

Latest Developments in NR-additives Technology

The application technology of Natural Rubber has a long history, going back more than 150 years. At that time it came in use as an elastomeric material by virtue of the invention of sulphur-vulcanization. Since that period, the majority of developments in rubber chemistry: reinforcement and vulcanization, were all triggered by technological requirements originating from the processing of NR. As of today still, NR represents about 1/3 of total world consumption of elastomers, in tires as well as in rubber goods. And so, we still witness many developments in rubber application technology today, which are closely related to the use of NR.

As a proof thereof, the following articles were prepared as short overviews of the latest developments in additive packages for Natural Rubber, for dry NR as well as for NR-latex. Reasons for continued developments in the additives field are e.g.:

- New applications;
- Implementation of more modern processing techniques;
- New legislative issues related to the rubber industry as a whole;
- The continuous need to save cost.

The rubber processor needs to keep abreast of all these developments in order to safeguard his competitive position and to guarantee profitability of his business on the long term. A few examples of trends and new solutions, as covered in the following articles are:

- The growing need for N-Nitrosamine safe compounding;
- Latest innovations as regards anti-reversion agents;
- Developments in the stabilization against aging of NR, in latex form as well as in the vulcanized state;
- Implications of the use of silica instead of carbon black for reinforcement;
- Latest developments in the field of processing additives.

The following articles clearly illustrate the continued efforts in research to upgrade the rubber technology; to develop the profitability, the versatility and the hygienic standards in the rubber industry as a whole and in NR-processing in particular.

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Special on Additives Contents

	Page		Page
Latest Developments in NR-additives Technology <i>J.W.M. Noordermeer</i>	1	Effective Protection of Natural Rubber <i>K.S. Reinartz and L.W. Ruetz</i>	5
Developments in Stabilisers for Natural Rubber Latex Compounds <i>C. Petri and T.D. Pendle</i>	2	Organosilanes and Silicas in Natural Rubber <i>R. Haddeman and R. Panenka</i>	8
Accelerators and Reversion Modifiers for Natural Rubber <i>A.J. de Hoog</i>	3	Processing Aids <i>B. Van Baarle</i>	9
		Resins in Natural Rubber <i>G. Prager</i>	11

Developments in Stabilisers for Natural Rubber Latex Compounds

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Stabilising additives for natural rubber 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, ie. 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 (eg. 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 stabilities. 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.

Synthetic fatty acids can be made quite easily and have well defined and consistent compositions and, unlike the natural acids which have a linear molecular structure, can have other molecular conformations. 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. In general the best synthetic acid soaps exhibit a combination of high solubility in water, low foaming tendency, and good resistance to destabilisation by zinc oxide.

Figure 1 compares the viscosity stability of a pre-vulcanized latex prepared with potassium laureate with that of similar

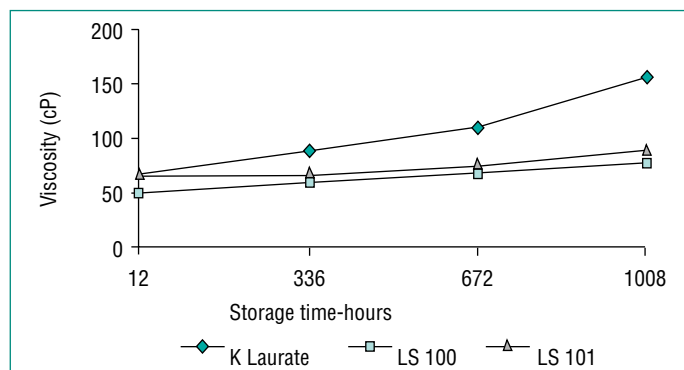


Figure 1. Effect of soaps on the storage viscosity increase of pre-vulcanized latices.

latices prepared using two synthetic fatty acid soaps (Struktol LS 100 and Struktol LS 101). The results clearly show that the latices prepared with the synthetic fatty acid soaps show much better stability of viscosity over a storage period of 6 weeks at room temperature. The improved stability being, presumably, due to a lower sensitivity to zinc oxide.

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 are another measure of the stability of the system. The mechanical stability values of the pre-vulcanized latices mentioned above were measured during six weeks' storage and are shown in Figure 2. Once again, it is clear that the synthetic soaps, particularly LS 100, are measurably superior to potassium laureate.

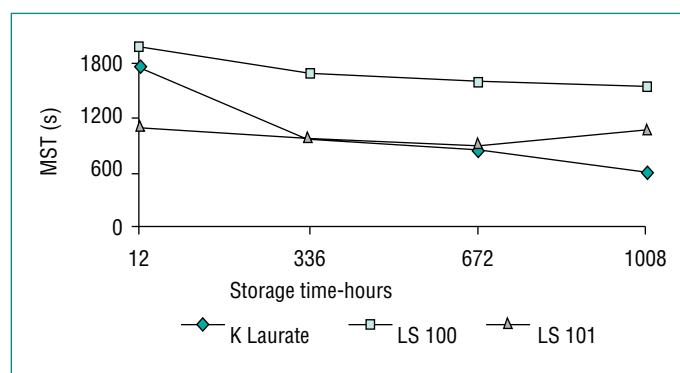


Figure 2. Changes in MST on storage of pre-vulcanized latices stabilised with various soaps.

Other work has shown that the superiority of these synthetic soaps is not confined to pre-vulcanized latices but, as would be expected, is also shown in vulcanizable 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. Comparisons of the foam stabilising behaviour of LS 100 and LS 101 with that of potassium laureate have shown that they are very similar, therefore the use of these synthetic soaps can be expected to cause no problems in this respect.

In 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 pre-vulcanized latices 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.

