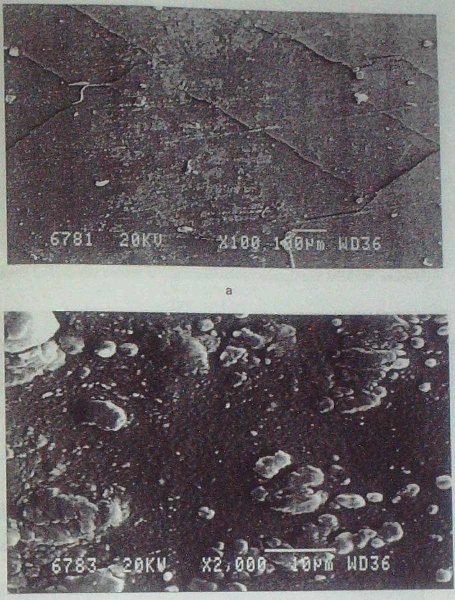
$$-CH_2-\overset{CH_3}{C}=CH-\dot{C}H- + -CH_2-\underset{CH_3}{C}=CH-\dot{C}H- \longrightarrow \begin{array}{l} -CH_2-\overset{CH_3}{C}=CH-CH- \\ \qquad\qquad\qquad\quad | \\ -CH_2-\underset{CH_3}{C}=CH-CH- \end{array}$$



$$-CH_2-\overset{CH_3}{C}=CH-\underset{\cdot O}{CH}- + -CH_2-\underset{CH_3}{C}=CH-\dot{C}H- \longrightarrow \begin{array}{l} -CH_2-\overset{CH_3}{C}=CH-CH- \\ \qquad\qquad\qquad\quad O \\ -CH_2-\underset{CH_3}{C}=CH-CH- \end{array}$$

The UV treatment also affects the morphology of the vulcanised lateces surfaces, and in a different way for the two materials. The SEM micrograph of the UV-5 cm-5 min treated latex 1 (Figure 14) shows a relatively smooth surface on which several filler particles and paraffin wax agglomerates are disseminated. The UV-15 cm-2 min treated latex 1 (Figure 15) shows a noticeable surface crosslinking giving a hard layer and several cracks. On top of this hard layer, some paraffin wax agglomerates can be also distinguished. Therefore, the UV treatment produces surface cleaning and noticeable crosslinking, favouring the migration of paraffin wax.

Figure 14. SEM micrograph of UV-5 cm-5 min treated vulcanised latex 1.



a

b

Figure 15. SEM micrograph of UV-15 cm-2 min treated vulcanised latex 2. **a.** X 100. **b.** X 2000.

UV treatment is more aggressive for vulcanized latex 2. Whereas noticeable surface ablation is produced by UV-15 cm-2 min treatment (Figure 16), extensive surface crosslinking and formation of cracks are produced by the UV-5 cm-5 min treatment of latex (Figure 17).

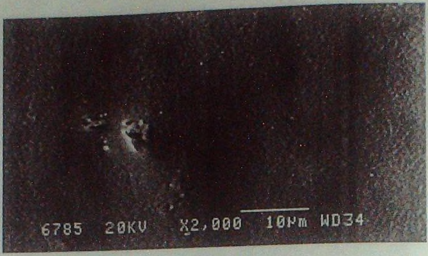
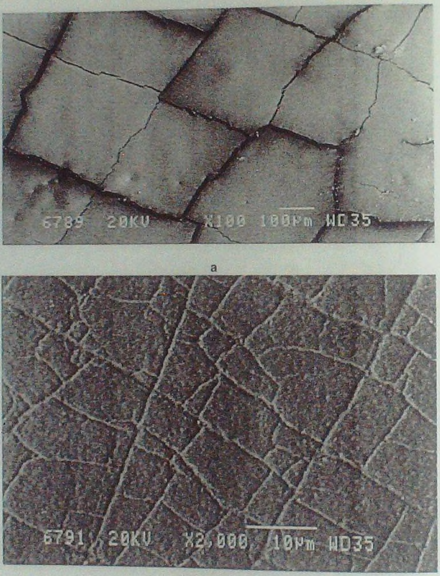


Figure 16. SEM micrograph of UV-15 cm-2 min treated vulcanised latex 2.



a

b

Figure 17. SEM micrograph of UV-15 cm-2 min treated vulcanised latex 2. **a.** X 100. **b.** X 2000.

The influence of the surface modifications on the adhesion properties of the two vulcanised lateces treated with UV radiation was monitored by T-peel tests on UV-treated latex/PU adhesive+5 wt% polyisocyanate/leather joints. The joints prepared with the as-received lateces show a very low peel strength (Table 2), and the treatment with UV radiation leads to a moderate increase in the T-peel strength. The increase likely arises from improved wettability and the surface chemistry produced by UV treatment, but the presence of antiadherent moieties and surface crosslinking inhibit adhesion of the two lateces. The differences in peel strength in the adhesive joints produced with the two vulcanised lateces also correspond to different loci of failure of the joints.

Table 2. T-peel strength values of UV treated vulcanized lateces/ PU adhesive+5 wt% polyisocyanate/leather joints.

Vulcanised latex	Treatment	Peel strength (kN/m)
Latex 1	As-received	0.8
	UV-15 cm-2 min	1.5
	UV-5 cm-5 min	1.0
Latex 2	As-received	1.1
	UV-15 cm-2 min	-
	UV-5 cm-5 min	1.7

All adhesive joints of vulcanised latex 1 show an adhesion failure, whereas for vulcanised latex 2, the failure was produced in the UV modified surface layer. In fact, the ATR-IR spectra of both failed surfaces of the UV-5 cm-5 min treated latex 2/PU adhesive+5 wt% polyisocyanate/leather joint (Figure 18) are similar between them and corresponds to the ATR-IR spectrum of the UV-5 cm-5 min treated latex 2. Figure 19 also confirms this kind of failure.

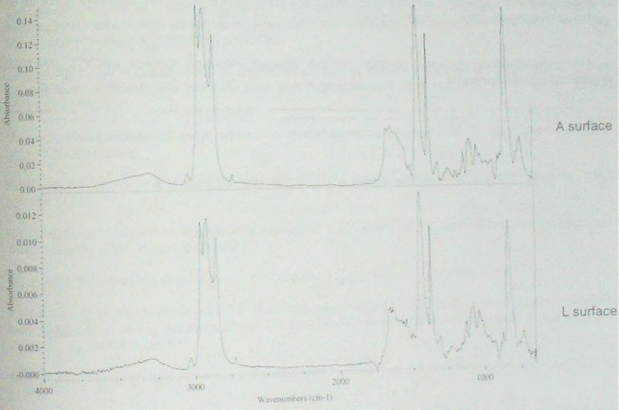


Figure 18. ATR-IR spectra of the failed surfaces obtained after peel test of UV-5 cm-5 min treated latex 2/ PU adhesive+5 wt% polyisocyanate/leather joint.

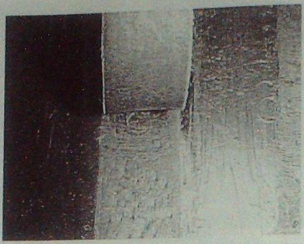


Figure 19. Photograph showing the failure of UV-5 cm-5 min treated latex 2/ PU adhesive+5 wt% polyisocyanate/leather joint.

CONCLUSIONS

Poor adhesion of vulcanised lateces soles is mainly due to the presence of antiadherent moieties (paraffin wax, zinc stearate) on the surface. Halogenation with ethyl acetate solutions of 3 wt% TCI effectively removes the antiadherent moieties, creates roughness and surface chemistry, and also improves wettability. As a consequence an adequate adhesion to polyurethane adhesive is obtained. UV treatment is not as effective in the surface modification of vulcanised lateces soles.

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MORPHOLOGY AND MECHANICAL PROPERTIES OF LAYERED SILICATE REINFORCED NATURAL (NR) AND POLYURETHANE (PUR) RUBBER BLENDS PRODUCED BY LATEX COMPOUNDING

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BIOGRAPHICAL NOTE

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ABSTRACT

Natural rubber (NR), polyurethane rubber (PUR) and NR/PUR-based nanocomposites were produced from the related latices by adding a pristine synthetic layered silicate (LS; sodium fluorohectorite) in 10 parts per hundred parts rubber (phr). The dispersion of the LS latices in the composite was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Further information on the rubber/LS interaction was received from Fourier transform infrared spectroscopy (FTIR) and dynamic mechanical thermal analysis (DMTA). Tensile and tear tests were used to characterise the performance of the rubber nanocomposites. It was found that LS is more compatible and thus better intercalated by PUR than by NR. Further, LS was preferably located in the PUR phase in the blends which exhibited excellent mechanical properties in spite of the uncompatibility between NR and PUR. Nanoreinforcement was best reflected in stiffness- and strength-related properties of the rubber composites.

INTRODUCTION

Nowadays rubber nanocomposites containing layered silicates (LS) as reinforcement are gaining importance
[1]. The interest behind this development is due to the nanoscale dispersion (the thickness of the layered
silicates is ca. 1nm) and very high aspect ratio of the silicate platelets (length to thickness ratio is up to 2000)
[2] enabling high reinforcing efficiency even at low LS loading. In order to make the polar LS compatible wit
nonpolar polymers and thus to facilitate the exfoliation of LS, the silicates are made organophilic [e.g. [2-3]
This occurs by exploiting the cation exchange capacity of the LS. Organophilic LS are, however expensiv
which forced the researchers to have a look at alternative methods. Non-organophilic (pristine) LS can b
dispersed in water which acts as swelling agent via hydration of the intergallery cations (usually Na^+ ions)
Note that several rubbers are available in latex form which is rather stable aqueous dispersion of fine rubbe
particles (particle size usually below 5 µm). Mixing of latex with LS followed by coagulation is therefore at
interesting way to produce rubber nanocomposites. This route has been already followed for natural (NR) [4
styrene/butadiene (SBR) [5-6], acrylonitrile/butadiene (NBR) [7] and carboxylated NBR [8]. On the othe
hand, no report is available on LS-reinforced latex blends. This is quite surprising as latex combinations ar
widely used to improve some praxis-relevant properties of the constituents. Note that NR has to b
filled/reinforced owing to its moderate tear strength [e.g. 9-10]. In order to improve the resistance to solven
(specially towards hydrocarbons), to abrasion and to UV-irradiation, NR is often blended with polyurethan
rubber (PUR). Accordingly, the aims of its present work were a) to produce LS-reinforced NR/PUR-base
nanocomposites via latex compounding, and b) to study their morphology-dependent mechanical properties

EXPERIMENTAL

Materials. As LS a synthetic sodium fluorohectorite (Somasif ME-100) of Co-op Chemicals (Tokyo, Japan) was selected. This LS had a cation exchange capacity of 100meq/100g and an intergallery distance of 0.95nm. Note that this LS exhibits a very high aspect ratio, viz.>1000 [4, 11].

Sulfur prevulcanized NR latex was procured from Rubber Research Institute of India (Kerala, India). This concentrated, high-ammonia (1%) NR latex contained 60% dry rubber. For prevulcanization this latex was mixed with the ingredients listed in Table 1 with slow stirring. The compounded latex was then heated to 70°C in a water bath with low stirring for 4h. The prevulcanized latex that obtained was cooled to room temperature and the initial ammonia content was restored by adding ammonia solution. The NR latex was then stored in tight plastic bottles until use.

PUR latex (Impranil DLP-R) containing ca. 50% polyester-based polyurethane was supplied by Bayer (Leverkusen, Germany).

Film casting. The prevulcanized NR latex was mixed with the aqueous dispersion of LS (10%) and stirred well. The dirt and coarse particles were removed by filtering through a sieve (opening 250µm) and the latex compound was cast in a mold build of glass plates (dimensions: 130mm x 100mm x 2mm). The casting was allowed to dry in air till transparent and post vulcanized at 100°C for 30 minutes in an air circulated oven. Fully vulcanized samples were then cooled and packed in sealed polyethylene bags for testing.

Aqueous dispersion of LS was added to the PUR latex stirred and cast as indicated above and air dried till transparent. Note that PUR has not been cured.

Latex blends with various PUR/NR ratios (viz. 1/1 and 8/2) with and without LS were produced in a similar way as described above.

