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Profile

Mould fouling of tyres

Introduction

Mold fouling is a phenomenon commonly seen in the rubber processing industry. During vulcanization, with each cycle another thin layer of mostly ZnS is deposited on the wall of the mold. By understanding the cause of mold fouling and of the underlying mechanism of the formation of ZnS crystallites on the metal surface of the mold it should be possible to adapt the process to reduce this ZnS formation and thus prevent mold fouling.

There are two possible solution routes to prevent or minimize the formation of mold fouling:

1) By adapting some of the compounding ingredients;
2) By modifying the surface of the mold.

Environmental benefits of the reduction of zinc oxide

Reduction of the amounts of zinc oxide used would be beneficial to the environment. By volume, tyre production worldwide consumes up to 75% of the total rubber production. Pollution of roads by rubber of tyres causes an environmental problem. Leaching of zinc components from the tyre rubber into the surface water locally disturbs or destroys the microbiological balance in the aquatic environment. Reduction of the amount of zinc oxide or by replacing of it by nano-zink oxide or the use of alternative vulcanization systems can lead to reduction of the deposits onto the mold. This gives longer stand times of molds (presumably up to at least 10 times) and therefore also a cost reduction in mold cleaning operations.

1 Reduction by adapting compounding ingredients

Sulphur and zinc oxide are ingredients commonly used in the production process of tyres. Most deposition products on moulds for tyres contain a lot of ZnS (zink sulfide) as a result of the use of high amounts of these ingredients. To minimize mold fouling the amount of zinc oxide or sulphur has to be reduced or eliminated. In the frame of reduction of ZnS by adapting compounding ingredients first of all a manageable method for the determination of ZnS was developed. By means of short run (vulcanization) experiments, the influence of changes in compounding ingredients was studied. Most experiments were carried out on blends of NR/BR compounds similar to those most often used in the manufacturing of tyres.

Determination of zinc sulphide (ZnS) content

Most of the methods to determine ZnS content are indirect. For this study a direct method was developed. To determine the ZnS content in a rubber compound the molded (vulcanized) rubber was cryogenic grinded into small granules. The granules were extracted with acetone and treated with a mixture of hydrochloric acid and acetic acid whereby the metallic sulphides are decomposed. The resulting hydrogen sulphide was absorbed in a buffered cadmium acetate solution and the cadmium sulphide formed was determined iodometrically. Then, the extracted rubber was digested with sulphuric acid/nitric acid in a microwave oven. In the digested solution an element scan was performed by ICP-ES.

From this result it was concluded that ZnS was formed as a reaction product from zinc oxide and sulphur.

The most acceptable hypothesis is a chemical formation of ZnS as a reaction product from zinc oxide and sulphur. This general reaction is described in different rubber handbooks, but now scientific approved. A simplification of the reaction mechanism is:

$$2\,RH + S_x + ZnO + (\text{accelerator}) \rightarrow$$
$$R\text{-}S_{(x-1)}\text{–}R + ZnS + H_2O$$

Tyre compounds usually contain 5 phr zinc oxide and about 2 phr sulphur. It can be calculated that a formulation of 100 phr rubber (total mass of about 175 phr) contains about 2.8 wt% zinc oxide and 1.1 wt% sulphur. It also can be calculated that 1 gram ZnO gives about 0.6 gram ZnS. As can be seen from these calculations a substantial amount of ZnS could be generated. In practice, only ZnS (in situ) in the ‘upper layer’ of the tyre gives ZnS crystallites (possibly induced by the metal

The R-S Information Center for Natural Rubber

Last year the R-S Information Center for Natural Rubber existed 10 years. Looking back, we are happy to see that so many people from all over the world showed their interest in Natural Rubber by subscribing to Natuurrubber, visiting our website or asking information by telephone or email. However, times change and so do we. The number of subscriptions to Natuurrubber appears to be almost constant over the last few years, whereas the number of visitors to our website still increases. At the same time, every year it becomes more difficult to find authors willing to contribute good articles. This is one of the reasons that the costs to produce Natuurrubber became higher and higher.

Therefore, regrettably we had to decide to end the production and circulation of Natuurrubber. So, at the same time we end the possibility to ask information by telephone or email. We will continue our website and will add to that in the near future a forum on Natural Rubber. There, everybody has the possibility to ask information on subjects related to Natural Rubber. So we hope to encourage a platform of free exchange of information. Of course, our experts will keep an eye on it and will allow only relevant questions and appropriate reactions. We hope to have finished the changes to the website in October.