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Accelerators and Reversion Modifiers for Natural Rubber

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Introduction

Natural Rubber in itself is in a thermoplastic stage. This means that it is sticky, easy to be deformed and smelly at higher temperatures and brittle at lower temperatures. That is the reason that the material was not much used in previous centuries. To improve the material properties rubber has to be vulcanized. By this vulcanization rubber get elastic properties, that means that deformations are reversible to a large extent. The process of vulcanization is known already for almost 160 years. The use of sulphur as a vulcanizing agent was invented by accident in 1839 by Charles Goodyear. Since then a wide variety of compounding ingredients has been developed. These include accelerators, the activators zinc oxide and stearic acid, black and white fillers, antidegradants, retarders, etc. The most important group of the additives used in vulcanization are accelerators. Since the first use of aniline in 1906 a lot of accelerators have appeared on the market.

Accelerator type	First use
Dithiocarbamates	1919
Guanidines	1920
Thiazoles	1925
Thiurams	1930
Sulfenamides	1937

As can be seen in the table all the important accelerators of nowadays originate already from before World War II and are still the workhorses in the rubber industry.

Accelerators

One could ask the question why there are so many accelerators and other additives.

The answer could easily fill quite a few pages. Rubber vulcanization is a very complex process and, although being in use for more than 150 years, not fully understood. Because of the complexity the process can be influenced by a variety of different types of accelerators.

Next there is the wide variety of application areas and as a consequence the wide variety of requirements on the rubber article. The application areas and products are shown in the table.

Category	Products
automotive	tires, v-belts, profiles, hoses, wipers
technical goods	o-rings, membranes, seals, valves
industrial products	belts, hoses, roll covers, shock absorbers
building industry	profiles
footwear	boots, shoe soles
latex applications	gloves, condoms, carpet backings, balloons
cables	insulations, jackets

Dependent on the area of application a product should fulfil requirements regarding physical properties. The most important physical properties are shown below.

The properties are determined by the composition of the compound and how it is vulcanized. Development of a compound

Physical properties of interest for rubber articles

hardness	wet and dry traction
tensile, modulus	flex and fatigue properties
elongation at break	heat build up
tear strength	ozone resistance
rebound resilience	heat ageing
compression set	swelling in solvents
abrasion resistance	(steel cord) adhesion

and a vulcanization recipe is the specific knowledge of the rubber compounder.

Within a basic compound recipe the processing safety (scorch safety), speed and extent of vulcanization, blooming characteristics, shelf life and costs can be fine tuned by the right choice of accelerator.

As was stated above many accelerators are already in use for decades. This demonstrates that innovations in the rubber industry are scarce. Innovations that occurred in the past were inspired by increased technology requirements or for instance by environmental issues.

An example of the latter is the nitrosamine problem. Many accelerators are based upon amines. Secondary amines can form carcinogenic nitrosamines. Although levels are quite low (in the order of $\mu\text{g}/\text{m}^3$) the level of extractable nitrosamines is restricted in baby teats, and – in Germany – also the level of airborne nitrosamines. These restrictions have lead to improved operating conditions in the rubber factories but also to the development of new products based upon safe amines. Perkacit TBzTD (tetrabenzylthiuramdisulfide) and Perkacit ZBEC (zinc dibenzylthiocarbamate) are examples of such new developments. Both products are based upon the nitrosamine safe dibenzylamine.

Another example of environmentally driven innovation is the development of much cleaner production processes for accelerators. Flexsys has for instance a new-technology plant for the production of thiurams in Cologne with a very much reduced waste production as compared to conventional plants, and with the additional benefit of a much purer product.

An example of a technology driven innovation is the introduction of radial tires. This had a very strong impact on the use of natural rubber in tires. An example is the application of NR in the belt compound. This is the compound in which the steelcord is embedded. Natural rubber is applied here because of its excellent green tack and green strength. The tack is required to give the tire the necessary dimensional stability when still in the unvulcanized state. The adhesion of the steelcord to the rubber is very important. Adhesion is improved when the vulcanization speed is not too high. For this purpose the relatively slow sulphenamides MBS and DCBS have been developed. In Europe the use of MBS is decreased because the product is based upon the carcinogenic nitrosamine forming morpholine.

Insoluble sulphur

The radial tire has lead also to the development of insoluble sulphur. The reason is that for the adhesion of the rubber compound to the steelcord a high level of sulphur is required.



Another application of natural rubber in tires is in tread compounds for heavy truck tires. Here NR is used because it has the lowest heat generation of all polymers used in tires. During running heat is generated in the tread because of the repeated deformations. This heat has to be dissipated and this dissipation in a poor heat conductor like rubber is increasingly difficult in a thick article like a truck tread. So running temperatures in truck tires are much higher than in passenger car tires. Temperatures of 100°C during long trips and heavy loads are not uncommon. Therefore an elastomer is chosen with a low heat generation e.g. natural rubber.

With normal sulphur this high level would lead to blooming during storage in the unvulcanized state. This bloom destroys the desired tackiness of the compound. Therefore instead of normal sulphur, polymeric sulphur is used. This is insoluble and hence cannot bloom. Crystex is the well known trade mark of insoluble sulphur.

Reversion Modifiers

Increased use of natural rubber has led to the development of another innovative group of products e.g. the anti-reversion agents. Natural rubber has in comparison with SBR and BR a much higher reversion tendency. This decrease in physical properties is due to prolonged cure at high temperatures. Especially NR compounds with a conventional cure system with sulfenamides as accelerator are prone to reversion. A conventional cure system contains a low amount of accelerator (typically 0.6 phr) combined with a relatively high amount of sulphur (typically 2.5 phr). With such a cure system mainly polysulfidic crosslinks are formed. These crosslinks can contain up to 8 sulphur atoms per crosslink. Such polysulfidic crosslinks are thermally unstable and degrade to mono- or disulfidic crosslinks and to sulphur containing main-chain modifications. This process is called reversion. Compounds with a high level of polysulfidic crosslinks have very good dynamic properties like flex fatigue resistance. Good dynamic properties are highly desirable in tires. Crosslinks with mono- and disulfidic crosslinks have a much higher thermal stability. Compounds with such short sulphur crosslinks can be formed when a higher accelerator-to-sulphur ratio is chosen, for instance 1.5 phr of both ingredients. This system is named a

semi-EV system (EV stands for Efficient Vulcanization) and indeed shows much less reversion. However, the dynamic properties are worse, so this is not an optimal solution.