Morphology detection. The dispersion of LS in the latex films was studied by X-ray diffraction (XRD) and transmission electron microscope (TEM). XRD spectra were obtained in transmission mode using Ni-filtered CuKα radiation (λ=0.1542nm) by a D500 difractometer (Siemens, Germany). The samples were scanned in step mode by 1.5°/min rate in the range of $2\theta<12^{\circ}$. For comparison purpose the XRD spectrum of the LS powder was also registered, however, in reflection.

TEM images were taken in LEO 912 Omega microscope with an accelerator voltage of 120keV. Thin sections (ca. 100nm) of the specimens were cryo-cut with a diamond knife at ca. –120°C and used without staining.

In order to get a deeper insight in the possible interaction between LS and rubber Fourier transform infrared spectroscopic (FTIR) measurements were also done. FTIR on the films was performed in attenuated total reflection mode (ATR) at a resolution of 4cm^{-1} using a Nicolet P 510 spectrometer. LS powder was pressed with KBr powder for FTIR measurements in transmission mode.

Property assessment. Dynamic mechanical thermal analytic (DMTA) spectra of the films were recorded by an Eplexor 25N device (Gabo Qualimeter, Germany) in tension mode at 10Hz frequency. The complex elastic modulus, its constituents (viz. storage, E'and loss parts, E") along with the mechanical loss factor (tanδ) were determined as a function of the temperature (T = -100°C...+60°C). The static and dynamic tensile load applied were 2 and ±1N, respectively and the heating rate was set to 2°C/min.

Tensile tests to determine the ultimate properties (strength, elongation) along with the moduli at selected elongations were performed at room temperature (RT) on dumb-bells according to ASTM D 412 using 500mm/min crosshead speed . The tear strength at RT was determined according to ASTM D 624 using crescent shape specimens at a crosshead speed of 500mm/min. The tensile and tear properties were determined also after heat aging (storage for 7 days at 70°C).

RESULTS AND DISCUSSION

Morphology. Figure 1 shows the XRD spectra of the LS and the LS-containing films of various compositions. Note that the LS shows two smaller peaks in addition to the major one. These peaks correspond to the following interlayer distances based on the Bragg's equation: 1.22, 1.10 and 0.95nm. So the LS used contained some small fractions with higher intergallery distance than the bulk material. LS has been intercalated by NR in the related compound as the interlayer distance of the LS increased to 1.19nm -

1.31nm. The appearance of the related broad peak suggests that the degree of NR intercalation is different. A considerably better intercalation was noticed for the PUR latex where two peaks were resolved. The major peak indicates that the interlayer distance of the LS widened to 1.73nm from the initial 0.95nm. This effect can be assigned to the higher polarity of PUR compared to NR which favors the compatibility with LS. Similar to PUR the NR/PUR latex blend shows also two peaks. Albeit they appear at slightly higher interlayer distances than in PUR, these peaks are likely the same. The intensity ratio of these peaks is, however, opposed to that of the pure PUR nanocomposite. Before discussing this aspect attention should be paid to results achieved by TEM and FTIR.

TEM pictures in Figure 2 evidence the good intercalation of LS by PUR. One may get the impression that a part of LS has been even exfoliated. Pictures in Figure 2 demonstrate further the high aspect ratio of the LS. This is becoming obvious when the size of the flat-one laying platelets (disks) in Figure 2b are considered.

The dispersion of LS in PUR/NR (1/1) latex blend differs considerably from that of the PUR. TEM picture in Figure 3 show that NR and PUR are not compatible. Note that particles from the sulfur prevulcanized NR appear dark in these TEM images. Layered silicate stacks can be located at the boundary of the PUR (light) and NR (dark) phases. Pronounced intercalation and possible exfoliation took place only in the PUR phase - see Figure 3b. The silicate layers and aggregates cover the NR particles resulting in a skeleton (house of cards) structure. This peculiar morphology is rather specific for NR nanocomposites produced by the latex route if the length of the LS is commensurable with that of the rubber particle size in the latex. Based on the TEM results we can now explain the difference in the XRD spectra of the PUR and PUR/NR latices. Recall that LS is less intercalated by NR than by PUR. So, in the case of the PUR/NR blend, PUR should intercalate the double amount of LS due the volume excluded by NR. Bearing in mind that there is an optimum in the LS content in respect to intercalation/exfoliation phenomena, a substantial increase in the LS may cause its reaggregation (confinement). However, this does not yield necessarily a deterioration in the mechanical properties. Recall that the prevulcanized NR particles force the silicate aggregates in the neighbouring PUR phase to cover their surface. This results in a skeleton morphology as the length of the silicate layers is higher than those of the diameter of the particles (Figure 3). The formation of this skeleton structure may yield improved mechanical properties.

Interesting information can be derived from the FTIR analysis, too. Several attempts to characterise PUR/clay [12-14] or NR/clay [15-16] nanocomposites using FT-IR spectroscopy have already been made. In most of the cases just the verification of the incorporation of the clay into the matrix was the outcome. Differences between the spectra of unfilled material and nanocomposite were searched among peaks corresponding to vibrations of the macromolecular chains of either PUR or NR. Chen et al. [12] tried to estimate the degree of interaction between the silicate layers and the PUR segments evaluating the ratio of the absorption peaks of the hydrogen bonded and the free groups of NH or C=O. Recently, Loo et al. monitored the stress-induced peak shift in the Si-O stretching vibration of montmorillonite clay in nylon-6/nanoclay nanocomposite [17]. The vibration of the Si-O bond was found to be sensitive to stress showing a shift to lower wavenumbers with increasing level of strain.

The absorption bands in the infrared (IR) spectrum of various layered silicates depend on their chemical composition [18]. In case of fluorohectorite the IR spectrum presents mainly two peaks corresponding to the Si-O stretching vibration at the 1005 cm^{-1} and the Si-O bending vibration at the 476 cm^{-1} [13, 17, 18]. The sensitivity of these peaks to intercalation/exfoliation phenomena is an aspect observed in the current paper.

As presented in Figure 4, the Si-O stretching vibration at the 1005 cm^{-1} in the case of PUR/LS system is appearing as a shoulder around 990 cm^{-1} superposed to the 967 cm^{-1} peak of PUR. Moreover, the Si-O bending vibration at the 476 cm^{-1} is shifted to the 467 cm^{-1} presenting a clear peak due to the fact that at that region the PUR does not present any peak. Considering the fact that the PUR is capable of intercalating the layers of LS (i.e. TEM and WAXS experiment), the peak position is likely due to the interaction of the macromolecular chain with the silicate layers.

Figure 5 presents the spectra in the case of NR/LS system. The Si-O stretching vibration at the 1005 cm^{-1} and the Si-O bending vibration at the 476 cm^{-1} are shifted to 998 cm^{-1} and 470 cm^{-1} respectively. According the TEM and WAXS findings, the NR/LS system showed less significant intercalation (and thus layer expansion) than PUR. This means that the interaction between the NR macromolecular chains and the layered silicate is rather low. Respectively, the peak shift in the IR spectra for the NR/clay nanocomposite was also slighter than the shift for PUR/clay nanocomposite.

The spectra of the PUR/NR blend reinforced with LS is presented in Figure 6. The Si-O stretching vibration at the 1005 cm^{-1} and the Si-O bending vibration at the 476 cm^{-1} are shifted to 994 cm^{-1} and 468 cm^{-1} respectively. This means that there is a rather good intercalation of LS in the blend, similarly to the neat

PUR. Considering the TEM images, the component that worked as intercalant in the blend was the PUR rather than the NR.

Consulting the above mentioned results, it is clear that PUR has two favourable peaks in the case of the XRD spectra. This means that there are two favourable and possible distances between the layers of the silicate during intercalation. In the case of the spectra from the blend these two peaks are also appearing but with totally opposite intensity. The volume during the mixing of the materials (glass plates) was each time the same and PUR is obvious that intercalates much better than NR (XRD spectra). Considering that in the case of the blend the volume that possess the two components is the half that they were possess alone in the glass plate, excluded volume phenomena should be present (also restricted mobility of macromolecular chains). The LS is mainly in the PUR area (TEM images), so the amount of LS that should be intercalated by PUR is not actually 10phr but something less than 20phr. Having in mind that there is an optimum in LS content in order intercalation/exfoliation phenomena to take place (enhanced properties at low filler level) [1, 19-20], the increase of LS content in the PUR area should act reversal to the phenomenon. The NR/LS system gives raise to a peak in the XRD spectra around 7 degrees. Thus, the main peak for the blend around 7 degrees is quite logical, presenting also a smooth peak around 4.5 degrees.

Thermomechanical properties. Figure 7 shows the course of the storage modulus (E', Figure 7a) and mechanical loss factor (tanδ, Figure 7b) as a function of temperature for the latices studied. Comparing the DMTA traces of the plain rubbers with that of the blend one can notice that PUR and NR are fully incompatible. This is based on the fact that no change in the related glass transition temperatures (T_g) occurs due to blending and the stiffness follows the composition at ratio. This finding is in harmony with TEM results. The nanoreinforcement proved to be very efficient below the T_g of the matrix (plain rubbers) and below the component with the higher T_g (blend rubbers), respectively. The stiffness of the plain rubbers was increased by 1200-1500MPa (depending on the temperature) owing to 10% LS. One can notice that the formation of a skeleton structure in NR and PUR/NR blend is as efficient as the markedly better intercalation, however, without skeleton structure in PUR. Figure 7b demonstrates that nanoreinforcement caused a dramatic decrease in the tanδ. This finding is in concert with the expectation: the molecular mobility is strongly hampered owing to the strong LS/rubber interactions. Note that in Figure 7a the major reason of blending NR with PUR is obvious: the blend exhibits a markedly higher stiffness than NR up to $T \approx 10^{\circ}C$ (T_g of PUR).

Tensile mechanical properties. Table 2 lists the mechanical properties of the rubbers and their nanocomposites before and after heat aging. Note that LS nanoreinforcement was very effective for PUR. The ultimate tensile strength as well as tear strength strongly increased (more than 3 times) and a dramatic improvement was found in the moduli at different elongations. As expected, the LS reinforcement strongly decreased the ultimate elongation. A similar scenario, however, with less improvement in the stiffness and strength was found for the NR. The most interesting results presented the PUR/NR (1/1 and 8/2) blend based nanocomposites due to their excellent mechanical performance. So, part of the expensive PUR latex can be replaced by inexpensive NR latex without sacrificing the mechanical response of the nanocomposites. A further advent of compounding NR with PUR is related to the aging of the latter. Heat aging of PUR accompanied with crosslinking (via interchange reactions) which enhances the stiffness and strength data of PUR, PUR-containing blend and related nanocomposites.

CONCLUSIONS

Based on this work devoted to study the morphology dependent mechanical properties of layered silicates (LS) reinforced NR-, PUR- and PUR/NR-blend based nanocomposites produced by the latex route, the following conclusions can be drawn:

- LS is more compatible and thus better intercalated by PUR than by NR. In the case of sulfur-prevulcanized NR latex and its blends with PUR the LS forms a skeleton (house of cards) structure. The onset of this structure is favored by the prevulcanization of the NR. The reinforcing efficiency of the skeleton-type structure (NR) was comparable with that of composed of LS layers and stacks (PUR).
- Albeit PUR and NR are completely incompatible, the mechanical properties of the nanocomposites based on their blends (PUR/NR ratios 1/1 and 8/2) agreed with those of the plain PUR. The effect of LS dispersion (intercalation/exfoliation) was best reflected in stiffness- and strength- related characteristics.

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Figure 1. XRD spectra of the layered silicate (LS) reinforced latex nanocomposites of various compositions

Note: for comparison purpose this figure contains the XRD spectrum of the LS (sodium fluorohectorite), as well

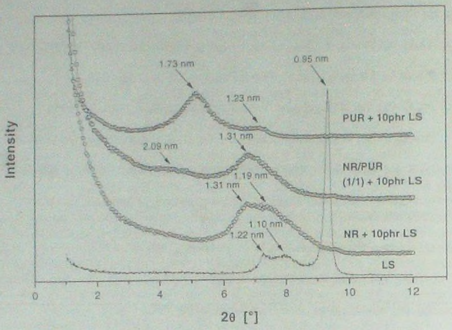

Figure 2a.

Figure 2b.

