

## Company visits

Seven years ago Wil Aben and Seel de Meij visited a range of Dutch and Flemish rubber trading and processing companies to find out if there was ground for the Rubber-Stichting to establish an information center on natural rubber. One of the results of that trip was that they found a strong demand for company visits. Not a strange finding really, considering the character of the usual relationship between natural rubber suppliers and natural rubber users. Contrary to what is customary with many other raw materials, where customers not only are acquainted with supplier's salesmen but also with its technologists and have (free) access to technological support, in the case of natural rubber the relationship is almost completely limited to commerce.

Therefore one of our first actions after the foundation of the R-S Information Center for Natural Rubber was to set up a visiting scheme for our consultants to visit once or twice a year a selection of companies in The Netherlands, Flanders and the adjacent border area of Germany in order to exchange technological information. Because we realized ourselves that it could take quite some time to establish firm contacts with the management and the technological staff of companies using natural rubber we continued this year after year.

Now, after more than five years, the kind of trust-based relationship we intended to realize is a reality with three companies. I shall not make a secret of it that we consider this, in quantitative terms, as a rather disappointing result. All the more as during these years we got the impression that the knowledge at many processing companies steadily decreases due to the departure of the old guard with lots of experience and the fact that newcomers are less prepared to do the same type of work for years on end. Of course the discontinuity resulting from people leaving a company also has often consequences for the relationships we try to build up.

In 2001 we are still available and willing to come. But we also think that we have to adapt to our findings. Therefore, from now on the initiative is at the companies who want to take benefit of this free service.

Jim van der Heijden

## Profile

### Annual report 2000 (concise version in English)

#### Introduction

This report relates to the activities of the R-S Information Center for Natural Rubber in the year 2000.

The departure of Ir. S. De Meij FPRI, the increasing role of the Internet as means of communication and the relocation of the Delft activities to Eindhoven required several adjustments to the operations of the Information Center.

#### Information Provision

The shift from telephone and mail to e-mail as the most common way to contact the Center that was noted in the previous annual report has continued in 2000. This development is expected to run its course.

In June 2000 the Rubber-Stichting website was provided with a counter to obtain a better understanding of the number of times this site is visited. In the year under review, this was 579 times (*this already has been equalled in the first three months of 2001!*). People from all over the world visit the site; the links to the TNO and the IRRDB websites undoubtedly will contribute to this.

The distribution is as follows:

The Netherlands 21%

#### Europe excluding the Netherlands:

Belgium	4%	
France	3%	
Germany	2%	
U.K.	2%	
Europe other	6%	17%

#### North America:

U.S. Commercial	7%	
U.S. other	5%	
Canada	2%	14%

#### Asia:

Thailand	3%	
Japan	3%	
Malaysia	2%	
Asia other	6%	14%

Not traceable		34%
---------------	--	-----

**Total 100%**

Many visitors will find their information on the website without further telephone or e-mail contact. Therefore, the exact number of times that active and passive information is provided is not really known. However, it is clear that the number is higher than in pre-Internet years.

In anticipation of the website renewal planned for 2001/2002, the editions of "Natuurrubber" will be made available on the site in their entirety.

#### "Natuurrubber"

As of 1 January 2000, Seel de Meij ceased his editorial activities for "Natuurrubber". It soon became clear that he had devoted a great deal of time to the newsletter since its launch. Seel usually acted as reviser of presented articles and the other editors were hardly aware of the time this, often very necessary, task needs. Following his departure, a lot of time had to be set aside for editing by the other editors, particularly where the theme issues were concerned.

In 2000, three information numbers (18, 19 and 20) and a theme number (17) were issued:

#### No.17, 1st Quarter, Content:

- "Special on NR Latex"
- "Natural Rubber Latex (preface)"
- "Production, Processing and Properties"
- "Latex Protein Allergy: Some Questions"
- "Environmental Issues and Challenges in the European Latex Industry"
- "Natural Rubber Latex Technology"
- "Natural Rubber for Medical Devices"
- "Natural Rubber in the New Millennium"

## Special issues

The next issue of "Natuurrubber" (no. 23) will be the yearly special issue. This year the theme is "Testing". Copies of special issues of preceding years are still available. Themes were "Natural Rubber, Health and Environment" (in Dutch only), "Papers presented at the 60<sup>th</sup> anniversary of the R-S", "Additives", "Engineering" and "NR Latex".