Research within Flexsys with the object of finding a solution for this problem has led to the development of the anti-reversion agent Perkalink 900. This product replaces polysulfidic crosslinks, broken because of reversion, by long (hence flexible) C-C crosslinks. As a result physical properties remain unchanged at overcure conditions, but also during high temperature operating conditions, which normally lead to a rapid decrease of properties.

This is of course an advantage in heavy truck tires with their high running temperatures. Also in the vulcanization of thick rubber articles the product can advantageously be used. The long vulcanization time, necessary to give also the inside of the article a sufficient state of cure, promotes reversion at the outer parts of the article with the unavoidable decrease of properties. Application of Perkalink 900 has as result that the physical properties at the outside remain at the required high level.

Another product with anti-reversion properties is Duralink HTS. This product repairs broken polysulfidic crosslinks. The repaired crosslink still contains various sulphur atoms and hence can break again. The process of reversion is very much delayed by this product. It has the additional advantage of increasing steel cord adhesion in belt compounds.

Perkalink 900 cure vs. peroxide cure

Earlier it was mentioned that Perkalink 900 forms long, flexible C-C crosslinks. This distinguishes the product from another group of C-C crosslinks forming vulcanizing agents namely the crosslinking peroxides.

The C-C crosslinks formed by peroxides have a very high thermal stability. However, they are also very short, just the length of a carbon-carbon bond, and inflexible, and therefore the dynamic properties of peroxide cured articles are poor. For under the hood applications with very high requirements on heat resistance peroxide cured systems can be of advantage. Because of the very stable crosslink peroxide cured products have an excellent resistance to compression set.

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Introduction

Rubber articles under severe service conditions undergo stresses which cause degradation of the rubber and its network. Therefore there is a demand for systems giving optimum protection of rubber goods.

Ageing is mainly caused by dynamic stress, oxygen, ozone and heat. These initiate different physico-chemical reactions in the vulcanizate.

In the following article a brief survey will be given to demonstrate the different ways of protecting rubber articles based on natural rubber. The chemical classes of antidegradants will be discussed.

Chemical Classes of Antidegradants

It is necessary to find an optimum solution in combining the activities of various antidegradants according to the intended application of rubber articles.

The antidegradants are selected from different groups. These groups can be classified by their activities against the different ageing processes (Table 1).

1. Staining antioxidants with anti-fatigue and antiozonant effects

example:

N-isoprpyl-N'-phenylene diamine IPPD
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine 6PPD

2. Staining antidegradants with anti-fatigue effects but without antiozonants effects

example:

octylated diphenylamine ODPA

3. Staining antidegradants without anti-fatigue and antiozonant effects

example:

2,2,4-trimethyl-1,2-dihydroquinoline, polymerised TMQ

4. Non-staining antidegradants without anti-fatigue and antiozonants effects

example:

2,2'-methylene-bis-(4-methyl-6-tert.-butylphenol) BPH

5. Specialties, e.g. non-staining antiozonants without antioxidant and anti-fatigue effects

Table 1: Classification of antidegradants by their protective properties (most important groups)

These groups of antidegradants will be discussed in the following article. For simplification, international abbreviations will be used (explanations given in the appendix).

Staining antioxidants with anti-fatigue and antiozonant effects

The para-phenylene diamines (PPDAs) fall into this class. IPPD and 6PPD are commonly used for dynamically stressed articles, giving a broad spectrum of protective activity. In addition, DTPD is often used to increase the long-term performance.

The antidegradants of this class reduce the scorch time to different extents. 77PD and IPPD reduce it most, 6PPD to a lesser extent, and DTPD practically not at all. The

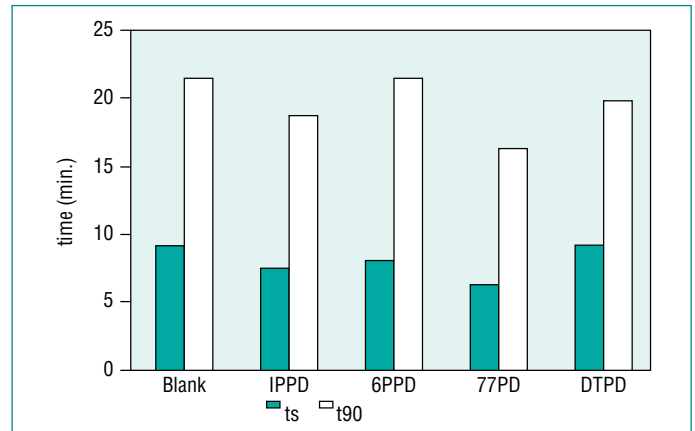


Figure 1: Scorch time t_s and vulcanization time t_{90} at 140°C (NR, formulation 1; 2.0 phr antidegradant)

vulcanization times are reduced almost proportionally (Fig. 1). At normal levels, the various PPDAs have practically no effect on the mechanical properties of the vulcanizates (see Table 2 “unaged properties”).