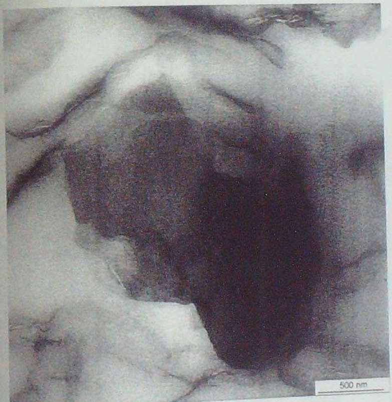

Figure 2. TEM images taken at various magnifications from the film cast of PUR latex containing 10phr LS

Figure 3a.

Figure 3b.

Figure 3. TEM pictures taken from the film cast of the PUR/NR (1/1) latex blend containing 10phr LS

Figure 4. FT-IR spectra of PUR, LS and PUR reinforced with LS 10phr

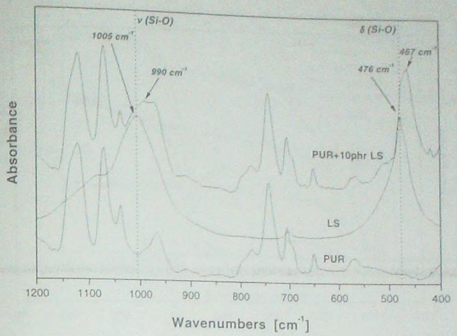

Figure 5. FT-IR spectra of NR, LS and NR reinforced with LS 10phr.

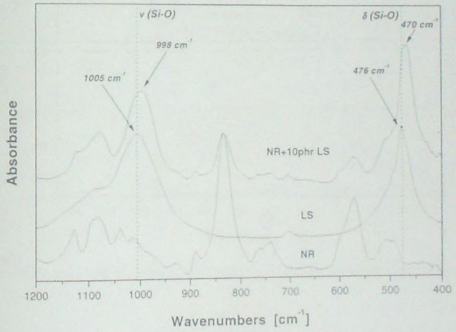

Figure 6. FT-IR spectra of PUR/NR (1/1) blend, LS and PUR/NR (1/1) blend reinforced with LS 10phr

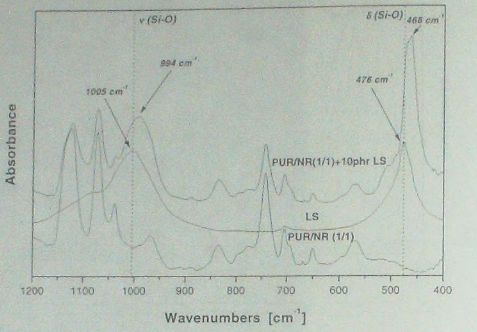

Figure 7a.

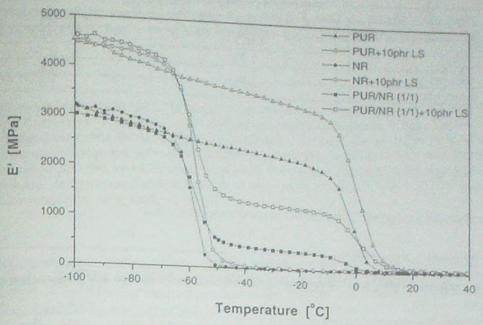

Figure 7b.

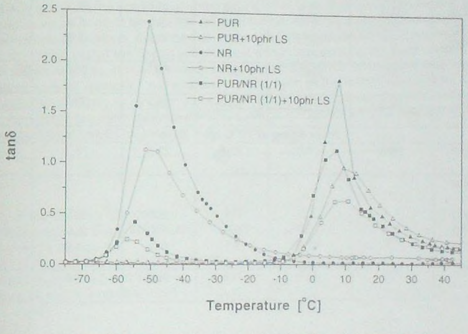

Figure 7. Storage modulus and mechanical loss factor as a function of temperature for pure and reinforced systems

Table 1. Formulation of NR prevulcanized latex. Designation: ZDMC is zincdimethyldithiocarbamate

	Formulation	
	wet	dry
NR latex (60%)	166.7	100.0
10% KOH solution	1.0	0.1
50% ZDMC dispersion	2.0	1.0
50% sulfur dispersion	2.0	1.0

Table 2. Mechanical properties of the rubber nanocomposites studied

Before aging						
Property	PUR	PUR+LS 10phr	NR	NR+LS 10phr	PUR/NR (1/1) +LS 10phr	PUR/NR (8/2) +LS 10phr
Tensile strength (MPa)	4.0	15.9	19.6	23.5	12.4	11.4
Tensile modulus (MPa)						
100% Elong.	0.8	5.6	0.7	2.1	4.3	4.9
200% Elong.	0.9	7.8	0.9	3.1	5.9	6.7
300% Elong.	1.1	10.1	1.1	4.5	7.5	8.4
Elongation at break (%)	932	543	881	697	556	469
Tear strength (kN/m)	12.3	54.5	28.0	36.7	59.9	50.7
After aging at 70°C for 7 days						
Tensile strength (MPa)	10.5	17.9	20.8	23.5	16.7	17.5
Tensile modulus (MPa)						
100% Elong.	1.1	7.6	0.7	2.7	6.7	7.4
200% Elong	1.4	10.7	0.9	4.2	9.4	10.4
300% Elong.	1.8	13.5	1.1	6.0	11.6	13.0
Elongation at break (%)	772	444	768	620	484	447

NATURAL RUBBER LATEX CONDOMS - REQUIREMENTS SET FORTH IN INTERNATIONAL STANDARD VS. REAL-TIME AGEING STUDIES

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ABSTRACT

As regards products made from natural rubber 1awx, the ageing process and - in connection with it - the shelf life is deemed an important aspect. Condoms fall within the regulations laid down in the Medical Device Directive 93/42/EEC, in which special requirements have been set forth with regard to the storage: period and the evidence provided for it. For that reason, after several years of discussions held in the international countries, an Arrhenius method - determination of the burst volume and the burst pressure after an artificial ageing carried out in an ageing oven - was added to the ISO standard to determine the period for which a condom type complies with the minimum requirements. At that time, the method was not validated. In the meantime, it has, however, been shown by means of test results presented from real-time studies and those received - both with anti-oxidants and without - from ageing oven tests that the real processes develop in a much more complex way. Owing to the fact that different temperatures at which the tests are performed entail completely different reactions, the Arrhenius method cannot be applied without any restrictions. It has turned out that, on condition that the ageing is carried out a high temperature, the burst pressure tends to decrease more remarkably than in reality, whereas the burst volume tends to decrease less remarkably than in real-time measurements. Moreover, some further aspects, such as the form of the condom, the lubricant and the packing format will have to be taken into account. It is true that this way, by means of a changing of the formulation, condoms can specifically be modified to be "in conformity with the standards", but this does not result in any additional benefit for the user.

CONTENTS

TS: DIN 58993 : 1991 7 > /
Force at b: EN 600 : 1996
Burst pres: ISO 4074 :

HISTORY OF THE CONDOM STANDARDS

The purpose of this lecture is to give you an impression of the present knowledge regarding the ageing behaviour of natural rubber latex condoms and to describe in which way the ageing tests are integrated into the standard quality tests.

When AIDS came into the mind of a wide public in the 1980s, the safety of condoms became more and more important as well. In Germany, the first national standard – DIN 58993 [1] - was released in 1991. Since 1993, condoms have been considered as medical products in Europe (Medical Device Directive 93/42/EEC) [2], and since that time, a lot of new regulative requirements arose also for condoms.

In 1996, the European standard EN 600 [3] superseded the national standards. The consensus included an accelerated ageing test (test of force at break after 2 days / 70°C, minimum 39 N) with partly lower requirements than those that were stipulated in the former standards. The former German standard included a tensile strength test to be carried out after 7 days / 70°C with a limit of 17 MPa, which approximately equals 40 – 50 N force at break. Real-Time tests were not carried out.

The CEN decision to draw up a condom standard that should worldwide be valid resulted in a lot of changes. The work regarding the next revision of EN 600 was in accordance with the Vienna agreement delegated to an ISO committee, which resulted in a clash of interests. It was decided that the tensile test carried out after artificial ageing should be replaced by the burst test after artificial ageing. This test is performed by filling the condom with airflow, and recording the volume and the difference in pressure between the inside and the outside of the condom. In the United States, this test used to be carried out already before the current revision of ISO 4074 for condoms came into force.

To observe both national laws and international regulations, the members of the ISO Technical Committee 157 also strived at finding methods to perform real-time ageing tests and also methods to estimate the shelf life of condoms. In EN 600, the shelf life was defined to 5 years, which was just a period taken from experience. After several years of discussions, ISO 4074:2002 [4] was finally released and adopted as EN. It includes a method to estimate the shelf life of condoms by performing burst tests after artificial ageing and calculating the shelf life by means of an Arrhenius approach.

TENSILE STRENGTH VS. BURST VOLUME AND PRESSURE

It is a widely used method in rubber industry to test the material properties by performing tensile tests with defined bodies like the well-known S2 body. The advantage of the method is that you can compare the properties of many different rubber articles. Since condoms are much thinner than S2 bodies, ring samples were used for tensile tests. They can easily be cut off the condom and either the thickness, which is independent from the tensile strength or the force at break can be measured simultaneously with the elongation. This was an established test method in nearly all the standards in European countries before EN 600 came into force. The ageing test was a tensile test carried out with artificially aged condoms and turned out to be advantageous to find out possible vulcanisation faults, but it was not possible to find a correlation between the shelf life and the tensile results before and after ageing.

In the USA, the ageing behaviour was tested by means of a burst test (see above) carried out with artificially aged condoms as stipulated in former editions of ISO 4074. It is also a stress/strain test, but there are many more parameters influencing the results, such as the shape of the condom (for example: contoured condoms and dotted condoms have lower burst volumes, small condoms have a relatively high burst pressure). The results of the burst tests are more dependent on film inhomogenities, as these are possible reasons for bursting.

Some experts argue that this test is a better test for the realistic performance of a condom, as the entire condom is tested. However, there is a limit to the test. The tip area, which is the part undergoing the highest stress during use, is elongated by 50 % only, whereas most parts of the condom are elongated by about 800 % [5].

The tensile test is more complicated to perform, as the results of the tests are remarkably influenced by the skill of the personnel who cut the samples. Moreover, the equipment required for the tensile test is more expensive than the burst testers.

However, it was decided to take the burst test as a basis for ageing studies and an estimating of the shelf life.

THE ARRHENIUS APPROACH

The discussions held in the ISO 4074 committee led to the following result: It was postulated that the degrading of burst pressure and burst volume follows an Arrhenius equation like most chemical reactions do. The method was successfully applied for the results of tensile tests for many hard rubber articles.

Practically, the burst volume and the burst pressure are plotted against the time at a given ageing temperature for different ageing times. In theory, the time values of different temperatures can be transformed to equivalent times at a reference temperature by multiplying them by a factor given by the Arrhenius equation:

$$a_T = e^{-(E_a{}^*(1/T_{ref}\quad 1/T_{age})/R} \qquad \text{Equation}$$

Where:

E_a is the activation energy (in J/mol)
R: is the universal gas constant (8.31 J/mol^{-1}K^{-1})
T_{ref}: is the reference temperature (in K, here: 303 K)
T_{age}: is the temperature at which the ageing is carried out (in K)

The Arrhenius energy was taken from the literature [6] and set to be 83 KJ/mol. Tests should be performed for different ageing temperatures at different ageing times. The property/equivalent time plots of different ageing temperatures should then theoretically superpose in one single master curve.

The shelf life should be calculated from the master curve as the time at which the burst properties are not any more in compliance with the standard requirements (18 l burst volume and 1.0 kPa burst pressure). The mean value of the properties minus 2 – 3 standard deviations shall be higher than the minimum limit.

The method was not validated before it was included in the standard. There were very few published data at that time.