**No.18, 2nd Quarter, Content:**

1999 Annual Report of the Rubber-Stichting Information Center; Accelerators; Publications; Fillers; Economy; Events

**No.19, 3th Quarter, Content:**

Economy; Events; Publications; Accelerators; Obituaries Tom Pendle, Gérard Loyen, Dietrich Brichzin; From the Rubber Economics Yearbook: Prospects for 2000; Fillers

**No.20, 4th Quarter, Content:**

From the R-S Board; Change of address; Fillers; Events; VKRT-jubilee; Special on Testing; Publications; Fillers; Economy; Accelerators; From the history of rubber

The number of subscribers continues to grow. As a consequence of opening the website, e-mail subscription requests for the magazine were also received in 2000.

In previous annual reports, it was noted that "Natuurrubber" is the calling card of the Rubber-Stichting and the Information Center at home and abroad. This was still the case in 2000. The expectation for the coming years is that in addition to "Natuurrubber", the website will play an increasing role in this respect and both R-S Information Center organs will complement and support each other.

**Company visits**

For many raw materials like for instance synthetic rubber, it is rather common that supplier and user have contacts not only on financial matters but also on technological ones. However, the contacts between the producers and sellers of raw natural rubber and the final buyer most often are only commercially. Producers of natural rubber almost never have technological (processing or application) know how, neither have most sellers; although it should be noted that some sellers to a certain extent indeed provide technological support to their customers. The aim of company visits as offered by the Information Center is to fill at least part of the technological vacuum in the relationship between supplier and user. We believe that this is the more important because from our contacts with users of natural rubber we have the strong impression that the knowledge about processing and application of natural rubber is fading away rapidly. The old guard of experienced staff is retiring or already retired and the replacing staff usually both don't have the opportunity to learn the tricks from their predecessors and don't stay long enough to build up themselves the experience required. We realize that

exchanging technological information requires an atmosphere of trust and confidence between parties that has to be built up over a long period. Also the consultants of the Information Center are well aware that they can only fill in part of the gap although they have access to much more information than most users. But we believe that every bit helps. Against this background, the Information Centers consultants again visited a number of companies in 2000.

**Relocation**

Since the last quarter of 2000 and as a result of the relocation of TNO Institute of Industrial Technology from Delft to Eindhoven, the consultants have been carrying out their Rubber-Stichting activities from the new TNO office in Eindhoven, which also houses the Information Center library and archive.

**Other***NR and art*

- A curator of a collection of three-dimensional objects was supported in establishing contacts that have led to a "spatial manuscript of rubber" in which the text "once upon a time" is visualised.
- For tutors and pupils of the combined art academies of Amsterdam, The Hague and Utrecht, an afternoon was spent advising on the processing of latex in textile design.

*Mandate extended*

The Board of the Rubber-Stichting decided in December 2000 to extend the mandate of the R-S Information Center to January 2003.

## Accelerators

### Relationships Between Mixing Method, Microstructure and Strength of NR:BR Blends

*J. Clarke, B. Clarke and P.K. Freakley, Rubber Chemistry and Technology, Vol.74, No.1, 2001, p.1-15*

Much published literature on the way in which phase morphology and filler distribution affect blend properties is contradictory or confusing. Experiments were carried out to elucidate the relationships and to determine whether the use of compatibilisers or special mixing techniques might have a beneficial effect on natural rubber:butadiene rubber (NR:BR) blend properties. NR:BR blends were prepared using both a masterbatch method and a single-stage mixing method. A cure system, which gave an even distribution of crosslinks between the phases, was used.

The morphology, tensile strength and tear strength properties of the blends were measured. Results indicated a high degree of compatibility with fine textured blends (domain sizes < 1µm) being quickly and easily produced, even from masterbatches of very different viscosities. Strength properties of these fine-textured masterbatch blends could be predicted by applying the simple rule of mixtures to properties of individual compounds mixed under the same conditions. Although in particular situations a coarse morphology could result in high tear resistance values, for most applications a fine textured morphology gives the most satisfactory overall tensile and tear strength properties. For blends mixed in a single-stage process, development of a fine textured morphology was much quicker than that of filler dispersion. For NR:BR blends containing an optimum cure system it was concluded that the mixing cycle should be chosen to optimise filler dispersion and that use of a compatibiliser will not significantly shorten the mixing cycle or improve the properties of the blend.