Antioxydant (2.0 phr)		blank	IPPD	6PPD	77PD	DTPD
Oxygen ageing: 21 bar O₂, 70°C						
Duration						
Tensile strength (MPa)	unaged	25.1	25.6	25.9	25.0	26.1
	7 days	2.6	18.7	19.4	15.7	17.1
	14 days	–	12.8	12.8	6.3	13.0
	21 days	–	7.1	6.5	3.6	8.9
Elongation at break (%)	unaged	580	550	580	540	610
	7 days	115	460	510	480	530
	14 days	–	400	450	290	485
	21 days	–	280	280	160	395
Modulus at 300% elongation (MPa)	unaged	11.3	12.5	11.7	12.5	10.3
	7 days	–	12.8	11.9	10.6	9.9
	14 days	–	10.6	9.5	–	8.8
	21 days	–	–	–	–	7.3
Hardness at 20°C (Shore A)	unaged	61	63	63	65	62
	7 days	72	68	65	65	63
	14 days	–	69	68	65	64
	21 days	–	69	68	79	65

Table 2: Protective activity of different PPDAs against oxygen ageing (NR, formulation 1)

A comparison of the physical properties after oxygen ageing (21 bar, 70°C) shows that this ageing process is inhibited best by IPPD and DTPD followed by 6PPD.

Flex cracking, which is caused by periodic mechanical stressing of vulcanizates while they are simultaneously exposed to oxygen in the air, was determined by the chain fatigue test. For a description of this method see lit. ref. 1. The cracking of the test specimen was assessed after a definite number of flexures (the rating 0 indicates no cracks, while 3 indicates very severe crack formation).

Figure 2 shows that the order in which the Pedals afford protection against dynamic crack formation under the chosen test conditions is IPPD, 6PPD, 77PD, DTPD.



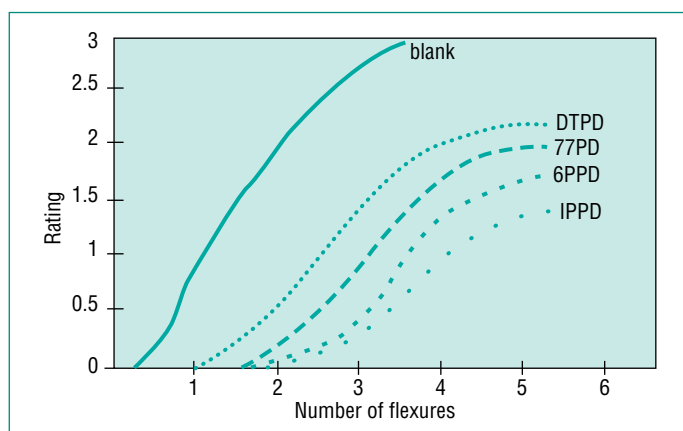


Figure 2: Crack formation versus test time (modification of the DuPont flexing test; NR, formulation 1; 0.7 phr antidegradant)

To determine the long-term effects of antioxidants, it is necessary to test vulcanizates that have undergone pre-ageing. At an ageing temperature of 80°C, it can be shown that DTPD gives the best long-term performance, although IPPD and even 6PPD are better at the beginning of the ageing cycle. To obtain the best results, the above described antidegradants are often used in combination.

PPDA's also give good protection against ozone. 77PD has the best protective effect; it is followed by IPPD, 6PPD and DTPD. This effect can be supported by the addition of antiozonant wax.

The use of PPDA's is limited to black articles due to their strong discolouring effect. In addition, the contact staining effect is also a limiting factor for their use.

Staining antidegradants with anti-fatigue effects but without antiozonant effects

An example of this class of antidegradant is octylated diphenylamine (ODPA). Used by itself, or preferably in combination with MMBI or ZMMBI, ODPA gives rubber goods outstanding resistance to heat.

ODPA is used for coloured rubber goods in which a slight yellow to brownish discoloration is not objectionable, especially those containing light-coloured reinforcing fillers.

Staining antidegradants without anti-fatigue and antiozonant effects

TMQ is the most effective product for simultaneous protection from oxygen and heat. By virtue of a synergism, the protective effect can be further improved by using TMQ in combination with MMBI.

Non-staining antidegradants without anti-fatigue and antiozonant effects

The products belonging to this group are based on sterically hindered phenols. The binuclear and polynuclear phenols are among the most effective non-staining antioxidants, such as BPH and SKF.

These antioxidants afford excellent protection against oxygen and heat, crazing and rubber poisons. They are not effective against flex cracking and ozone cracking.

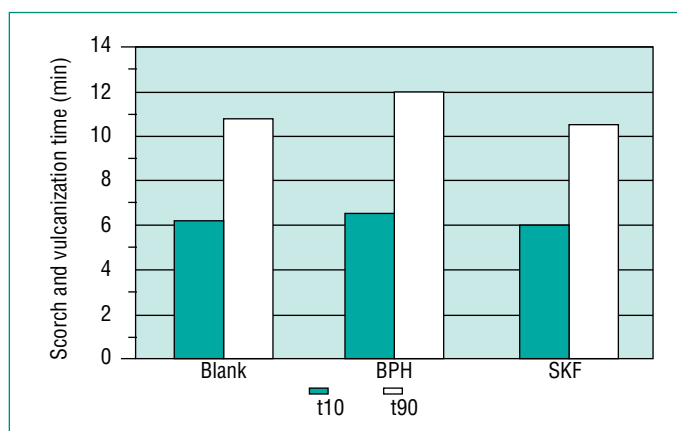


Figure 3: Scorch time t_{10} and vulcanization time t_{90} at 140°C (NR, formulation 2; 1.0 phr antioxidant)

The mechanical properties of vulcanizates are hardly affected by the antioxidants. The scorch time and the vulcanization time are only slightly influenced (Fig. 3).

The products of this group are classified as non-staining. BPH, however, has a pinking effect in vulcanizates that are exposed to light. SKF causes no discoloration of any kind in goods exposed to sunlight. Neither of these antioxidants causes contact staining.

In Table 3 the protective activity of the phenolic antidegradants is summarized.