RESULTS OF ACCELERATED AGEING BURST TESTS

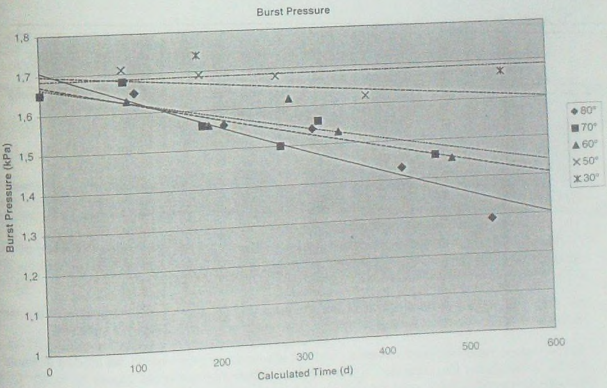

Figure 1 – Burst Pressure

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In the meantime, we have different measuring data available that we obtained from condom batches that show significant results. If we calculate with the postulated Arrhenius energy of 83 kJ/mol (and use the time shift factors from ISO 4074), we find that the burst pressure strongly decreases at high temperatures, whereas it decreases much more slowly at lower temperatures like 50 °C. This is demonstrated in figure 1 for temperatures between 50°C and 80°C. For each temperature/time point, 32 condoms were burst and the mean values of the burst pressure and the burst volume and their standard deviation were recorded. The 30°C values are those obtained from real time studies, which will be analysed in the next chapter. The condom is a cylindrical smooth condom with tip, coloured and flavoured (yellow / banana flavour). The described behaviour was stated in nearly every batch that was examined. The curves resulting from the single measuring data points are exponential fittings.

As regards the burst volume (figure 2), we stated the opposite behaviour. Although the tolerance of the burst volume values is higher and there is a higher variety in the results, we find that at high temperatures, the burst volume decreases more slowly than it does at low temperatures. The curves obtained for 50°C and 60°C are nearly the same as those obtained for 70°C and 80°C. Again exponential fittings are used. In this case, the results are obtained from a contoured smooth uncoloured condom with tip and silicone lubricant.

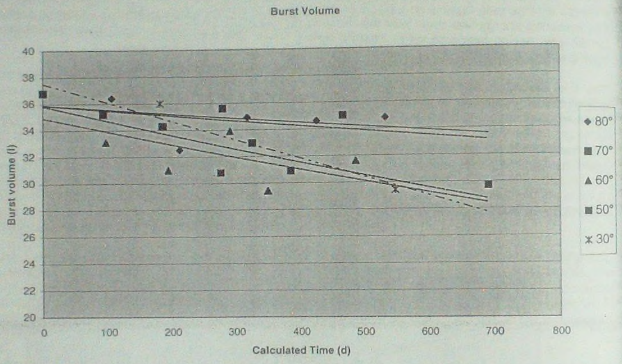

Figure 2 – Burst Volume

Experience has shown that the curves do not superpose for different temperatures. Furthermore, in ISO 4074, the product of burst pressure and burst volume is also taken into consideration, although this value is of no physical importance, the more so as the behaviour is different, because the graphs so not superpose.

The next step in our work was to examine if the superposing of the temperature curves could be realized by using a different Arrhenius energy. In case of the burst pressure, this will theoretically be possible (figure 3) if the Arrhenius energy is remarkably higher (about 120 KJ/mol).

But does this make a physical sense? If yes, the burst volume must show superposing of the temperature curves at the same Arrhenius activation energy. The results we obtained were not sufficient.

As the method described is not mandatory and it is allowed to vary the method, we tried to estimate the shelf life by extrapolating the decreases of the curves at different temperatures (figure 4) to 30 °C. It is then theoretically possible to calculate the shelf life from the decreases at 30 °C. But the result extremely depends on the fitting that is used. It is not applicable for the standard, because the user has a lot of freedom to obtain the results he prefers.

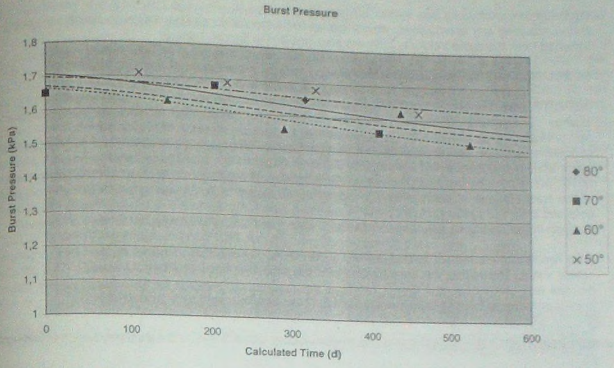

Figure 3 – Burst Pressure at Different Activation Energy

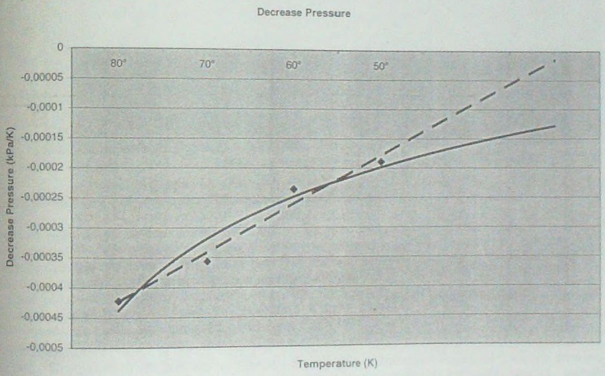

Figure 4 – Decrease of Pressure at Different Temperatures

Before drawing any conclusions, we compared the accelerated ageing results to real-time ageing results obtained from the same batches. They are also included in figures 1 and 2.

RESULTS OF REAL-TIME BURST TESTS

ISO 4074:2002 requires that real-time ageing measurements are performed at 30°C in order to simulate the storage conditions given in many southern countries. As this method is new and since we started our real-time studies at 30°C in 2001 only, we have at present no results for the proclaimed maximum shelf life of 5 years (a longer period is not allowed). But the results obtained from tests carried out with samples 2 ½ years after production at 30°C show that the tendency from the accelerated ageing studies continues: At 30 °C, the burst pressure nearly shows no degradation within 2 ½ years. On the other hand, the mean value of the burst volume is decreasing significantly by about 20 to 25 % compared to the original test result obtained after the production. Problems concerning non-compliance of the condoms with the requirements set forth in the standards can thus be expected after some time only with regard to the burst volume.

If we revert to the standard ageing test of 7 days / 70°C, we see that in this case, the burst pressure is the critical value. The higher the temperatures are, the more the burst pressure decreases. The conclusion is that the test carried out at 7 days / 70°C can be used as a crash test for the stability of the batch under special conditions, but it is not a good prediction of the real-time behaviour of the batch.

There was a consensus made at the last ISO TC 157 meeting in Denver about this point [7]. Several presentations of data showed that an estimation of the shelf life cannot be done in this way.

The Arrhenius equation is normally valid for one defined reaction. But in this case, several chemical reactions influence the product. The vulcanisation leads to different results depending on the reaction temperature, the accelerator system and the concentrations of sulphur and zinc oxide. The most important factor is the chain length of the sulphur in the bonding between different polymer chains (figure 5).

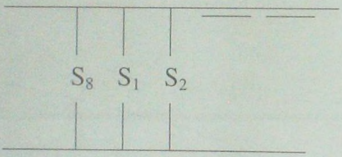

Figure 5 – Different Sulphur Chains

At low vulcanisation temperatures, most sulphur chains have eight atoms; at higher temperatures the chains become shorter because of degradation. This has an influence on the flexibility of the polymer. The ratio of mono-, di- and polysulfid bondings is a characteristic value for the physical properties of the polymer, because this ratio is different at different accelerated ageing temperatures.

The main ageing mechanisms in NR are reversion (thermal ageing), oxidation, UV ageing and ozone ageing. The condoms are well protected from UV, oxygen and ozone in their sealed packages that are usually made from foil, consisting of different polymers and an aluminium layer, but there is nearly no protection from heat. That is why we can assume that the degradation of polysulfid bondings to mono- and disulfid bondings and, as a result, the reaction of cyclic thioethers with the polymer chain (the so-called reversion) is the most important ageing mechanism for condoms in sealed packages (according to the standard they should be aged in closed packages). At higher temperatures, a cracking of carbon–carbon bondings is not impossible either. But in the standard ISO 4074, the Arrhenius energy of 83 kJ/mol was taken from an examination about an oxidation process of rubber, a completely different reaction.

More arguments against the Arrhenius model are the influence of lubricants (swelling effects) and of the sealing format. When a condom is sealed into a square format package, the ageing behaviour is significantly better than in a rectangular package in which one side is remarkably smaller that the other one. 30 X 70 mm used to be a widely used format for condoms. But in this case, the condom is forced into a special position, and viscoelastic effects also influence the ageing performance.

In the tensile test, the stress that the condom undergoes is defined and uniaxial, whereas, as regards the burst test, the stress behaviour is three-dimensional and complicated, which is one more reason for the fact that an Arrhenius approach is not successful. As mentioned before, special shapes have a significant influence on the burst test results, but not really on the results of the tensile test.

INFLUENCE OF ANTI-AGEING CHEMICALS

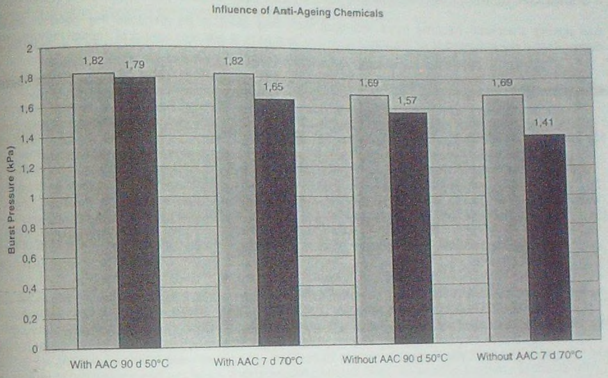

Figure 6 – Influence of Anti-Ageing Chemicals: Burst Pressure

The new requirement set forth in ISO 4074:2002 to the effect that real time ageing should be performed at 30°C instead of room temperatures leads to higher requirements regarding the condoms if a manufacturer wants to stipulate the same shelf life as before. This can be influenced by changing the sulphur/accelerator ratio or by using anti ageing chemicals. Anti ageing chemicals - we do not use the word antioxidants, as the process in question is not an oxidation - were often not used in the condom compounds, especially by European manufacturers. However, the importance of these chemicals has come to grow. As regards our experiments, we used a well-dispersed mixture of a highly active polyphenolic additive and alkylated phenols that does not have any colouring effect on the product and that is well effective against both oxidation and thermal mechanisms. In figure 6 some results can be seen for smooth, cylindrical non-pigmented condoms.

The ageing conditions were 7 days / 70°C and 90 days/ 50°C, which is obviously closer to the conditions that should be simulated. The results were obtained at the same dipping line under nearly the same conditions, but a different batch of latex was used. This fact and a different wall thickness seem to be the main reasons for the different burst pressures in the beginning. As a result, we can see that it is possible to improve the probability of complying with the standards if anti ageing chemicals are used. It seems that also real-time ageing results will get better, but this needs further investigations. So far no negative influences on other properties have been found. Another important test for condoms is the bio-burden test that has not been done yet, but as the concentration of the anti-ageing chemicals used was very low, it should be no problem.

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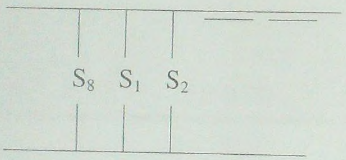

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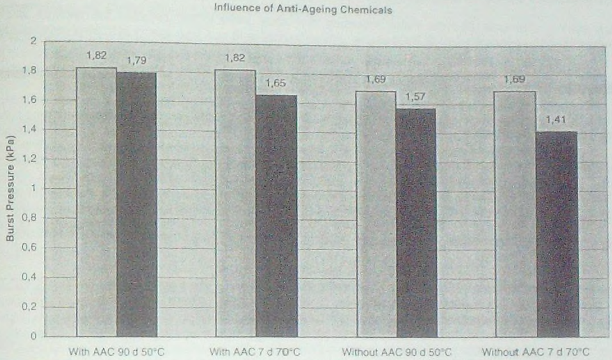

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CONCLUSIONS

We wanted to show in this lecture that only validated methods or at least those where a long-time experience is available should be made integral parts of standards. In ISO 4074, there is a method described for the estimation of the shelf life that may result in wrong predictions and lead to recalls or claims regarding condoms that comply with all the requirements regarding real-time tests. A second disadvantage of the method is that some problems, such as negative effects on the burst volume, might not be found. A scientifically serious estimation of the shelf life is not possible. Condom suppliers usually have a quality management system according to ISO 9001. This standard requires that all new processes, including testing procedures – be validated before they are established. But in this case, the testing standard is not validated.