### In Situ Filling of Silica Onto "Green" Natural Rubber by the Sol-Gel Process

*S. Kohjiya, K. Murakami, S. Iio, T. Tanahashi and Y. Ikeda, Rubber Chemistry and Technology, Vol.74, No.1, 2001, p.16-27*

The sol-gel reaction of tetraethoxysilane produced the fine and well-dispersed in situ silica particles in the "green" natural rubber (NR) matrix before curing. This new method was developed for a NR/silica composite material, and a good reinforcement effect of in situ silica was observed on the NR vulcanizate. The method is expected to be an industrially practical technique. The in situ silica did not much inhibit the accelerated sulphur curing. Thus, it is estimated that the concentration of silanol groups on the in situ silica surface was smaller than those on the conventional silica surface. The silica-silica interaction of in situ silica seems to be weaker to result in better dispersion in the rubber matrix compared with the conventional silica. Atomic force microscopy suggested that the wettability of NR onto in situ silica was higher than that onto conventional silica. The hardness, modulus at 50% elongation and the storage modulus at room temperature of in situ silica-filled NR vulcanizate were smaller than those of conventional silica-filled NR vulcanizate, although the crosslink density of the former was larger than that of the latter and their silica contents were comparable. These unique characteristics of in situ silica-filled



vulcanizate seem to be ascribed to the fine and well-dispersed in situ silica particles in the NR matrix. These observations suggests that NR (a renewable resource)/in situ silica composite has much potential as an ecologically “green” material in the rubber industry.

### Ozonation of Unstretched Natural Rubber: Part 1. Effect of Film Thickness

*F.H.A. Rodrigues, E.F. Santos, J.P.A. Feitosa, N.M.P.S. Ricardo and R.C.M. De Paula, Rubber Chemistry and Technology, Vol.74, No.1, 2001, p.57-68*

Unstretched films of natural rubber from *Hevea brasiliensis* were exposed to ozone flow of 15 mL/min for 4 to 60 min. The effect of reaction time and the film thickness was studied by viscometry and gel permeation chromatography (GPC).

For film thicknesses, in the range of 40 to 350  $\mu\text{m}$ , an initial in the intrinsic viscosity  $[\eta]$ , was observed within 8 min of reaction, followed by a decrease for longer times. For thin films, only a decrease in the  $[\eta]$  was observed. The viscosity increase, followed by its decrease, suggests the formation of crosslinking and chain cleavage, respectively, both expected by Criegee mechanism. The plot of  $[\eta]$  versus film thickness and the chromatographic analysis, related either to 8 or to 60 min of reaction, show that the ozone penetration and the ozone reaction progresses into deeper layers than those previously described in the literature ( $\sim 0.5 \mu\text{m}$ ), in this case, 170 and 250  $\mu\text{m}$ , respectively. One model was proposed to explain the viscosity, GPC and attenuated total reflection (ATR) results.

### Aging of Natural Rubber in Air and Seawater

*P.H. Mott and C.M. Roland, Rubber Chemistry and Technology, Vol.74, No.1, 2001, p.79-88*

Accelerated aging experiments were carried out on a natural rubber vulcanizate exposed to air and to seawater. Failure strain, shown to correlate well with the fatigue lifetime, was used to monitor the extent of degradation. The effect of temperature on the rate of aging followed an Arrhenius law, with activation energies equal to  $90 \pm 4$  and  $63 \pm 3$  kJ/mol for air and seawater aging,

### Questions

**Q: “How long can Natural Rubber function in an application?”**

**A: “ This depends completely on the product and its application.”**

Being a natural organic product, Natural Rubber is sensitive to many kinds of ageing. Whether ageing will take place and influence the function of a product depends on a number of details. To begin with, the composition of the rubber, the compound. To limit ourselves to only the influence of oxygen or ozone, does the compound contain anti oxidants and anti ozonants and if so which type(s) and how much? Beside that, the shape and dimensions of the product and the way it is used play an important role. For example, condoms are made of a very thin layer of natural rubber containing only a little amount of anti oxidants. Because they are well packed this will usually be sufficient for retaining all properties during their storage life. Indeed, condoms are intended to be used just once for only a short period of time. For most brands however, exposure of condoms to the open air would lead to a complete degradation within two or three weeks. On the other hand mounting blocks for car engines are often made of natural rubber. Although they have to function in the open air in oil containing surroundings they last for at least ten years, which is the normal life time of a car. Of course here the compound contains more anti oxidants and anti ozonants but especially the bulky dimensions of such a product make natural rubber suitable. Ageing is often the result of oxidation. This means that oxygen has to penetrate the rubber to make this process happen. The same goes for oil. The outer layer of mounting blocks will rapidly take up some oxygen and oil and will degrade within several months. But this applies only to the outer layer of at first less than a millimetre, after several years some millimetres. Compared with the over all dimensions of the block this will have no significant influence on its service behaviour, the change in behaviour being less than 10%.