Another important change is in the Information Center’s staff. Personally, I will leave TNO in September. Ben van Baarle will take over as manager and Hans Naus will assist him as a consultant. I wish both of them good luck for the future and I am sure that they will be able to ensure the continuity of the R-S Information Center for Natural Rubber.

For now, I thank you, the readers of Natuurrubber, for the interest you over the years have shown in Natural Rubber and I hope that you will make good use of our website in the future.

Jaap Havinga
Manager of the R-S Information Center for Natural Rubber

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surface). About 500 moldings can be performed in the tyre industry before a mold cleaning operation has to be carried out.

Experiments

To generate crystallites, vulcanization experiments were carried out on a series of compounds based on a blend of NR/BR. The formulations are shown in table 1. Experiments using inserts (small metal plates) as a mold wall show that the surface of the insert contain zinc sulphide crystallites. The presence of such crystallites can be verified easily by means of RMA, but this is a rather expensive method. Therefore a more simple test was developed to determine the first (visible) crystallites on the inserts. By means of a light microscope at a magnitude of 500x, individual crystallites down to 0.5 to 1 micron are visible.

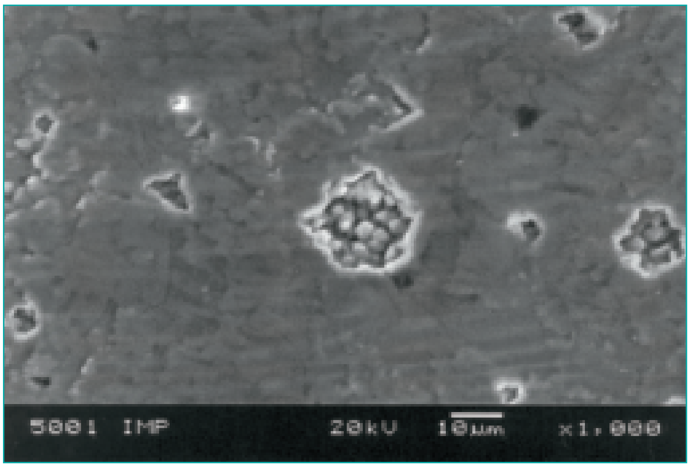
Influence of compounding ingredients

Zinc alternatives

Experiments were carried out on zinc oxide alternatives. As already shown, ZnS is formed as a reaction product of zinc oxide (or zinc containing ingredients) and sulphur. It is not be easy to eliminate sulphur or zinc oxide completely from the formulation, because both ingredients are essential in rubber (tyre) compounding. Elemental sulphur gives high mechanical strength and good bonding behaviour, zinc oxide activates the vulcanization system.

Rheometer experiments showed that the zinc oxide level may be reduced from 5 phr to 3 phr without significant changes in rheometer maximum, meaning that in principle almost a reduction of a factor 2 is possible. However, even with such a reduction no change in the deposit of ZnS was visible (Table 2). Also, by replacing ZnO by a type with a smaller particle size (Silox AC 40) no difference in deposit was visible. But when the ZnO is replaced by 0.25 parts of Nano ZnO of 40 nm (with the same rheometer maximum), thus reducing the zinc oxide level by a factor 20, short run vulcanization experiments up to 20 cycles with Nano ZnO in a compression mold showed no deposition of ZnS), table 2.

Figure 1
Porous PTFE surface with ZnS crystallites



2 Reduction by mold modification

Different parameters were investigated by means of short run experiments. Stainless steel with a roughness from 0.1 Ra to 2 Ra gave no reduction in mold fouling. Also, metallic coatings did not help to reduce mold fouling. Therefore, other coatings were investigated, like hybrid (chromic and chromic nitrid layers) coatings, PVD or CVD coatings (coatings prepared from a physical or chemical vapor damping process), diamond coating (DLC), ceramic coating (Enamel), and plastic coatings such as polyphenylenesulphide (PPS) and PTFE's.

All of the metal inserts with thin PTFE coatings showed crystallites (figure 1). For tyre molds thick ceramic coatings and thick PTFE coatings cannot be applied because of the design of the profile and the venturies involved. Another problem is the bad heat transfer from the mold through the coating to the rubber compound. For tyre molds a thin coating is advisable.