Antioxydant (1.0 phr)		blank	BPH	SKF
Oxygen ageing: 21 bar O₂, 70°C				
	Duration			
Tensile strength (MPa)	unaged	20.8	22.9	21.7
	1 day	17.0	19.5	17.9
	3 days	13.9	17.8	15.5
	7 days	-	17.1	14.8
	14 days	-	16.9	9.1
	21 days	-	13.0	-
Elongation at break (%)	unaged	715	755	745
	1 day	665	680	665
	3 days	675	635	620
	7 days	-	640	640
	14 days	-	640	570
	21 days	-	620	-
Modulus at 450% elongation (MPa)	unaged	7.2	6.1	5.7
	1 day	7.4	6.9	6.9
	3 days	6.2	7.7	7.4
	7 days	-	7.7	6.6
	14 days	-	8.3	5.7
	21 days	-	7.6	-
Hardness at 20°C (Shore A)	unaged	52	51	51
	1 day	52	52	53
	3 days	48	54	53
	7 days	-	53	51
	14 days	-	53	47
	21 days	-	51	-
Stress relaxation at 120°C in oxygen t_{75} (min)		24	160	75

Table 3: Effect of ageing on physical properties (NR, formulation 2)



From this table it can be seen that the protecting effect of BPH is better than that of SKF to some extent.

The ageing behaviour of vulcanizates can also be assessed by stress relaxation tests. An unstretched strip of the vulcanizate is exposed to oxygen at elevated temperatures. Also in this test the protection of BPH is better than that of SKF.

Although these antioxidants do not prevent static ozone cracking, they are highly effective against crazing. This effect is caused by oxygen and light on the surface of light-coloured vulcanizates. BPH is more effective than SKF.

Specialties

Many specialties are available to protect vulcanizates against different ageing processes.

Non-staining antioxidants are an example. When used in combination with antioxidant waxes, these products are very effective non-staining protective agents, though without antioxidant or anti-flex cracking effects.

Due to their non-staining character, the main application of these antioxidants is in light-coloured goods.

Literature:

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The Board of
the Rubber-Stichting and
the staff of
the R-S Information
Center for Natural Rubber
wish you a
Merry Christmas
and a prosperous and
happy 1998



Appendix

Formulation 1:

NR		100
Zinc oxide	Zinkoxyd aktiv®	5.0
Stearic acid		3.0
Black N 220		48.0
Aromatic mineral oil		2.5
Ozone wax	Antilux® 111	1.0
Sulphur		2.5
Accelerator CBS	Vulkacit® CZ	0.5

antidegradants:

IPPD	Vulkanox® 4010 NA)
6PPD	Vulkanox® 4020) as indicated
77PD	Vulkanox® 4030)
DTPD	Vulkanox® 3100)

Formulation 2:

NR		100
Zinc oxide	Zinkoxyd aktiv®	10.0
Stearic acid		1.0
Blanc Fixe N		60.0
Titanium dioxide	Bayertitan® A	10.0
Sulphur		2.0
TMTD	Vulkacit® Thiuram	1.0

antidegradants:

BPH	Vulkanox® SKF)
SKF	Vulkanox® BKF) as indicated

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Abbreviations:

The following abbreviations have been used in the text:
 PPDA: para-phenylene diamine (general classification)
 IPPD: N-isopropyl-N'-phenyl-p-phenylene diamine
 6PPD: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine
 77PD: N,N'-di(1,4-dimethylpentyl)-p-phenylene diamine
 DTPD: mixture of N,N'-diaryl-p-phenylene diamines
 MMBI: 4- and 5-methyl-2-mercapto-benzimidazole
 ZMMBI: zinc salt of 4- and 5-methyl-2-mercapto-benzimidazole
 ODP: octylated diphenylamine
 TMQ: 2,2,4-trimethyl-1,2-dihydroquinoline, polymerised
 BPH: 2,2'-methylene-bis-(4-methyl-6-tert.-butylphenol)
 SKF: sterically hindered polynuclear phenol

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Today rubber products fulfil important functions in almost all areas of life, in the household just as much as in the aviation and space industries. Their performance depends on the right combination of polymers, rubber chemicals and reinforcing filler systems.

Industrial carbon blacks are the classic reinforcing fillers for rubber products, approximately 90 % of the world's carbon black production is used in rubber compounds to improve tensile strength, abrasion resistance, skid resistance and other physical properties. A typical rubber compound for car tires contains approximately 35 % carbon black.

As carbon blacks can only be used in black rubber articles the search for alternative active fillers which permit the production of highly durable coloured products led to the development of precipitated silicas.

In the beginning, the use of silicas as reinforcing fillers instead of carbon blacks caused various problems:

- higher compound viscosity
- more difficult processing
- longer vulcanization times
- lower crosslinking density.

On the other hand compound properties like tear resistance or elasticity could be improved by the use of silicas.

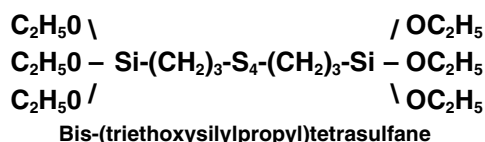
The reason for the differences in behaviour exhibited by carbon black and silica compounds lies in the different chemical surface groups and the filler interaction with the polymer.

General purpose rubbers like natural rubber are non polar materials. Silicas with their polar surface are less compatible and lead to lower physical compound properties in comparison to carbon black. It was therefore essential to modify the hydrophilic filler chemically. It was found that bifunctional organosilanes can be used for this purpose.

The silane's ethoxy groups are able to react with the silanol groups on the silica surface creating a stable bond between the silane and the filler. The second functional group permits the formation of crosslinks with the polymer which result in filler/rubber crosslinks via the organosilane.

The most common organosilane in the rubber industry is Si 69.

Its chemical formula is:



Si 69 reacts through ethoxy groups with the silica in the internal mixer during the mixing process. During vulcanization it forms crosslinks with the polymer by its sulphur group. The result of both reactions leads to the following optimized properties:

- reduced compound viscosity near to the level of carbon black
- improved processability
- increased vulcanization rate
- improved crosslink density and tensile values
- excellent tear resistance
- considerably improved abrasion resistance
- significantly improved elasticity and dynamic properties.