The ISO standard will be revised. Owing to the fact that there is no other validated method for the time being, we think that the only reasonable method is to estimate the shelf life from real time data by extrapolating real time data to the indicated shelf life. The ageing test for a batch can be regarded as a crash test. It is no prediction for the real time behaviour, but it can be a statement about how the properties of the batch react to a defined input of heat. Therefore the number of samples can be reduced.

Anti-ageing chemicals become more important than they used to be, because the condom standard demands that the indicated shelf life must be verified by means of real time ageing at tropical temperatures.

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THE ANATOMY OF INTER-MATERIAL COMPETITION IN SYNTHETIC LATEX POLYMERS: JAPAN AND CHINA

LaVerne W. Ellerbe & Ian Butcher
Kline Group, USA & Ian Butcher, Kline Group, Belgium

BIOGRAPHICAL NOTE

LaVerne W. Ellerbe is an industry manager in the Chemicals and Materials Practice of Kline & Company's Syndicated Research Division. Kline & Company, Inc. is a global consulting firm serving the chemical, materials, petroleum and consumer products industries. Prior to joining Kline, Ms. Ellerbe held management positions at FIND/SVP, Strategic Analysis, ARCO Chemical, and Dow Chemical USA. Her experience includes strategic planning, commercial development, technical services, R&D and manufacturing plant support in the chemical and materials industries. Ms. Ellerbe earned an M.B.A. from the Wharton School of the University of Pennsylvania and a B.S. degree in Chemistry from Norfolk State University. She can be reached at laverne_Ellerbe@klinegroup.com, or by calling 973-435-3431.

Ian Butcher is a Vice President and Officer of Kline & Company and the Managing Director of Kline Europe SA, Kline's European subsidiary. In his 22 years with Kline, Mr. Butcher has completed or managed hundreds of assignments in the chemicals, polymers, lubricants and related businesses. Since 1979 Kline has regularly produced a global series of syndicated studies on Synthetic Latex Polymers (SLP). This series covers the markets in North and South America, Europe, China and the Asia Pacific region. A companion series covers manufacturing Costs Analyses of SLP. Kline frequently provides its consultancy expertise on a proprietary basis to the SLP industry. Mr. Butcher's previous experience includes posts at the Université de Nice in France, several institutions of the EU in Brussels, the SLS consultancy in York and Executive Director at WS Atkins Management Consultants. He has been a regular conference speaker on specialty and fine chemicals and Customer Satisfaction Benchmarking techniques. He has a degree from the University of Kent, a post-graduate qualification from the University of York and a business diploma through the University of Leeds. He can be reached at ian.butcher@kline-europe.com The Kline website is www.klinegroup.com .

ABSTRACT

This paper will discuss the impact of inter-material competition on the net consumption volumes of synthetic latexes and emulsions used in paper, paints and coatings, and adhesive applications in Japan and China. A comparative analysis of industry structure, pricing trends, raw material issues and end-use market needs will be presented, along with differences in future growth prospects for styrene butadiene, acrylic-based emulsions, and vinyl acetate-based emulsions. The impact of inter-material competition on the long-term value of selected latexes and emulsions and projected changes in market position for these products will also be examined.

Introduction

In 2002, the Asia-Pacific region represented about 20% of global SLP demand, with more than two-thirds of this total coming from Japan and China. North America and Western Europe generated 75% of worldwide demand. (Figure 1)

Through 2007, global SLP demand will closely track the growth of key regional economies, and similar to forecast GDP in the highest consuming regions, is expected to grow at about 3% per year. During this time, growth in the Asia-Pacific region is expected to outpace that of North America and Western Europe by more than 60%. Although North America and Western Europe will continue to dominate global SLP demand, these regions are expected to lose market share to the Asia-Pacific region. (Figure 2)

Following industry growth, SLP suppliers with global market positions have increased activity in the Asia-Pacific region. In the process, differing business objectives from multinational, regional and local suppliers are converging to create an increasingly competitive marketplace. As divergent suppliers develop and earmark more products for the same end uses, a highly favorable environment for intermaterial competition is created, which is driven by the following factors:

- Rising and falling growth prospects in key end use markets
- Achieving economies of scale
- Cost-performance tradeoffs
- Concentration and balance among suppliers

Although similar fundamentals drive intermaterial competition in Japan and China, differences in industry structure and market conditions prescribe differential impacts on synthetic latex polymers with respect to product consumption volumes and their related market values. (Figure 3)

Drivers of Intermaterial Competition

The drivers of intermaterial competition and related impacts on different categories of synthetic latexes and emulsions consumed in Japan and China will be examined below.

Rising and Falling Growth Prospects in Key End Use Markets

In paper, paints and coatings and adhesive end uses, one or two core synthetic latex polymers typically account for the lion's share of total demand. (Figure 4) Notwithstanding magnitude, changes in end use market demand always impacts the growth of consumption volume and/or market value of associated synthetic latex polymers. For example, in Japan, styrene butadiene recently experienced net gains in general adhesives as a result of intermaterial competition stimulated by slow growth in traditional paper markets. Likewise, as the nonwovens and textiles markets contracted, styrene acrylic emulsions accrued gains in paints and coatings over vinyl acetate-based emulsions. (Figure 5)

Against a backdrop of robust economic expansion in China, intermaterial competition between styrene butadiene and styrene acrylics in paper and styrene acrylics, pure acrylics and vinyl acetate-based emulsions in paints and coatings has negatively impacted the market value of styrene butadiene, styrene acrylic and vinyl acetate ethylene emulsions. (Figure 6)

Achieving Economies of Scale

SLP capacities tend to be added in large increments, resulting in supply cycles that alternate between periods of excess capacity and insufficient supply. In 2003, both Japan and China experienced periods of excess capacity. While Japan's excess capacity can be associated with reduced demand in a sluggish economic environment, China's can be directly linked to capacity overbuilds in anticipation of increased demand. In both countries, as suppliers with high fixed costs try to utilize a significant fraction of full capacity to achieve breakeven economics, price wars and intermaterial competition are triggered. In 2003, average operating rates for synthetic latex polymer plants operated by the top nine suppliers in Japan and China were 74% and 70%, respectively. Plants operated by small local and regional suppliers tended to have capacity utilization rates below 70%. (Figure 7)

Cost-Performance Trade-offs

Acceptable performance at a given price level is another critical factor in intermaterial competition, since many customers in key end use markets for synthetic latexes are frequently price sensitive. Understanding the relevance of price sensitivity, SLP suppliers typically offer non-core products at lower price points. As customers within a particular end use market gain experience, switching costs decline, increasing the relative ease by which customers can choose differentiated products based on price. For example, price differentials for pure acrylic and styrene acrylic emulsions with comparable % solids range from 30% to 51% in the paints and coatings market in China. Price differentials for styrene butadiene and vinyl acetate ethylene emulsions range from 42 % to 44% in the paper market in Japan. (Figures 8 & 9)

Concentration and Balance Among Suppliers

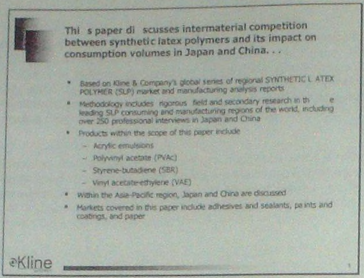
Competition in concentrated markets is typically more orderly than competition in highly fragmented markets. However, although the top nine suppliers control 70% of the market in Japan, intermaterial competition is a still a factor. The effects of consolidation and migration of end use markets offshore have raised the bar on product development and increased consumption of synthetic latex polymers in alternative end use markets.

In China, the top nine SLP suppliers only control 37% of the market. As expected under these conditions, intermaterial competition is not only prevalent, but also provides a vehicle for emerging market leaders to increase overall market share. (Figure 10)

Conclusions

Although at different stages of growth, the markets for SLPs in Japan and China are both subject to a high degree of intermaterial competition. In Japan, the recipe for intermaterial compeition includes low growth prospects in core end use markets, relatively high fixed costs, a variety of product differentiating capabilities and a concentrated base of suppliers. By contrast, China has highly attractive prospects for end use market growth and a fragmented base of suppliers. The common factors driving intermaterial competition in both Japan and China include product differentiation capabilities and the need to utilize excess capacity to cover fixed costs. (Figure 11)

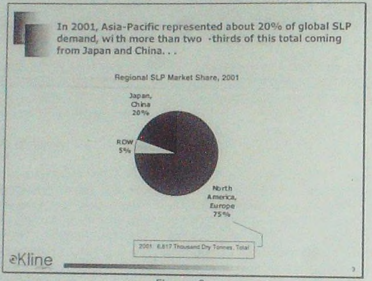
Intermaterial competition is being integrated into the fabric of the synthetic latex polymer industry as suppliers target non-core end use markets for growth, and end users gain experience with different classes of synthetic latex products. Longer term, as market growth normalizes in Japan and stabilizes in China, the prospects for continued intermaterial competition appear to be highly favorable. (Figure 12)



This paper discusses intermaterial competition between synthetic latex polymers and its impact on consumption volumes in Japan and China. . .

- Based on Kline & Company's global series of regional SYNTHETIC LATEX POLYMER (SLP) market and manufacturing analysis reports
- Methodology includes rigorous field and secondary research in the leading SLP consuming and manufacturing regions of the world, including over 250 professional interviews in Japan and China
- Products within the scope of this paper include
  - Acrylic emulsions
  - Polyvinyl acetate (PVAc)
  - Styrene-butadiene (SBR)
  - Vinyl acetate-ethylene (VAE)
- Within the Asia-Pacific region, Japan and China are discussed
- Markets covered in this paper include adhesives and sealants, paints and coatings, and paper

Figure 1

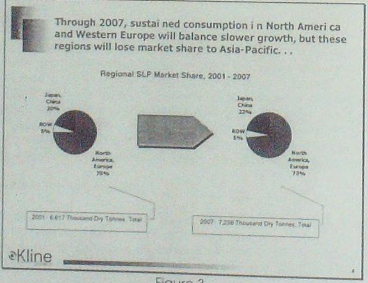


In 2001, Asia-Pacific represented about 20% of global SLP demand, with more than two-thirds of this total coming from Japan and China. . .

Regional SLP Market Share, 2001

2001: 6,817 Thousand Dry Tonnes, Total

Figure 2



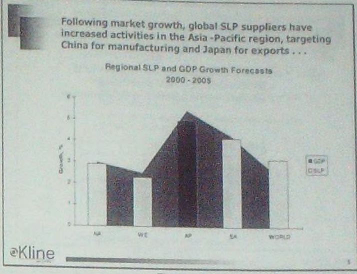
Through 2007, sustained consumption in North America and Western Europe will balance slower growth, but these regions will lose market share to Asia-Pacific. . .

Regional SLP Market Share, 2001 - 2007

2001: 6,817 Thousand Dry Tonnes, Total

2007: 7,298 Thousand Dry Tonnes, Total

Figure 3



Following market growth, global SLP suppliers have increased activities in the Asia -Pacific region, targeting China for manufacturing and Japan for exports . . .

Regional SLP and GDP Growth Forecasts
2000 - 2005

Figure 4

Diverse suppliers in fractured end use markets must leverage market and manufacturing options to gain competitive advantage. . . .

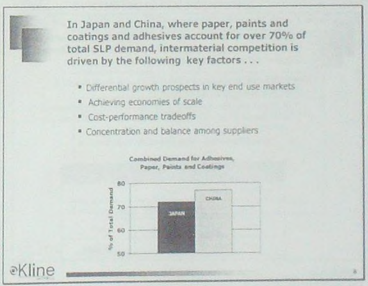
MARKET FACTORS

- Product differentiation
- Political climate
- Alliances
- Logistics
- Technical Service

MANUFACTURING FACTORS

- Technology
- Capacity utilization
- Raw material costs
- Labor costs
- Plant size
- Degree of integration
- Operating flexibility

Figure 5

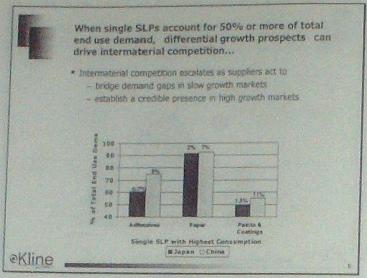


In Japan and China, where paper, paints and coatings and adhesives account for over 70% of total SLP demand, intermaterial competition is driven by the following key factors . . .