This means that ageing by oxygen is most important in those applications where the rubber is rather thin.

A stretched natural rubber surface is sensitive to ozone attack. Ozone attack will continue as long as the rubber is stretched and therefore even bulky products can fail rapidly.

Dynamic fatigue, microbiological degradation and wear are other degradation phenomena that may influence lifetime. In general there is no easy way to predict the life time of a rubber product because it depends not only on the composition of the rubber but also on the service conditions of the product, such as time, temperatures, contact with certain media and so on. Nevertheless, with sufficient knowledge both of the rubber and the service conditions of the product made of it, lifetime often can be estimated from the results of a series of tests each covering a certain aspect. In *Natuurrubber*'s special issue on testing some aspects of such tests will be explained more in detail.

(Jaap Havinga)

### Events 2001-2002

**July 31-August 1 International Latex Conference.** Akron, USA. Tel

+1 330 836 9180. E-mail  
cstevens@crain.com

**September 10-12 ECCMR 2001: Second European Conference on Constitutive Models for Rubber.** Tel +43 1 47654 5255.

Fax 43 1 47654 5292.

**October 1-2 Automotive Fuel & Rubber Conference.** Frankfurt. Tel

+44 1939 250383. Fax +44 1939 251118.  
E-mail conferences@rapra.net

**October 25-November 1 K2001.**

Düsseldorf. Tel +49 (0)211/4560-01.

Fax +49(0)211/4560-668.

**November 6-7. 9th Brazilian Congress of Rubber Technology.**

Sao Paulo, Brazil. Tel +11 253 3832.

Fax +11 253 3774.

**November 20-21. Rubber Bonding 2001 Conference.** Turin, Italy. Tel +44 1939

250383. Fax +44 1939 251118. E-mail  
conferences@rapra.net

**October 1-4 ATT – Automotive and Transportation Technology Congress and Exhibition.** Barcelona, Spain.

Tel +44 13 72 72 06 20.

Fax +44 1372 720101. E-mail

enquiries@attce.com

**October 15 Service Life Prediction of Elastomer Components.** London, U.K.

Tel +44 20 7451 7304.

Fax +44 20 7839 2289. E-mail

Angela\_Douglas@materials.org.uk

**November 6-9 4th International Rubber Technology, Machines and Articles Exhibition.** Sao Paulo, Brasil. Tel

(5511) 7291 8188. Fax (5511) 7291 0200.

E-mail lcoml@francal.com.br

**December 4-5 Latex 2001 Conference.** Munich, Germany. Tel

+44 1939 250383. Fax +44 1939 251118.

E-mail conferences@rapra.net



respectively. The difference can be accounted for by the difference in oxygen concentration for the two environments.

### Effects of Chlorination on Nitrosamines and Nitrosatable Substances in Natural Rubber Gloves

*A.H. Eng, Journal of Rubber Research, Vol. 4(1), 2001, p.11-16*

Chlorination at room temperature can accelerate the reduction of nitrosamine and nitrosatable contents of natural rubber gloves. The extent of the reduction for double-surface chlorinated gloves was found to be higher than that for single-surface chlorinated gloves. When compared to leaching of the rubber glove at room temperature, chlorination can remove much more nitrosamine and nitrosatable substances from the glove. A study of the model reaction between nitrosamine and chlorine indicated that the positive effects of chlorination on the reduction of nitrosamine and nitrosatable concentrations were possibly due to the formation of a more soluble salt in the presence of chloride in the acidic medium. A survey of commercial chlorinated and powdered gloves produced by the same manufacturer indicated that the nitrosamine content of chlorinated gloves was higher than that of powdered gloves. The discrepancy could be due to different formulations and processing conditions used in producing the two different types of gloves.

