New anti-ozonant - 6PPD - IPPD - Migration - Release of physical properties

Currently available antiozonants such as N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD) and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD) migrate either during vulcanization or during service, thus affecting ageing protection and fatigue resistance. A slow migrating antiozonant and also a relevant test protocol for screening antiozonant protection was developed.

In this paper a comparison has been made with regard to migration of anti-degradants such as 6PPD, IPPD and development products in typical sidewall compounds using a recently developed test protocol. The combination of 6PPD and the development product provide longer lasting and better appearance of tire black sidewalls. Physical and dynamic properties are better retained in presence of the newly developed antidegradant. A good migration correlation was found between outdoor ageing and the dynamic ageing test method.

A Novel Slow Release Antidegradant for the Rubber Industry

Part 1: Migration behavior of newly developed anti-ozonant compared to conventional antidegradants

The migration of antidegradants (especially antiozonants) is an important feature in the protection of rubber formulations used in the tire industry and other industrial rubber products.

There are numerous theories outlined in the literature [1, 2] describing ozone protection both under static and dynamic environments. For achieving sufficient ozone protection under static environments, the waxes (paraffinic wax for temperature below 40 °C and microcrystalline wax for temperatures above 40 °C) are the best choice. However, rubber articles face dynamic environments and hence waxes alone cannot protect the article from ozone attack. For dynamic applications, the chemical antiozonants have been developed and are widely used today. The mechanism of protection is migration to the surface and reaction with ozone keeping the rubber unreacted [3].

The speed of migration of antiozonants plays a dominant role in protection against ozone. Several reports [4] indicate however that diffusion is not the sole criteria. Also the products formed by reaction with ozone are excellent and effective antiozonants themselves.

Currently, the most accepted mechanism of antiozonant action is a combination of the scavenging theory and protective film theory [5–7]. Therefore, it is obvious that the major characteristics required as antiozonant properties are migration to the surface of a rubber vulcanize and reactivity towards ozone.

Although, conventional antidegradants as N-(1,3-dimethylbutyl)-N'-phenyl-phenylene diamine (6PPD) are still the most widely used antidegradants in rubber, there is a trend and demand for longer-lasting and non-staining products [8].

Over the years, Flexsys has been working on the development of slow diffusion antiozonants with the aim to protect rubber articles for longer duration and to provide longer lasting tire black sidewalls with better appearance [9]. The research is culminated in the development of 6PPD-C18, a salt of 6PPD and stearic acid. In this paper, a comparison has been made with regard to migration of antidegradants such as 6PPD, IPPD and the 6PPD-C18 salt in typical sidewall compounds using a recently developed test protocol. Physical and dynamic properties were determined before and after a dynamic ageing test protocol. A comparison has been made to correlate the lab ageing test and outdoor ageing performance.

Experimental

Characterization of 6PPD-C18

6PPD-C18 was produced in the laboratory according to the procedure reported earlier [9]. The product obtained has a melting range of 40–50 °C. Infrared (IR) analysis indicated the disappearance of NH bands between 3370 and 3390 cm⁻¹.

The composition of 6PPD-C18 was also estimated by DOSY-¹H NMR (Diffusion Ordered Spectroscopy). This two-dimensional spectroscopic technique can differentiate between products having similar chemical shifts in a NMR spectrum but have different molecular weights. This technique is based on differences in diffusion or mobility. Lower molecular weight products are more mobile than those with a higher molecular weight and generate signals at higher values on the y-axis of the ¹H NMR spectra. It is obvious from the spectra plotted in Fig. 1 that the proton signals for both the stearic acid part (1.2–2.6 ppm) and the 6PPD part (7.0–
7.6 ppm) of PPD-C18 are located at approximately the same level on the y-axis of the Dosy 1H NMR spectra. The proton signals at 3.7–3.9 ppm are related to the methylester of stearic acid. This product is formed during the synthesis of 6PPD-C18 with methanol as a solvent. The proton signals of the methylester of stearic acid are positioned at a higher level (lower molecular weight) on the y-axis. These facts indicate that PPD-C18 is present as a complex rather than as a mixture of 6PPD and stearic acid.

Formulations, mixing and curing
Compound formulations are shown in Table 1 and 2. All the ingredients except sulfur and accelerators were mixed in a 1.6L internal mixer. Sulfur and accelerator were mixed on a two-roll mill at 50±65 °C according to standard laboratory mixing conditions. Compounds were cured to optimum cure by compression molding at 150 °C/190.

Ageing
Dynamic ageing:
Rubber test pieces (2 mm thickness) were flexed on a Monsanto fatigue to failure tester for 24 hours, at 23 °C, 1.67 Hz and 10 % strain. After the flexing, bloom was removed with acetone (not extracted but wiped off with a tissue that was saturated with acetone). Finally, the test pieces were aged in an air circulation oven for 7 days at 70 °C. This procedure was done once or repeated several times as indicated in respective tables.