- Differential growth prospects in key end use markets
- Achieving economies of scale
- Cost-performance tradeoffs
- Concentration and balance among suppliers

Combined Demand for Adhesives, Paper, Paints and Coatings

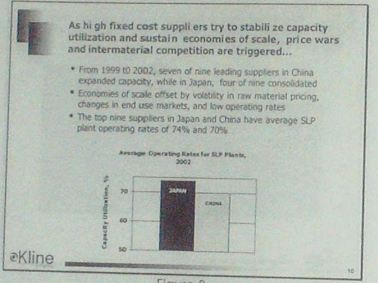
Figure 6



When single SLPs account for 50% or more of total end use demand, differential growth prospects can drive intermaterial competition...

- Intermaterial competition escalates as suppliers act to
  - bridge demand gaps in slow growth markets
  - establish a credible presence in high growth markets

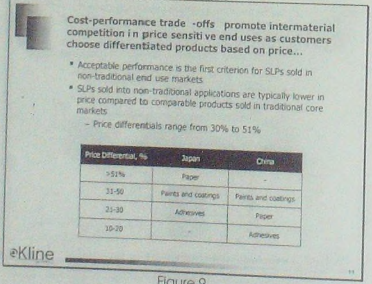
Figure 7



As high fixed cost suppliers try to stabilize capacity utilization and sustain economies of scale, price wars and intermaterial competition are triggered...

- From 1999 t0 2002, seven of nine leading suppliers in China expanded capacity, while in Japan, four of nine consolidated
- Economies of scale offset by volatility in raw material pricing, changes in end use markets, and low operating rates
- The top nine suppliers in Japan and China have average SLP plant operating rates of 74% and 70%

Figure 8

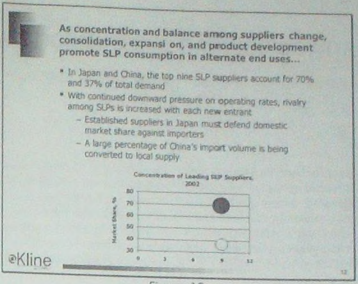


Cost-performance trade-offs promote intermaterial competition in price sensitive end uses as customers choose differentiated products based on price...

- Acceptable performance is the first criterion for SLPs sold in non-traditional end use markets
- SLPs sold into non-traditional applications are typically lower in price compared to comparable products sold in traditional core markets
  - Price differentials range from 30% to 51%

Price Differential, %	Japan	China
>51%	Paper	-
31-50	Paints and coatings	Paints and coatings
21-30	Adhesives	Paper
10-20	-	Adhesives

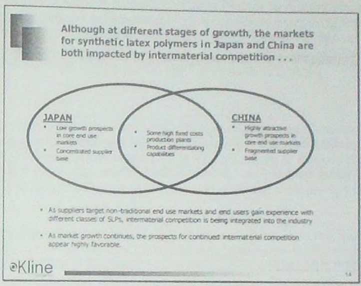
Figure 9



As concentration and balance among suppliers change, consolidation, expansion, and product development promote SLP consumption in alternate end uses...

- In Japan and China, the top nine SLP suppliers account for 70% and 37% of total demand
- With continued downward pressure on operating rates, rivalry among SLPs is increased with each new entrant
  - Established suppliers in Japan must defend domestic market share against importers
  - A large percentage of China's import volume is being converted to local supply

Figure 10



Although at different stages of growth, the markets for synthetic latex polymers in Japan and China are both impacted by intermaterial competition . . .

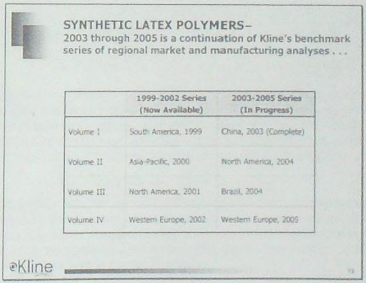
JAPAN
- Low growth prospects in core end use markets
- Concentrated supplier base

- Some high fixed costs production plants
- Product differentiating capabilities

CHINA
- Highly attractive growth prospects in core end use markets
- Fragmented supplier base

- As suppliers target non-traditional end use markets and end users gain experience with different classes of SLPs, intermaterial competition is being integrated into the industry
- As market growth continues, the prospects for continued intermaterial competition appear highly favorable.

Figure 11



SYNTHETIC LATEX POLYMERS–
2003 through 2005 is a continuation of Kline's benchmark series of regional market and manufacturing analyses . . .

	1999-2002 Series (Now Available)	2003-2005 Series (In Progress)
Volume I	South America, 1999	China, 2003 (Complete)
Volume II	Asia-Pacific, 2000	North America, 2004
Volume III	North America, 2001	Brazil, 2004
Volume IV	Western Europe, 2002	Western Europe, 2005

Figure 12

Sports Balls
Improved Tires
Chemical process,
Packaging.

Improved solvent, oil and flame resistant - protective gloves.
30-6000 times improvement
in barrier properties.

Ozone, UV, sunlight.
steam, brake fluid
Water [illegible]

dip coating
soccer balls bladders.
Spray coating
Tires
Tennis balls
Roll to Roll coating
packaging, [illegible]

NANOCOMPOSITE BARRIER COATINGS

Harris A Goldberg, Carrie A. Feeney, Douglas P. Karim, & Michele Farrell
InMat Inc, USA

BIOGRAPHICAL NOTE

Harris A. Goldberg received his Ph.D. in condensed matter theory from the University of Massachusetts in 1975. After a post-doctoral position at the University of Toronto, he began an industrial research career at the Celanese Summit, New Jersey research center in 1978. Working first for Celanese and later for Hoechst Celanese, he made technical contributions and led business development teams in numerous material science areas including carbon and graphite fibers, intercalated graphite, optical recording, non-linear optics, photorefractive polymers, packaging materials, and dielectric composites. He has over twenty patents, and has co-authored over forty technical papers as well as a book entitled *The Physics of Carbon and Graphite Fibers.*

In 1999, he co-founded InMat LLC with his partner, Dr. Carrie Feeney, and with the support of their technical team. InMat has continued to lead the development of nanocomposite barrier coatings, and had its first commercial success when Wilson Sporting Goods introduced their Double Core tennis ball, the official ball of the Davis Cup, in July of 2001. In April of 2003, InMat LLC became InMat Inc. with Pangaea Ventures, NGEN Partners, and DSM Venturing making a significant financial investment.

ABSTRACT

InMat has developed a unique family of nanocomposite barrier coatings based on aqueous dispersions of several polymers. Its first commercial product line (Air D-FenseÔ) is commercially used by Wilson Sporting Goods in its Double CoreÔ tennis ball (the official ball of the Davis Cup) to improve the air pressure retention of that product. That product is 30 times less permeable than the unfilled butyl rubber on which it is based. Up to 300 times reduction in permeability has been achieved while still maintaining the flexibility required of most rubber products.

InMat has also developed nanocomposite barrier coatings based on several other elastomeric and glassy matrices. All achieve large reductions (up to 6000 times) in oxygen permeability relative to the unfilled matrix because of the excellent dispersion of exfoliated clay in the coating. Applications that are currently targeted include sports balls, chemical protective gloves, tires, and packaging. The essential elements of InMat's technology will be reviewed, along with the key advantages of InMat's coating technology for each application.

---

1. INTRODUCTION

The addition of large aspect ratio plates of inorganic filler to polymer in order to reduce the permeation rate of gases and other chemicals has been known for many years[1-6]. Nano-dispersed clay minerals are often used as the filler because of their large aspect ratio, and because they are only about 1 nanometer thick. This means that the particle size can be kept small enough to facilitate processing and to maintain important secondary properties such as clarity. In coatings, the small particle size is critical to obtaining uniform coatings.

Most of the reported work on clay polymer nanocomposites has targeted the production of resin suitable for thermal processing. In such nanocomposites, both mechanical and barrier properties are significantly modified. A coating approach enables one to separate the mechanical characteristics of a product from the barrier properties by providing the barrier in a thin layer. This means that product redesign can be minimized while still providing large improvements in barrier properties.

There are two fundamentally different approaches to nanocomposite barrier coatings. The most straightforward is to dissolve the matrix in a solvent, and use exfoliated clay that has been functionalized so that it can be dispersed in the same solvent. Such organically modified clays are also used in the thermoplastic approach to clay polymer nanocomposites, as they are critical to obtaining good dispersion of the clay in the polymer. One of the earliest coating examples of this approach was described by Ward et. al[2].

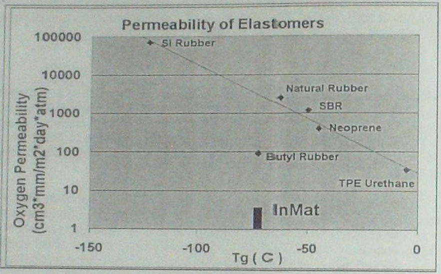
InMat's approach is to start with an aqueous dispersion of a polymer that is not soluble in water. Many layered silicates can be exfoliated and form reasonably stable dispersions in water. We have found that exfoliated clay and suspended polymer can be formed into a single stable dispersion, and that the clay will remain well dispersed in the polymer when these dispersions are dried into coatings. In this paper, we will describe the performance of coatings developed by InMat using this approach.

2. TECHNOLOGY BACKGROUND

The initial issue we addressed was the high permeability of rubber in products that require flexibility but which also function as barriers, either to gases or to chemicals. The most important example was tires, which continuously lose air pressure because of the high permeability of the rubber. The tire industry uses butyl rubber innerliners in order to minimize the air pressure loss in tires. They spend $1 billion / year on the innerliners, and have explored numerous approaches to developing alternatives. We set out to develop a coating that could provide the same barrier as the currently used butyl innerliners, but at lower cost and weight.

Since butyl rubber is the least permeable rubber that remains flexible at low temperatures (see Figure 1) we used it as the matrix for our first formulations. We then chose vermiculite as the first nano-dispersed clay because it has the largest aspect ratio of any commercially available silicate. The aspect ratio of exfoliated vermiculite is approximately 10,000. This means that the plates are locally aligned even at relatively low concentrations in our suspensions. The mesoscopic nature of exfoliated vermiculite suspensions is demonstrated by viewing it between cross polarizers as shown in Figure 2.

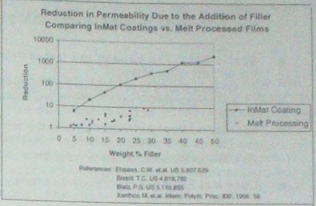
Figure 1:



If one simply mixes exfoliated vermiculite with a commercially available butyl rubber dispersed in water, one would find that the butyl rubber and the vermiculite agglomerate quickly. Careful attention to formulation details such as solid content, surfactants, and other additives, as well as proprietary modifications of the initial clay and polymer suspensions has enabled InMat to produce stable formulations over a wide range of clay to polymer ratios. These formulations are typically sprayed onto polypropylene film for initial oxygen permeability evaluation.

Figure 2: 0.02% dispersion of Microlite™ in water showing oriented domain structure.

Figure 3:



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Bissot T.C. US 4,818,782
Blatz P.S. US 5,110,855
Xanthos M. et al. Intern. Polym. Proc. XIII, 1998, 58

An example of the results achieved is shown in Figure 3. The number of times reduction in oxygen permeability relative to that of the unfilled polymer (butyl rubber) is plotted versus the weight fraction of exfoliated clay in the dried coating. The large reductions achieved by InMat's patented coating technology[7,8] are compared to the reductions achieved using the thermal processing using the same weight percent filler. This shows that the filler remains well dispersed in not only the coating formulation but also the dried film.

o„ol exldatad

In addition to getting large permeability reductions, it was essential that we control the surface interactions of the clay platelets so that the nanocomposites would be flexible enough for applications in elastomeric products. Many elastomeric products must withstand limited strains of no more than 15%. This includes tires and most protective gloves. Fiber re-enforcement always limits the strain that a product can undergo. Nonetheless, it was still a challenge to develop formulations that could have high loadings of nano-dispersed clay and still not be damaged by strains in the 10-20% range. InMat has achieved that through proprietary treatments and formulations, and the results have been presented in earlier articles[9].

We believe that the large reductions in permeability are our best evidence that we maintain good dispersion not only in the formulation, but also throughout the drying process. Significant efforts to obtain micrographs of these nanocomposite coatings have not been successful.

3. TARGET MARKETS

InMat is currently targeting the four market areas shown in Figure 4. The first two, sports balls and tires use butyl nanocomposite formulations. Because of the need in the chemical protective industry for improved resistance to solvents, oils and flames, new nanocomposites based on other elastomers are being developed.