The first application for Si 69 in the rubber industry was found in the mid 1970s in adhesion compounds for mining belts, based on natural rubber.

Investigation in the performance of silica/organosilane filler systems exhibited, that Si 69, on account of its polysulfidic sulphur group, was able to act as a sulphur donor. This effect was used to develop reversion-free curing systems, the so called "Equilibrium Cure System". This was adopted by the tire industry for the manufacture of truck tires, OTR-tires and solid tires.

The experience with the above mentioned applications has shown that the hysteresis of rubber compounds could be reduced when carbon black was stepwise replaced by precipitated silica in combination with Si 69. This knowledge was further developed and applied to cool running truck tires with an increased service life.

Natural rubber is the preferred raw material for the production of truck tires. In order to reduce the heat generation of the tread compound under service conditions, a part of carbon black is substituted by the silica/organosilane system. As the hysteresis also influences the rolling resistance truck tires were developed with reduced rolling resistance and therefore reduced fuel consumption.

These initial developments in natural rubber have also led to new possibilities in other fields of the rubber industry. Today the car industry demands low rolling resistant passenger car tires and the tire industry responds with totally new tread compounds based on S-SBR, highly filled with silica and modified with Si 69. The tire industry is even developing coloured tires for passenger cars.

Today the organosilanes and especially Si 69 form an established group of rubber additives with still increasing demand. Besides the tire industry there is a variety of different mechanical rubber goods where silica in combination with organosilane is used.

The success of the organosilanes in the rubber industry started with the use of Si 69 in natural rubber compounds. Nowadays these products find their application in almost all polymers.

¹ Degussa AG, Rubber Chemicals and Pigment Division, Hürth-Kalscheuren, Germany



Processing aids are substances that improve the processability of a rubber compound without (adversely) affecting its mechanical properties, as long as only small quantities are added to the compound.

From 1990 till 1992 TNO carried out a multisponsor project on processing aids. One of the sponsors was the Rubber-Stichting. The results of the project have been published in 3 reports (in Dutch), covering:

- Literature Review (TNO-report 544/90),
- Peptizers (TNO-report 579/91)
- Dispersion agents and lubricants (2 parts, TNO-reports 845/91 and 71/92).

In a paper of B. van Baarle LPRI and Ir T.H. van der Burg, published in "Kunststoffen en Rubber" (1993, nr. 3, p. 34/36) titled "Verwerkingshulpmiddelen" a summary of the results was given. This summary and the 3 reports are free available from the R-S Information Center for Natural Rubber.

The following article is a shortened version of the summary in "Kunststoffen en Rubber".

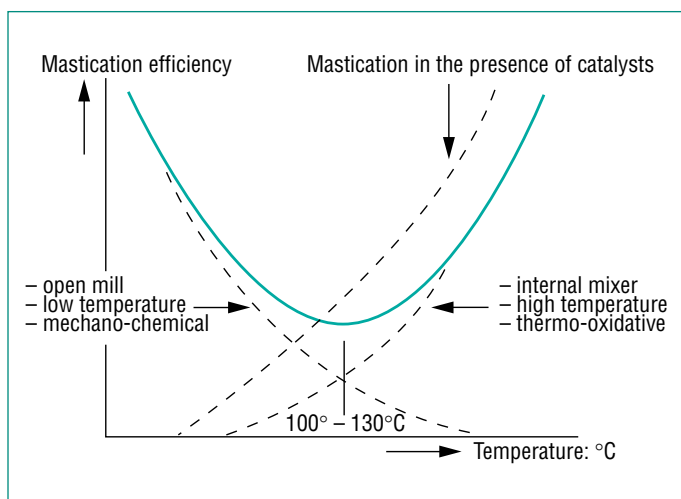


Figure 1: The effect of temperature on the mastication behaviour of NR.

Literature review

Normally, processing aids are only used in the rubber industry as a last resort in the processing of compounds. To acquire a better understanding of the way in which these processing aids are used, it is imperative to conduct a literature review to:

- gather knowledge on the mechanisms that play a role in the use of processing aids;
- formulate a general set-up as to the application of these aids;
- determine the concentrations in which these substances can be added.

The review has shown that processing aids can be categorized into a number of groups, which include: peptizers, dispersion agents, resins and release agents. The research programme compiled on this review was concentrated on the two main groups, i.e.:

1. peptizers;
2. dispersion agents and/or lubricants.

Peptizers

Peptizers are processing aids that are used to speed up the breakdown of polymer chains during the mastication process. They can be subdivided into chemical and physical peptizers.

The chemical peptizers (disulphides and metal complexes) are highly reactive. Their physical counterparts are not as reactive and are consequently added in higher concentrations. Physical peptizers spread throughout the compound more effectively, because they also act as dispersion agents. Figure 1 shows the difference between mastication at low and high temperatures. Mastication in an internal mixer (high temperature) is energetic and quicker than mastication in an open mixing mill (low temperature).

Dispersion agents and lubricants

The effect of dispersion agents and lubricants overlaps, so they are classified in a single category. These substances can be used both to disperse and to lubricate. A dispersion agent always has