A further look at thin coatings with a 'non-porous' closed surface may give a solution to the mold fouling problem.

Magnetite coating

Also the electro mechanisms were studied. However, these cannot account for the formation of zinc sulphide (ZnS). This implies that the formation of ZnS at the interface of mold and rubber compound has to be caused by a physical or chemical reaction at the mold surface (ZnS crystallizes at the interface).

Vulcanization experiments at high temperature confirmed that the ZnS was formed as crystals on the mold surface. In this investigation it was already shown that nano-sized ZnS crystallites were formed (determination of ZnS) in the rubber and diffused from the rubber compound to the mold surface to interact on a molar basis with iron (Fe_2O_3) present at the surface, probably forming a marmetite (ZnSFe) lattice. This could then act as a grafting point for the build-up of ZnS crystallites. One would expect that the formation of ZnS crystallites by physical chemical reactions depend on oxidized or sulphurized iron atoms present on the surface of a mould. Then, it might be possible to prevent the formation of ZnS crystallites by changing the haematite (Fe_2O_3) surface of the iron of a mould to magnetite (Fe_3O_4). It is known that in central heating systems or boilers a magnetite coating is applied to prevent corrosion.

Table 1 Tyre compound (NR/BR blend)

Ingredients	Phr	Phr	Phr	Phr
NR	70	70	70	70
BR	30	30	30	30
Zinc oxide (ZnO)	5	3	-	-
Zinc oxide (Silox AC 40)	-	-	3	-
Zinc oxide (Nano ZnO)	-	-	-	0.25
Stearic acid	2	2	2	2
Carbon black (N375)	50	50	50	50
Oil (high aromatic)	5	5	5	5
Accelerator (TBBS)	1.25	1.25	1.25	1.25
Sulfur (S)	2.25	2.25	2.25	2.25

Table 2 Deposition of ZnS crystallites by using ZnO alternatives (NR/BR blend)

	ZnO (RS) 5 phr	ZnO (RS) 3 phr	ZnO (Silox) 3 phr	Nano ZnO 0.25 phr
As such	0	0	0	0
After 5 cycles	2	2	2	0
After 10 cycles	2	2	2	0
After 15 cycles	4	4	4	0
After 20 cycles	4	4	4	0
RMA	ZnS	ZnS	ZnS	-

0 = no deposition 1 = few small crystallites 2 = many crystallites covering <50%
3 = small and large crystallites 4 = crystallites covering >50%

For our study, a passivated iron mold (insert) was prepared. The passivation can be carried out chemically (alkali) or physically (steam). Two different magnetite coatings were investigated, both based on an alkali surface preparation method, and two PTFE-coatings. Initially, short run vulcanization experiments were carried out. Later, large scale runs were carried out in an injection mold machine. It was shown that no ZnS crystallites were visible at the mold surface. Not only the formation of ZnS (mold fouling) was observed, but also the mold release behavior. In Table 3 the mold fouling and release behavior is summarized for the most interesting coatings. The stainless steel coating is used as a reference material. As can be seen from the table after about 500 cycles no mold fouling was visible on the magnetite coatings and the thick PTFE coatings. Also a plastic coating (PPS) and a metal multi-layer from earlier investigations in this project were summarized in the table. On the PPS-coating and the multi-layer of chromic /chromic nitrid coating some crystallites were visible. During vulcanization experiments, all coatings showed good release properties.

Table 3 Evaluation of the most promising coatings

Coating	Thickness (micron)	Mold fouling	Mold release
Stainless steel	n.a.	-	+/-
Magnetite (thin1)	2.5	+	+
Magnetite (thin2)	4	+	+
PTFE (thick1)	25	+	+
PTFE (thick2)	18	+	+
PPS	26	+/-	+
Cr/CrN	11	+/-	+

\+ = no fouling resp. very good release
+/- = little fouling resp. good release
\- = fouling resp. bad release

3 Conclusions

Mechanism of mold fouling

It can be concluded that ZnS crystals are formed on the surface of metal molds through in situ formation of ZnS in the compound as a reaction product during vulcanization. Possible solutions might be:

Adapting a compound

- Mold fouling may be reduced by reduction of the zinc oxide level;
- Mold fouling can be eliminated or reduced by using nano-zinc oxide.

However, for optimal mechanical and dynamical properties of the compounds more investigations have to be carried out.