Packaging applications require lower cost and much better oxygen barrier than that provided by the elastomeric nanocomposite formulations. Starting with non-elastomeric matrices dispersed in water, InMat has been able to make coatings with much lower permeability that will be cost effective alternatives to currently used barrier materials in the packaging industry

Current Markets for InMat Technology

- **Sports Balls: The bounce and feel of natural rubber with the air retention of butyl**
  - ☐ Wilson's Double Core™ ball (the official ball of the Davis Cup) using InMat Air D-Fense™ coating is available worldwide
- **Improved Tires: Air retention without weight, rolling resistance and cost penalties of butyl rubber innerliners**
  - ☐ Coatings are being tested by many of the leading tire companies
- **Chemical Protection: Improved dexterity and flexibility**
  - ☐ Phase 2 SBIR for Army – improved solvent, oil, and flame resistant protective gloves
- **Packaging: Improved protection with thinner coating**
  - ☐ A superior oxygen barrier when compared to commercially available products

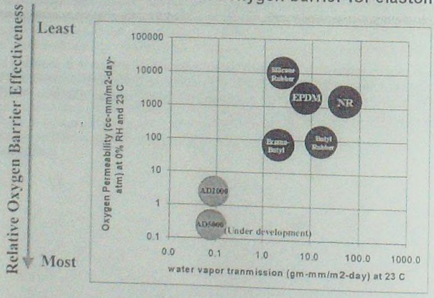
Figure 4

4. PERFORMANCE

BUTYL NANOCOMPOSITES

Figure 5:

InMat's butyl nanocomposite coatings provide a unique combination of moisture and oxygen barrier for elastomers



The performance of InMat's butyl nanocomposites as air barriers is shown in Figure 3, and has been discussed previously[9]. In Figure 5, we show how the oxygen barrier performance relates to that of other commonly used elastomers. In addition, we show the moisture barrier performance for the first time. It is important to note that the moisture barrier properties of these nanocomposites depend upon the moisture content of the coating. When the coating is in a relatively dry (< 50% humidity) environment we observe the large improvements in moisture barrier shown in Figure 5. When the coating is in a high humidity environment, we do not observe any significant improvement in moisture barrier. This is presumable due to the moisture absorption of the nano-dispersed clay, and the fact that it will absorb a layer of water on its surface.

OTHER ELASTOMERS

Although butyl is one of the lowest permeability elastomers, it is very susceptible to oil, fuels, and hydrocarbon solvents. Coatings that provide good barrier based on other elastomers are therefore required. The table below shows results on three alternative elastomeric matrices. These formulations are still under development by InMat.

The results shown in the table are not on fully optimized formulations. They are merely shown to demonstrate that low permeability coatings based on a variety of elastomeric matrices have been produced, and that using InMat's approach, barrier coatings can be developed for a large variety of applications.

Table: InMat Nanocomposite Technology Utilized in Aqueous Elastomeric Latices

Latex Type	% Filled[1]	Permeability[2]	Reduction[3]	% Strain[4]	Key secondary properties
Neoprene	30	1.5	83	12	Ozone, UV, oil, and solvent resistance
Neoprene	0	125			
Nitrile	30	2.3	57	14	Solvent, oil and fuel resistance
Nitrile	0	130			
EPDM	20	17	11	15	Ozone, UV, sunlight, steam, brake fluid, and weak acid resistance
EPDM	0	185			

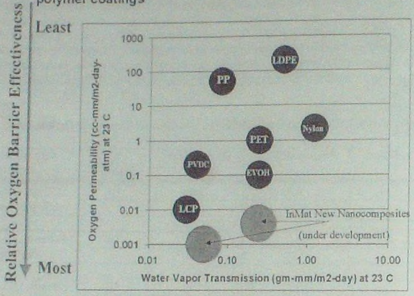
Notes:

1. Weight % of dried film.
2. Permeability is oxygen permeability reported in units of cc mm/m2 day atm @ 23C and 0% relative humidity.
3. Reduction is the times the oxygen permeability is reduced from the unfilled elastomer.
4. % Strain is reported as the strain to first damage under biaxially elongation and evaluated under a microscope.

NON-ELASTOMERIC NANOCOMPOSITES

As shown in Figure 1, there is a typical tradeoff between the flexibility of a polymer and its permeability. In applications that do not require elastomeric flexibility, one typically gets improved barrier properties by using higher Tg and partially crystalline polymers. The permeability of InMat's butyl nanocomposite filled with 20-30% nano-dispersed is comparable to unfilled polyester.

Figure 6 **InMat's new high barrier nanocomposites provide a superior O2 barrier when compared to the best available thermoplastics and polymer coatings**



Thus, if one wants to obtain superior barrier properties for applications that do not require large deformations of the coating, one should start with polymers that are good barriers, and further improve them by adding nano-dispersed clay. This approach has been examined by numerous companies. For example, Honeywell has commercialized its Aegis polymers that contain nanocomposites of nylon[10].

InMat has extended its approach for making aqueous based nanocomposite coatings to several non-elastomeric matrices. The data shown in Figure 6 represents results on formulations under development based on aqueous dispersions of PVDC and polyesters. The improvements obtained in oxygen barrier are large, reaching several thousand times. The improvements to date in moisture barrier properties have been much smaller, but development work continues.

5. APPLICATION PROCESS

The coatings described in this paper can be applied using most standard application processes. Spray coating has been used in the tire and sporting goods industries. It provides thickness control while enabling uniform coatings to be applied to relative complex shapes (tires and tennis balls, for example).

Dip coating is used to manufacture gloves and bladders for soccer balls. InMat formulations can be applied using a similar process, and often using the same equipment.

The flexible packaging industry typically uses high-speed roll coating in order to minimize the cost of applying coatings to large amounts of flexible packaging film. Formulations suitable for roll coating of packaging film are under development.

6. SUMMARY AND CONCLUSIONS

InMat has demonstrated that nanocomposite barrier coatings based on aqueous dispersions of polymers and nano-dispersed exfoliated clay can be developed and commercially manufactured. Building on its first product line based on butyl elastomers, new nanocomposites coating formulations utilizing a variety of elastomers and non-elastomeric polymers have been made and characterized. These results demonstrate the applicability of InMat's approach to solving a wide variety of customer needs.

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QUANTUM LEAP POLYMER INNOVATION PERFORMANCE THROUGH ADVANCED TECHNOLOGY MANAGEMENT

Dr. Wolfram Keller, *Principal German Management Team*
Product Development Practice Area, P R T M, Germany

BIOGRAPHICAL NOTE

Wolfram Keller is a core member of PRTM's German management team and of the European Product Development Practice Area. He has over eight years consulting experience. His work at PRTM has focused on the assessment, design and implementation of innovation and business strategy processes. His experience includes strategic and operational innovation processes, e.g. R&D and technology portfolio management, resource management, IP management, and R&D controlling. Wolfram also facilitated numerous project teams managing specific technology and product development projects in the chemical, pharmaceutical, vaccines and engineering industry. He also facilitated several project teams in supply chain management engagements, mainly in the sourcing area.

Prior to joining PRTM, Wolfram spent eight years in the chemical and pharmaceutical industry in Germany and Taiwan. He initially focused on R&D in the area of ultra-pure chemicals, before he joined the management team of a German-Japanese-Taiwanese joint venture in order to set up a high-tech electronic chemicals plant in Taiwan taking responsibility for the manufacturing and quality assurance processes. Back in Germany he focused on new business development at the interface of the chemical and semiconductor industry.

Wolfram has a PhD in biochemistry and a diploma in chemistry from the Technical University in Darmstadt, Germany. He is a certified DIN ISO 9000 auditor for quality assurance systems by the TÜV Rheinland, a certified six sigma black belt and among the first certified Next Generation Product Development consultants across PRTM.

Industry Focus

Wolfram's experience spans a range of industries including chemicals, pharmaceuticals, medical devices, engineering, semiconductors, electronics, and telecommunication devices. He has been working in projects in 12 European countries and in the U.S.

Publications and Presentations

Publications
Wolfram Keller, "IP Management als Prozeß – ein Hoffnungsträger in der chemischen Industrie" *CHEManager*, Germany, 2001
Wolfram Keller, "Six Principles of IP Management for Chemicals Companies" *The Chemical Engineer*, UK, 2001
Wolfram Keller and Stephen O'Donnell, "Using patent management as a competitive weapon" *Screening, UK*, 2001
Wolfram Keller, "Decoding the value of technology platforms", *Teknoscienze*, Italy, 2003
Wolfram Keller and Brian Gibbs, "Increasing the Value of Technology Platforms", *Insight*, US 2003

Presentations
"R&D Benchmarking", Fraunhofer Gesellschaft, Berlin, Germany, 1999
"Strategic R&D Management", Management Circle, Wiesbaden and Mainz, Germany2000
"Efficiency in inbound logistics", Management Circle, Düsseldorf, Germany, 2002
"Improvement opportunities through VMI", Management Circle, Munich and Cologne, Germany, 2002
"The Supply Chain Manager", Management Circle, Oberursel, Germany, 2002
"Best Practices in Product Stewardship", RAPRA-Rubberchem, Munich, Germany 2002
"Managing Elastomer Technology Platforms" RAPRA-HPE, Cologne, Germany 2002
"Technology Management & Benchmarking –Ingredient and Catalyst to Improve Innovation Performance", Euro Med Forum Capri, October 2003
„Technologiemanagement als Innovationsmotor der Medizintechnik", Medica Düsseldorf , November 2003

Project Experience

- Led the assessment, design and implementation of next generation product development at a leading, international manufacturer of sweets. Focusing on advanced product development, portfolio and resource management the client achieved a 30% TTM reduction, a 25% increase in R&D productivity and a 10% increase in Operating Profit
- Led the implementation of franchise life cycle management, (a long-term strategic planning process) at a leading vaccines manufacturer. Designed management process to define, manage, and control the franchise's technology and market playing field, their mutual interfaces, and the appropriate organization. Developed a platform approach to new vaccine development (saving potential >$ 50 million) and identified and valuated new market opportunities suited to close the major part of a $ 1 billion+ gap the client was facing due to formerly poor business planning and lack of control
- Led the post-merger alignment of technologies at a medical devices client. Implemented an approach to valuate current and future technologies to effectively facilitate the required rationalization. Shifts in technology strategy and locations are expected to result in R&D savings of approximately 10% or $10 million/year.
- Led the implementation of an innovation strategy process in a multi-billion chemical company. Responsible for process design, subsequent implementation and management of the steering committee. Results included a best-in-class industry oriented innovation strategy contributing to a revenue growth of twice of that of the main competitors. New IT enabled portfolio management and new intellectual property process helped achieve these strategic objectives
- Led the product platform strategy project in a multi-billion telecommunication company. Supported the definition and implementation of an initial platform based product strategy. The new way of working in platform and platform element teams is saving the company $100 million over the next decade in R&D investments
- Established a robust approach for the product development department at a leading semiconductor manufacturer, targeting to reduce time-to-market by 40% and improve pipeline throughput by 30–40%
- Led a project at a major engineering company specializing in large-scale biochemical processes. Facilitated the client through the change from a pure line R&D organization to a matrix organization, ultimately leading to a cycle time reduction for the processes of up to 50%
- Redesigned the supply line of a major telecommunications company and four of its key suppliers. The supply chain operations reference-model (SCOR) based improvements resulted in a reduction of sourcing costs of $20 million through a highly effective inventory management process and introduction of IT based order management systems
- Implemented in a pharmaceutical pilot plant new planning process and significant improvements in the go-into-plant, processing and transfer phases resulting in throughput improvements of up to 50% and cost reduction per batch in the magnitude of 30%
- Conducted a strategic asset management & technology management survey in the chemical industry
- Conducted a benchmarking survey in the chemical industry on IP/patent management practices
- Conducted a benchmarking survey on order processing costs in the chemical industry
- Conducted a benchmarking survey on pilot plant effectiveness

ABSTRACT

Overview

In the polymer industries, innovation management is increasingly being seen as the "holistic backbone of the business." The term describes a process chain that encompasses research, technology management and product development as well as the key process enablers of IT systems and performance management. Historically product development has been a major focus for the polymer industries. In contrast, the lack of emphasis on technology and performance management has left few companies with a structured framework in place to adequately define, manage and measure their technology processes. The majority of companies are therefore under utilizing their existing resources. This paper will provide a guide to the steps to achieving a strong technology position, the results of which are productivity improvements and the doubling of new product revenue.