### Proceedings and Reviews

#### Simulation of materials processing: Theory, methods and applications

*Proceedings of the sixth international conference, NUMIFORM '98, Enschede, Netherlands, 22-25 June 1998, J.Huétink & F.P.T.Baaijens (eds), 90 5410 970 X*

#### The R-S Information Center for Natural Rubber

**Manager** Jim van der Heijden  
**Consultants** Ben van Baarle LPRI  
 (Tel TNO +31 40 2650351),  
 Ing. Jaap Havinga (Tel TNO +31 40 2650914)  
**Delegate from the Board** Ing. Wil Aben  
**Postal Address** P.O. Box 6235, 5600 HE Eindhoven,  
 The Netherlands  
**E-mail** rs@ind.tno.nl  
**Internet** www.rubber-stichting.ind.tno.nl

#### The Information Center

- Provides **Information** by telephone about properties and processing of natural rubber and about products manufactured on the basis of this material. The first three hours spent on researching a question are without charge.
- Publishes the free **Newsletter** "Natuurrubber".
- Supplies **Technical Service**, via free company visits.

#### Editors "Natuurrubber"

Jim van der Heijden and Ben van Baarle (co-editor)



### Ozonolysis of Natural Rubber: A Critical Review

*S.S. Solanky and R.P. Singh, Progress in Rubber and Plastics Technology, Vol.17, No.1, 2001, p.13-57*

## Fillers

### IRSG's Panel of Associates continues to expand

The International Rubber Study Group announced in February and March that the Japan Rubber Manufacturers Association, Pirelli Pneumatici SpA and Felda Rubber Industries Sdn Bhd joined IRSG's Panel of Associates.

### Key Rubber Indicators

The International Rubber Study Group published the 2000 Edition of "Key Rubber

Indicators" (ISBN 0 900936 49 5).

Information: IRSG, Heron House, 109/115 Wembley Hill Rd., Wembley, HA9 8DA, U.K. or IRSG@compuserve.com

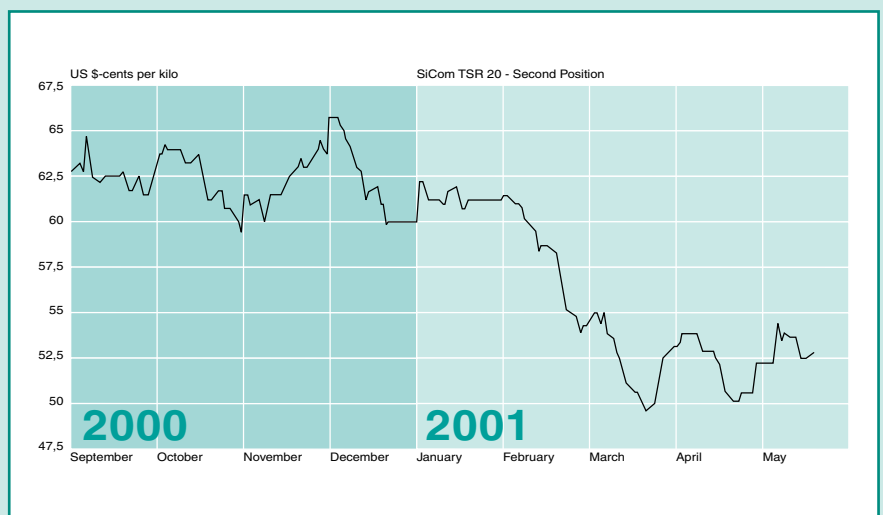
### SSL Healthcare Nederland N.V.

This is the new name derived from the merger between Seton, Scholl and LIG. Everything else including the address will remain unchanged, as the announcement stated.

### Advances and developments in NR

*Abdul Aziz S.A. Kadir, Rubber World, November 2000, p. 44-50*

The activities of the Malaysian Rubber Board over the years have contributed significantly to the progress of the Malaysian rubber industry. Malaysia will shift from primarily being a producer of NR as an agricultural material to being a provider of NR industrial materials and products.



### The Price of Natural Rubber

Another quarter with little to no interest, and overall a further slide in price. During April I.N.R.O. managed to dispose of the stocks left, and so all looked set for a rise, but poor vehicle sale figures in both Europe and the USA dampened prices.

The political uncertainty in Indonesia caused some consumers to be worried, and when the Rupiah collapsed from around 9,700 against the dollar in March to over 12,000 in May, the Indonesian rubber looked very vulnerable, but again poor demand and reasonable production kept levels low.

Late Chinese purchases and further rumours of government intervention also tried to raise hopes, but during late May the Thailand/Chinese countertrade for the Thai buffer stock fell down, leaving a rather embarrassed Thai government to dispose of their stocks in a depressed market, where buyers could dictate terms. The outlook for the coming months is slack, and we expect levels to just maintain around the bottom, or even drop further unless there is some unexpected buoyant factor that is so far unseen.

*Alec.F.S.McDougall, Trading Director  
 L.Wurfbain & Co b.v.*