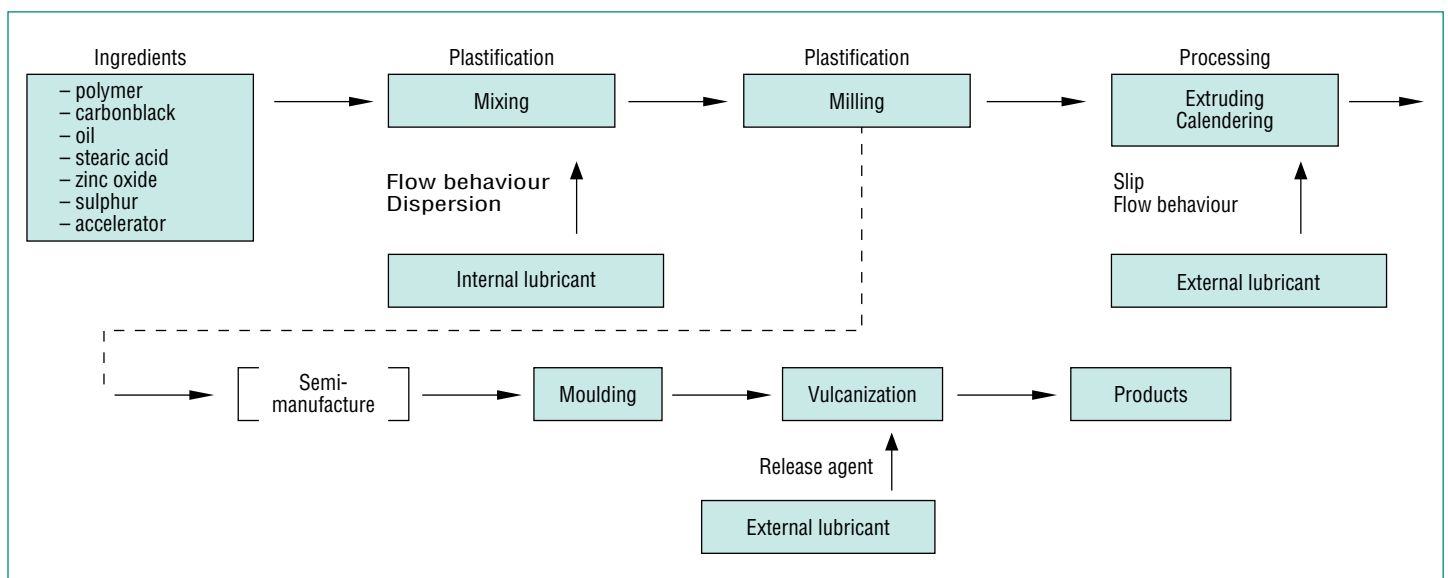


Figure 2: Processing rubber compounds with dispersion agents and/or lubricants.

to be compatible with the polymer, a lubricant can be either compatible or incompatible. A compatible (internal) lubricant is used primarily to reduce the viscosity of the mass. An incompatible (external) lubricant is mainly used to reduce the friction on the wall of the mixer.

Figure 2 shows where dispersion agents and/or lubricants can be applied during processing. The difference between dispersion agents and lubricants becomes evident in the processing behaviour. Dispersion agents should be added to the mixing process as early as possible, and lubricants as late as possible, because this reduces the shearing force and decreases the filler dispersion as a result.

The effectiveness of dispersion agents and/or lubricants depends on the shear rate. For example, a substance may be highly effective at low shear rates (compression moulding) but less effective at high shear rates (injection moulding).

Figure 3 depicts the viscosity as a function of the shear rate, as well as the shear rate for each process. The figure also shows that all processes can be studied with a capillary rheometer.

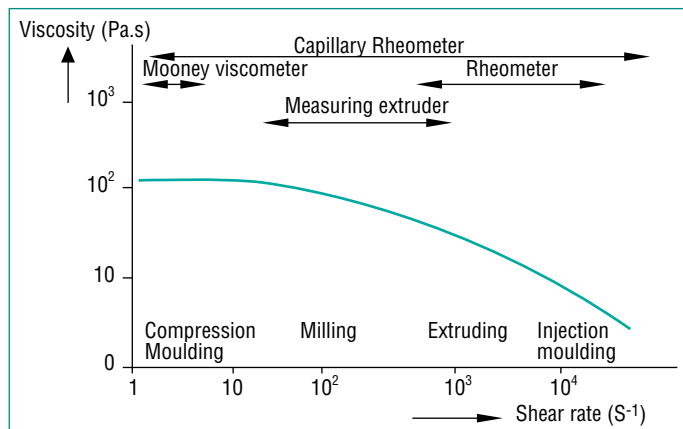


Figure 3: Shear-dependent behaviour of viscosity

The literature provides a method for studying whether a lubricant works internally or externally. This method is based on determining the Mooney-viscosity of a compound and the Brabender moment. It is assumed that the Mooney-viscosity is proportional to the energy dissipation in the material, while the Brabender moment is a measure of the (external) friction on the wall. This is shown in figure 4.

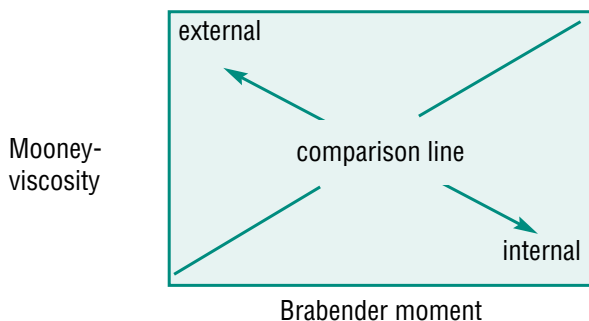


Figure 4: Relationship between Mooney viscosity and Brabender moment of an internally and an externally working lubricant

Multifunctional additives

In addition to the most commonly known processing aids, there is also a group of special additives (fatty acid amides) which, apart from improving the processability, can also play a role in the vulcanization. Fatty acid amides are formed by replacing a hydroxyl or carboxyl group with an amino group. Fatty acids can be wholly or partially replaced by fatty acid amides. One of these substances, SAPA (Surfactant Accelerator Processing Aid), has been studied during the project. SAPA works at low temperatures up to approximately 100°C as a processing aid and at high temperatures (>135°C) as a vulcanization accelerator for a-polar polymers (NR). SAPA can be added in low concentrations (≤ 3 parts). The use of zinc oxide can be reduced and stearic acid is unnecessary. Although the project does not enter into the vulcanization properties, it is clear that SAPA does speed up the vulcanization process.