Understanding Performance

On average only every second technology project is transferred into product development within twelve months of its completion. Even best-in-class companies suffer from significant time-to-market delays of new products due to the technology development being behind schedule. Benchmarking is a preferred method of performance management, providing on going visibility into a company's innovation performance, and an understanding of the profit potential of products that are the derivatives of the underlying technologies.

Best-in Class Seven Step Framework
The best-in-class seven-step technology management process helps polymer companies improve R&D productivity by up to 50%. Re-allocating the thus freed up resources to support additional projects, increases project pipeline throughput, leading to additional new product revenue of up to 50%. In this context, benchmarking provides the transparency for management to evaluate the significant improvements made.

Commitment to Change
Implementing technology management successfully requires a committed approach to change. A clear, frequently time-staggered implementation strategy is essential, as is the investment in skilled resources, progress tracking, facilitation by process specialists, and management support. This commitment is vital to drive through the implementation of technology management, and the resulting increased productivity and revenue will ensure that the investment is worthwhile.

Conclusion
By adopting a technology management process framework, i.e. leading technology management practices supported by on going process enablers such as performance measurement or IT-systems, companies can achieve technology leadership and improve their overall performance in innovation. Overall this lecture will show how technology management can be part of an integrated approach to innovation management in the polymer industries, and boost business results.

There are three main reasons why polymer companies have to improve their technology management performance now.

1. The need to increase productivity in the execution of technology management: Revenues from new products can be as much as 50% higher for the top 20% polymer companies than for average companies. These have to catch up in order to close the competitive gap before it increases any further. Their R&TD productivity is currently 50% lower than that of their competitors that operate best-in-class technology management already. The challenge for them is finding the best way to re-allocate freed-up resources for other technology projects, to increase pipeline throughput, and generate more new product revenue and profits.

2. The need to increase return on capital investment, a more strategic issue: The market cycle is gradually turning more favorable. Capital spending, which can be considered an equivalent for investment in new technologies (i.e., plants and equipment), will rise again. Those who systematically get better returns on their capital expenditures will find themselves in fundamentally stronger positions than their competitors. Especially important in today's business climate is to understand how to achieve high returns on CAPEX.

3. The need to adhere to requirements implied by politics ("political needs"): The European Commission's white paper charts a new strategy for chemicals policy: "... changes to existing procedures should limit R&D costs and encourage technological innovation." What may sound as a very positive mission in the first place is in fact a threat to more than 36,000 Europe-based chemicals companies, a significant number of which are in the polymer business. Early estimates from within that industry indicate the manufacturers will have to spend ca. Euro 8 billion on 30,000 substances whose production volume exceeds one ton, and on 5,000 products manufactured in quantities above 100 tons. To match the new regulatory requirements, we expect polymer manufacturers to make massive changes to their processing technologies.

These three needs are closely interrelated. Political needs define some of the business boundary conditions. Within these boundaries a polymer company has to find and maintain most feasible way— technically and economically—to manage its technologies. In other words, a company has to decide what technologies to invest in, why, and how to do it.

While the needs to significantly improve the way of managing technologies are clear, few polymer companies are managing technologies along their lifecycle effectively enough yet.

Begin with a definition of holistic technology management

We define technology management as:

- Defining and selecting the technologies needed to sustain business success (technology and capital asset strategy)
- Developing, maintaining, and replacing those technologies as directed by the technology strategy (technology management execution)
- Selecting and putting in place the best organization for managing technology (technology management organization)
- Measuring the costs and benefits of the technologies you own (performance management)
- IT-enablement of technology planning, decision-making, execution, and monitoring through advanced web-based IT systems

From a business perspective, we distinguish two aspects of technology management

- The strategic component or "strategic capital delivery"
- The operational side of technology management or its "execution," what I refer to as technology management in the narrow sense

Execution of technology management is a key driver of R&TD productivity that is becoming increasingly important, as the frontrunners of technology management in the polymer industry have begun to show over the last five to ten years.

Polymer companies have spent a lot of time and money creating better polymer manufacturing technologies and products over the last two decades, and performance improved dramatically. This was mainly due to the emergence of the stage-gate process in the late 1980s, and to a shift in focus from individual projects to project portfolio and resource management.

Because of these achievements, time to market for new polymers decreased quite markedly between 1997 and 2000. It improved by

- 10% for high-complexity projects
- 28% for projects with medium complexity
- 17% for projects with low complexity

Companies were able to get polymer products out the door 27 weeks faster on average. This was excellent progress.

However from a business perspective, technology management was traditionally much less valued than what appeared to be the more appealing product development. Because of this overriding focus on product development, today relatively few polymer companies do a good job of technology management and capital spending management and miss a great opportunity to achieve superior business performance.

Since there is a close correlation between the complexity of a new technology and the time to market of the derivative products, it doesn't come as a surprise that time to market for complex projects improved by only 10% between 1997 and 2000. Better product development practices alone aren't enough when you're seeking a first-to-market position for new, complex products. We estimate that ca. 20% of time-to-market delays for new polymers are related to delays in technology development. In other words every fifth product is not launched on time, since the technology is not ready.

Polymer companies with strong technology management capabilities don't only hit the window of opportunity better. They also use newly developed technologies 100% more often in product development than average firms. Only one out of every two new technologies on average finds its way into product development—a huge waste of resources.

R&TD productivity and efficiency does improve by 40% to 50%, if a company is able to:

- Execute 20% more technology projects with the same number of resources
- Utilize the newly developed technologies 50% more often to create new products
- Accelerate time to market of their technology-based products by 20%

Benchmarking data and project experience show that very few polymer companies have already managed to do this.

Once the developed technologies have come to life, a top tier of polymer companies outperforms their peers when it comes to capital investment. These companies are the "High ROGFA" (ROGFA = Return On Gross Fixed Assets) companies because they get superior returns on their capital investments in fixed-technology related-assets (plants and equipment). That is the key principle of asset management in the polymer industry or, as we phrase it, strategic capital delivery. High ROGFA performance is a fundamental driver of overall company performance, such as higher sales growth, better margins, higher asset productivity, and higher shareholder returns.

In particular, High ROGFA polymer companies

- Have slightly newer assets than average companies, as calculated by accumulated depreciation divided by annual depreciation. For polymer companies, the average asset age is 9.3 years for the average population, versus 5.8 years for High ROGFA companies.
- Had an average cumulative shareholder return of 15.8%, compared to an average company return of 5%, from October 1998 through October 2003.
- Are not only more productive with their assets, but are able to run their businesses with a lower level of capital investment. Capital intensiveness has been steadily decreasing over the past five years for polymer companies
- Have consistently shown lower overall capital intensiveness during this period, while capital spending trends have been uniform across all polymer companies. Average-performing polymer companies decreased spending by 48%, while the High ROGFA companies' spending decreased by 42%.
- Are more productive with their assets and generate higher returns; they generate more cash flow and therefore have to spend less of it on capital expenditures. They are able to have more cash flow to spend on other value-creating activities (e.g., R&TD) or to put the extra cash flow into dividends for investors.

Since strategic capital delivery and the execution of technology management are so closely interrelated, it is accurate to assume that those companies are likely to be the technology leaders that have understood to manage both components equally well applying a holistic technology management framework.

We have developed and already implemented several times **a seven-step technology management methodology** that helps polymer companies achieve quantum leap improvements in technology performance:

- Portfolio of technologies is on average only 60% as old as that of competitors
- CapEx Intensiveness Ratio (Capital Expenses per Sales) is only half that of average competitors
- Productivity per employee is 20% to 25% higher
- Cumulative shareholder return is three times that of others over the five year period from October 1998 through October 2003

Those companies are the true technology leaders. Let's now try to understand how the technology leaders achieve this superior performance.

Step 1: Technology strategy definition. In this step, you outline which technologies to invest in, which technologies to keep, and which ones to retire—and why. This is documented in technology portfolios, technology roadmaps, mid- to long-term resource requirements, and long-term business goals. Technology strategy definition addresses both:

ROGFA, mainly through the selection of and decision for the right technologies

R&TD productivity, mainly through providing the organization with the budgets and infrastructure to create and maintain the technologies

Step 2: Trend scouting helps identify technology threats and opportunities arising from science, competition, or changes in legislation using technology mapping and patent mapping techniques. This step is aiming at identifying the right technologies required in the future, whether by in-house development or by acquisition.

Step 3: Technology planning effectively optimizes both the efficient creation of a technology and its high return on investment (or ROGFA). It facilitates a company's utilization of its planned and existing assets in the most technically and economically feasible way. Consolidating standardized plans for technology platforms, individual technologies, and technology elements into technology roadmaps is instrumental to better manage technology cost drivers such as the:

- Design for re-use
- Technology leverage across entities, locations, and product platforms
- Performance improvement programs aimed at increasing yield, process cycle time, and quality while reducing the amount of side products, energy, process down time, or money

Most of the savings achieved here directly improve the company's bottom line.

Step 4: Technology portfolio management operationalizes the company's technology strategy. It applies to both existing technologies and those planned and in development. It coordinates all technology development, acquisition, and technology lifecycle projects to minimize duplication of effort, better using resources, improving R&TD productivity and, again, the return on these investments. Probably the strongest lever in technology portfolio management is fact-based decision-making, a key principle in strategic capital delivery.

Step 5: Technology development is similar to new product development, but has a higher level of uncertainty or "entropy." It spans a wide range of different technologies, i.e., engineering technology, process technology, product technology, and application technology. Executing technology development in the right way, i.e., on time, on budget, and with the desired project results, is an ultimate technical and economical success factor. There is a direct correlation between the capabilities of technology development execution and R&TD productivity.

Step 6: Technology transfer in the polymer industry includes three types of transfer:

- First is the scale-up from lab to production via a pilot plant to confirm product parameters and set process parameters for mass production
- The second type of transfer is across different companies through mergers or acquisitions. They don't usually require that the technology be physically moved
- The third type of transfer includes a physically movement of a technology (where cost and practicality become critical issues) and is simplified if the technology is designed for re-use and has a modular structure that can be easily taken apart, moved, and rebuilt

Up-scaling is part of technology development and, thereby, belongs to technology management in the narrow sense, whereas transfers across businesses are mainly driven by business strategy and thereby are part of the strategic capital delivery process.

Step 7: Technology lifecycle management does offer huge financial benefits for leading polymer companies, since they take the total cost of ownership throughout the lifecycle of their technologies into account. They manage the ongoing use, upgrade, replacement, or ramp-down of their technologies in a more cost-effective way and do so without disrupting their supply chain (or ongoing business) and productivity.

If you want to measure how well you are managing your technologies and what the impact on your companies P&L / Balance Sheet is, you need to measure your technology process performance. If you don't measure, you'll have a hard time knowing if the yield, reliability, cost, and timelines of your technology projects are competitive, where your performance gaps lie, and what improvement targets are realistic.

The latest benchmarks about technology management execution are widely available already. By the summer of this year we expect to finalize a comprehensive, first-of-its-kind, worldwide benchmarking survey that will describe the strategic capital delivery performance across the chemical and polymer industry in much more detail than outlined here already.

To summarize:

Technology management and strategic asset management practices have greatly matured over the last few years in the polymer industry. Today, only a handful of frontrunners are adopting these practices as part of a holistic framework. The longer they maintain this critical advantage, the more the gap between the top tier and the rest of the polymer companies will widen, simply because the top-tier companies grow faster and achieve higher shareholder returns. For the remaining 80% of the polymer companies it is time to measure competitive and technology positions. Determine root causes and the impact of any performance gaps. Make use of the advanced and proven technology management practices available. Taking the impressive results into account they help achieve, they have truly deserved the often-used attribute of "best practices".

SUGGESTED FURTHER READING

Emulsion Polymerisation and Latex Applications
Rapra Review Report 160

Health and Safety in the Rubber Industry
Rapra Review Report 138

Latex 2001
Rapra Conference Proceedings

Latex 2002
Rapra Conference Proceedings

Natural and Synthetic Latex Polymers
Rapra Market Report

The Rubber Formulary
Plastics Design Library

Rubber Products Manufacturing Technology
Marcel Dekker

Rubber Technologist's Handbook
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Toxicity and Safe Handling of Rubber Chemicals, Fourth Edition
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