Applying a coating

- A magnetite coating is a very likely candidate. Results of tests are very promising but experiments in tyre molds are necessary to verify the potential of magnetite coatings in preventing mold fouling.

References

1) Mould fouling during vulcanization. B. van Baarle, Rubber World, December 2001.
2) Mould fouling during vulcanization (part 2), B. van Baarle, Rubber World, December 2004.

B. van Baarle LPRI, TNO Science and Industry, the Netherlands

Nitrosamines (continuation)

Following the article ‘Eliminating nitrosamines in natural rubber latex products’ also other producers have found solutions for eliminating nitrosamines and nitrosatable amines in natural rubber latex products.

Struktol (Schill & Seilacher) has demonstrated that it is possible to produce commercially acceptable HA and LA latex concentrates, containing no nitrosamines or nitrosatable amines, and causing no contact dermatitis if the new bactericidal chemicals are used to replace the TMTD. This bactericide has a FDA approval for food use. It is believed that the development of a new, more *“user friendly”* and *“environment friendly”* type of natural latex may help to improve the *“image”* of natural rubber latex.

Table 1 VFA Numbers: Changes on field latex

Time (days)	Latex A (TMTD/ZnO)	Latex B (LB219/ZnO)
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

Two latex samples were prepared in Malaysia. Latex A, a conventional sample containing TMTD and ZnO and latex B, containing Struktol LB219 and ZnO. When necessary, the MST levels of the compounds prepared with LB219 (which is a 50 (weight) % solution of synthetic carboxylates) were boosted by the addition of low amounts of Struktol LS100, an aqueous solution of a synthetic soap. To evaluate the relative performance of the preservative systems various characteristics of the samples were measured during 7 days. In table 1 a better per formance of Latex B (Struktol LB219) is shown when compared to Latex A (TMTD/ZnO). Also properties such as MST, VFA and KOH show no large differences after storage.

Table 2 Nitrosamine analysis of TMTD and LB219

	NDMA* (ppb)	NDEA** (ppb)
Latex A (TMTD/ZnO)	100-430	1-5
Latex B (Struktol LB219/ZnO)	nd	nd

*NDMA = nitrosodimethylamine
**NDMA = nitrosodiethylamine
nd = not detectable

To confirm that the new preservative is free of nitrosatable amines prior to use, samples were analysed (method BGVV (Bundesgesundheitsamt) by Rubber Consultants analytical laboratory in the UK). In addition, cast raw rubber films prepared from these lattices were tested to determine the nitrosatables present (table 2).
Comparative measurements of certain properties show no significant differences in compound properties and vulcanizate properties (table 3).

Condensed version from additives for the latex industry, Latex April 2004,
Clara Petri, General Manager - Latex Additives (Struktol, Schill & Seilacher, Germany)

Table 3 Compound and vulcanizate properties from lattices A and B

Properties	Latex A	Latex B
	Compound	
DRC (%)	49.4	49.5
Visc. (Cup #3)	25.3	25.3
MST (sec)	1720	1780
pH	11.4	11.3
	Vulcanizate	
TS (MPa)	28.2	27.6
M 300% (MPa)	1.7	1.7
EB (%)	870	870

Accelerators

Effect of Antioxidants and latex Vulcanising Agents on the Environmental Degradation of latex Films

A.Ikram, et al. Rubber research Institute of Malaysia, Kuala Lumpur, Malaysia.

The role of antioxidants and latex vulcanizing agents on the environmental degradation of NR latex gloves and films was studied. In agar plate culture, more than 80% of bacteria grow on the phenolic antioxidants. The dithiocarbamate accelerators, ZDEC was more inhibitory than ZDBC. The growth of fungi except yeast was unaffected by the presence of the antioxidants and accelerators. Increasing the level of crosslink concentrations increased their resistance to environmental degradation.

Physical property changes in commercial Natural Rubbers during long term storage

J. Yunyongwattanankorn, and J. T. Sakdapipanich, Mahodol University, Thailand.

Standard Thai Rubbers (STR) i.e. XL, 5L and CV 60 were investigated for 14 months, for Mooney viscosity, gel content and initial plasticity. The findings indicated that storage-hardening occurred in all the rubber samples. There was no clear relation with gel content with respect to storage time, indicating that the depth or position of specimens in a rubber bale did not affect the storage-hardening.