¹ TNO Institute of Industrial Technology, Delft, The Netherlands

Symposium on Rubber Technology

The Rubber Technology group at the University of Twente in Enschede (Faculty of Chemical Technology) organizes a one-day symposium at February 5th 1998 with the title: "Networking in Rubber Technology". The symposium deals with various aspects of network formation, characterization and degradation.

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Obituary

Dr Leonard Mullins

Every rubber technologist is familiar with the 'Mullins effect'. Mullins discovered in 1947 this effect of stress-softening, induced by pre-stressing filled rubber.

Mullins died on 19 September 1997, aged 79. He was however more than a world-wide recognized rubber scientist, among others Director of Research at MRPRA from 1962 to 1983.

A full account of his life and personality and his scientific natural rubber career is given in Materials World of November 1997, wherein W.F. Watson also gives a fascinating description of the Golden Age of rubber science around the 1950's.



Resins are useful products in the formulation of natural rubber based compounds. Due to the various polymerization techniques resulting in different types of resins – aliphatic C5, aromatic C9 and phenolics – a wide range of products is available, differing in both chemical and physical properties. For example, softening points range from as low as 10°C to as high as 140°C and colours vary from yellow to black.

The use of resins in rubber compounds has the following functions:

- as a tackifier;
- as a plasticizer;
- as a dispersion agent;
- as a property modifier.

This division in functions is not clearly defined, a resin may be used to promote one or more functions at the same time.

Although natural rubber possesses tack to some degree, temperature and humidity can affect the degree of tack. For tack and tack-retention, resins are added.

Depending on the type of resin, at normal levels, they generally affect the unvulcanized properties of compounds based on natural rubber as follows:

- Lower compound viscosity.
- Faster dispersion of black and non-black fillers.
- Lower mixing temperature.
- Improved calendering, extrusion and flow characteristics.
- Promote building tack.

Quantities have to be controlled. Too much tackifying resin changes the visco-elastic state of the natural rubber compound and consequently will have influence on the properties after curing. The best balance between tack and cohesion is reached by liquid resins. Because of the high viscosity of these resins at room temperature, the material should be pre-heated before addition. Another option is to bring the liquid resin on a carrier (dry liquid).

The effects of resins on the vulcanized properties of compounds based on natural rubber can generally be summarized as follows:

- Somewhat lower hardness.
- Lower modulus.
- Higher elongation.
- Tensile.
 - Higher with non-black fillers.
 - Somewhat lower with blacks.
- Higher tear strength.
- Good ageing characteristics.
- Higher resistance to compression set.
- Improved flex resistance.

The influences of the use of a resin (Nècires TR 100) on the properties of (un-)vulcanized rubber are shown in the following example. Nècires TR 100 is a thermoplastic resin based on cycloaliphatic monomers modified with hydroxyl groups.

Body ply

SMR 10	60.0
SBR 1500	40.0
GPF-black	55.0
Stearic acid	1.0
ZnO	5.0
Flectol H*	1.5
Process oil	5.0
CBS	1.3
DPG	0.3
Sulphur	2.0
Resin: 3.0 and 6.0 PHR	
Cure at 160°C	

* *Monsanto*

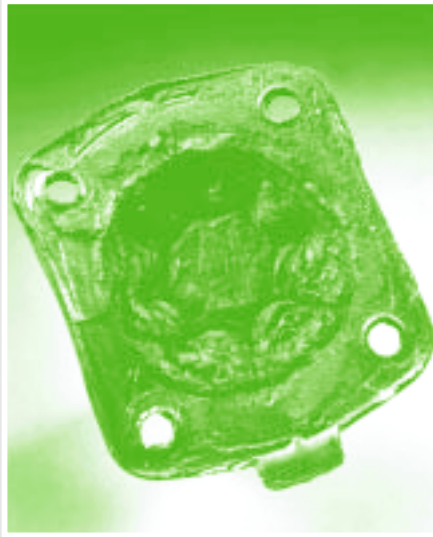
Resin type	Without resin	Nècires TR 100	Nècires TR 100
PHR	-	3.0	6.0
Cure at 160°C*			
Sopt., min.	6.3	6.7	6.8
Ts2, min.	3.8	4.2	4.2
Unaged properties			
Tensile strength, MPa	17.4	18.4	18.2
Modulus 300%, MPa	12.9	10.7	9.5
Elongation at break, %	390	440	500
Tear strength, N	67	69	72
Hardness Shore A	68	66	64
Aged properties			
3 × 24 hrs. at 100°C-air			
Tensile strength, MPa	14.0	14.7	15.7
Modulus 300%, MPa	-	-	14.3
Elongation at break, %	230	280	330
Tear strength, N	31	43	51
Hardness shore, A	74	72	70
Tack, N/2.0 cm			
Carcass-Carcass**			
After 1 x 24 hrs., RT	14	40	55
After 3 x 24 hrs., RT	21	44	70
After 7 x 24 hrs., RT	30	40	50
Heat build up, °C***			
	17	17	17
* Monsanto Rheometer			
** Stored 'open'. As to the determination of the green tack we refer to our data sheet no. 225 E/2			
*** ASTM D-6			

¹ *Nevcin Polymers B.V., Uithoorn, The Netherlands*



TNO Institute of Industrial Technology

Do you invest in research or claims for damages?



It could have been prevented. The investigation shows that materials have failed to meet specifications. Or specifications were met but application has caused problems no one anticipated. The results: the project is behind schedule, legal battles are tying down resources and claims for damages are threatening you with astronomical costs.

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Making technology work.

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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.

Under certain conditions the Rubber-Stichting enables companies to receive a reimbursement of fifty percent with a limit of Dfl. 5000,- of the **Consultancy** fees charged, for desk or laboratory research carried out at TNO.

More information is available from the Information Center.

Editors 'Natuurrubber'

Jim van der Heijden and Seel de Meij

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