Heat ageing:
Test pieces were aged in an air circulation oven for 14 days at 70 °C. Samples were kept for 24 hours at room temperature before final measurements.

Outdoor ageing:
Rubber test specimen (2 mm thick sheets) were exposed to weathering on the rooftop in Deventer, The Netherlands from December 2001 onwards.

Testing
Rheologic properties:
Cure data were determined on a Monsanto MDR 2000E according to ISO 6502-1991.

Stress-strain properties:
Stress-strain properties were determined on a Zwick tensile tester 1445, according to ISO-37:1995.

Fatigue to failure:
Fatigue to failure properties were measured on a Monsanto fatigue tester at 23 °C, 1.67 Hz and 100 % dynamic strain.

Ozone resistance:
Resistance to ozone cracking was measured in an Argentox ozone cabinet type 3MR-3R according to ISO 1431-1 ‘89 (static test) and ISO 1431-2 ‘89 (dynamic test).

Crosslink density distribution:
The crosslink density distribution was determined by measuring the crosslink density before and after chemical probe reactions as described by R.N. Datta [10] and references 11 to 17 cited therein.

Migration
Migration was studied by placing a plate of control vulcanizate (without antiozonant) in-between two plates of vulcanizate containing the experimental antiozonant. The three plates were placed in a metal mold and put in an air circulation oven as described by Kavun, Lehocky and Syrovy [11, 12]. The dimensions of the rubber plates are 10·10·1 cm. Experiments

Table 1. Formulations (Migration test)

<table>
<thead>
<tr>
<th>INGREDIENTS / MIXES</th>
<th>01</th>
<th>02</th>
<th>03</th>
<th>04</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BLANK</td>
<td>6PPD</td>
<td>PPD-C18</td>
<td>IPPD</td>
</tr>
<tr>
<td>NR SMR CV</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Buna CB 10</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Carbon black N-550</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Santoflex 6PPD</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Santoflex 6PPD/C18</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Santoflex IPPD</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Santocure CBS</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Note: Compounds contain equimolar amounts of PPD

Table 2. Formulations (Rubber test)

<table>
<thead>
<tr>
<th>INGREDIENTS / MIXES</th>
<th>05</th>
<th>06</th>
<th>07</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BLANK</td>
<td>6PPD</td>
<td>6PPD / PPD-C18</td>
</tr>
<tr>
<td>NR SMR CV</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black N-550</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Na. oil Synth. 4240</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Velex Sunolite 240</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Santoflex 6PPD/C18</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Santoflex IPPD</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Santocure TBS</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Figure 1. Dosy 1H NMR of Santoflex 6PPD-C18 (no solvent used)
were carried out at constant temperatures of 40° and 80° C. The amount of antiozonant that migrates to the center rubber plate was monitored by determination of the weight increase of the center plate and by analyzing the toluene and/or dichloromethane extractables of cryogenic ground rubber using GC and Flow Injection Analysis Mass Spectroscopy (FIA-MS). This was done after several fixed time intervals.

Quantification and identification by GC/FIA-MS

The amount of 6PPD present in the toluene and dichloromethane extractables of the rubber vulcanizates was quantified using a capillary gas chromatograph equipped with a split injector and a flame ionization detector. Identification of the different peaks was done by FIA-MS using the Platform-II quadrupole ex Micromass. In positive ESI, components should give [M + H] + or [M + Na] + adducts, so m/z values of M + 1 or M + 23 are expected. Ionization was done by electrospray positive/negative (scan range 200–1500 Da; capillary voltage 3.50 kV; HV lens 0.5 V; skimmer 5 V; Cone voltage 10/30 V/60 V; source temperature 60 °C). Methanol was used as a carrier solvent.

**GC-conditions:**
- Column: fused silica column WCOT, 17 m - 0.32 mm ID
- Stationary phase: Sil 5 CB, 100 % polydimethylsiloxane, crosslinked
- Film thickness: 0.4 μm
- Injector: Split, 250 °C
- Detector: FID, 330 °C
- Temp. program: 120 °C (1 min.)
  - 10 °C/min.
  - 320 °C (25 min.)

Results and discussion

**Migration behavior of antiozonants**

The type of rubber and fillers influences the migration behavior [13]. The stronger the intermolecular interactions of antidegradants are with the matrices, the slower the migration rates. In this study the amount of fillers and polymer is kept the same. The level of antidegradants used was maintained equal in mmoles (15 mmoles/100 phr rubber) as can be seen in Table 1. The migration characteristics at 40 °C for 6PPD, IPPD and 6PPD-C18 in a typical passenger sidewall compound are shown in Fig. 2. The weight increase of the center plate (in mmoles) is plotted against the square root of the time. The slope of the curve is directly related to the migration rate of the antiozonant.