Preparation and Evaluation of Thermally Depolymerized Natural Rubber in Rubber Compound Formulations

F. Cataldo, Trelleborg Wheel Systems, Rome, Italy.

Natural rubber was depolymerized into a viscous oil by a low temperature pyrolytic process. The liquid natural rubber was tested as plasticizer in rubber formulations. The performances offered by depolymerized natural rubber as plasticizer was satisfactory in comparison to aromatic oil and surprisingly it was found that the natural rubber oil gives higher hysteresis (tan@ 60°C) in comparison to a traditional aromatic extract.

Fillers

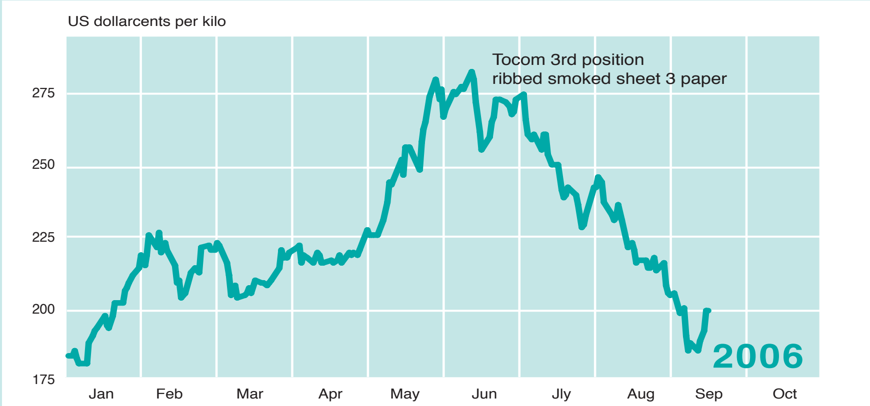
Pirelli making tyre division a stand-alone company

Pirelli & C. Spa's board of directors are planning to spin off the firm's tyre business into a separate, publicly traded company - but one in majority owned by Pirelli (erj).

Michelin spending $94 million to expand Thai tyre plant

Michelin is investing $94 million to expand capacity for passenger tyres by about a third at its Michelin Siam Cp. Ltd plant in Thailand (erj).

Natural rubber prices during 2006 and the current outlook



2006 started the year on a buoyant note, as prices were at record highs, influenced by both the all time highs in oil and gold, and also the Japanese speculators, who were riding a rubber market which had been on a three year not uninterrupted, but certainly steadily constant rise. Rubber producers were all enjoying very good returns, and even the main tyre companies were getting used to the high prices, and some were even buying forward. February saw the peak, and then the long awaited fall started. Again, nothing in natural rubber is totally constant, but with the odd rise occurring for profit-taking, prices fell from February to September by around 30%. Producers were at first slow to follow this trend, and tried through reports of poor weather etc. to keep the record high prices, but with speculators and dealers willing to discount the forward positions, the producers also reluctantly jumped on the bandwagon, and took any orders as the market fell. Reports of Chinese letters of credit either being delayed of just defaulted on for high prices rubber purchases also added fuel to the fall, and some weeks saw two or three limit-down movements.

Currently, early October, prices have steadied up, and are now approx 5% up from the September lows, and appear confidently steady backed up with wet weather in Thailand, and a lower than usual field crop. The outlook is now more uncertain than ever, as if one compares the current levels to those of the past five years, then prices are still very high, but if the comparison is just prices this year, then prices still look low, and current levels could be considered attractive. Short term prices seem to look like rising higher, but most are still long term bears.

Apollo to bring truck radial capacity on stream

Apollo tyres Ltd is adding truck- and bus capacity to its radial tyre plant in Limda, India. The company expects the line on steam in October (erj).

IRSG-Government of India

India is a producer of both NR and SR, but with the former accounting for, by far, the largest portion of total rubber output. Indian production of NR has grown at a rate of 8% a year from around 25,000 tonnes in 1960 to 745,700 tonnes in 2004, taking almost 9% of the world share and making the nation the fourth largest producer, behind Thailand, Indonesia and Malaysia.

www.rubber-stichting.info for rubber platform and regular updates of the Events list

The R-S Information Center for Natural Rubber

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The aim of the **R-S Information Center for Natural Rubber** is to give information to **companies and institutions** about properties and processing of natural rubber and about products manufactured on the basis of natural rubber. Information is provided by publishing the free newsletter *"Natuurrubber/Natural Rubber"*, by maintaining the Center's website and by answering questions asked by e-mail.