As expected, it is evident from this figure that IPPD migrates faster than 6PPD, which can be explained by the lower molecular weight of IPPD compared to that of 6PPD [14]. The development product, 6PPD-C18, however showed a slower migration rate compared to that of 6PPD.
slower migration rate should result in long-term protection when applied in tires. The rubber plates were analyzed by FIA-MS before and after the migration test. It could be clearly demonstrated that the center plate in the 6PPD-C18 experiments contains a lower amount of 6PPD than that of the 6PPD reference (Fig. 3). On the other hand, similar amounts of stearic acid were found in the center plate for all the tested antiozonants (control (1B), 6PPD (2B) and 6PPD-C18 (3B)) as can be seen in Fig. 4. Based on these observations, it can be concluded that stearic acid is not migrating and that 6PPD-C18 is working as a slow release agent for 6PPD.

**Dynamic ageing test protocol**

A test protocol was developed that would correlate long-term ageing and could be used for the comparison of different long-lasting antiozonants. It is well known in the rubber industry that results obtained from accelerated ageing tests should be used only for the relative comparison of compounds rather than for the prediction of long-term service life. Reliable information regarding long-term service life can only be obtained by carrying out field-testing.

Antiozonants migrate to the surface during ageing. The migration rate of antiozonants increases at increasing temperatures and might also increase during deformation. Therefore, it was investigated if a combination of dynamic flexing and heat ageing could be used as an accelerated ageing procedure. Compounds were aged at different temperatures and at different dynamic extensions. After ageing, compounds were extracted and analyzed for the remaining amount of antiozonant. A comparison was made to outdoor ageing (top roof ageing).

As can be seen from Fig. 5, one ageing cycle of 24 hours dynamic flexing at 10% strain and subsequent heat ageing in an air circulation oven for 7 days at 70°C corresponds well with three months outdoor ageing. It can be seen from Fig. 5 that approximately 10% PPD is lost during mixing and another 10% during vulcanization. Approximately 20% PPD is lost during the first ageing cycle. More PPD is lost during subsequent ageing cycles. Long-lasting antiozonants are supposed to migrate slower to the surface of rubber compounds than conventional antiozonants as 6PPD and IPPD and should therefore perform better after dynamic ageing.

The evaluation of different antiozonants by using the described dynamic ageing procedure is described in the next section.

**Physical and dynamic properties**

The effect of antiozonants on the physical mechanical properties was studied in a typical truck sidewall compound before and after several ageing procedures (heat ageing and dynamic ageing). The compound composition is tabulated in Table 2. A comparison was made between 6PPD and a mixture of 6PPD and 6PPD-C18 (a development product of Flexsys). The 6PPD-C18 was not tested as such but in combination with 6PPD because 6PPD is expected to provide short-term and 6PPD-C18 longer-term protection against ozone attack.

Compounds were mixed and cured to optimum cure (t90) at 150°C. As can be seen from Fig. 6, hardly any difference in cure characteristics could be observed between compounded 6PPD and the mixture of 6PPD and 6PPD-C18. Both compounds showed slightly decreased scorch times and torque rates compared to the control compound without antiozonant. The effect of PPD’s on the scorch time was expected and can be explained by the Pkb value of these products. The lower Delta torque can be explained by a lubricating effect of the PPD’s.

The effect of the tested antiozonants on the tensile strength is demonstrated in Fig. 7. It is obvious that in the presence of the combination 6PPD/6PPD-C18 better properties were obtained than in the presence of 6PPD. The difference is most pronounced after dynamic ageing. Similar observations were made for the resistance against ozone (Fig. 8) and for the fatigue properties (Fig. 9). 6PPD-C18 showed better retention of physical and dynamic properties. Besides improved retention of properties, also a better appearance of the 6PPD/6PPD-C18 containing compound was observed compared to that of the 6PPD-containing compound.

The better retention of physical and dynamic properties can be explained by elucidation of fine structure of the network before and after ageing. Before ageing, hardly any difference in crosslink density...
nor in crosslink density distribution was observed between compounded 6PPD and the mixture of 6PPD and 6PPD-C18. However, after dynamic ageing a significantly higher amount of polysulfidic- and a lower amount of monosulfidic crosslinks was observed in the presence of the 6PPD/6PPD-C18 combination. The improved fatigue properties can be explained by the higher ratio of polysulfidic/monosulfidic crosslinks. Polysulfidic crosslinks are thought to break up under strain and upon removal of the load rearrange to form new crosslinks at different sites [15]. The improved tensile properties can also be explained by the higher amount of polysulfidic crosslinks, according to investigations done by Brown [16], where hypothesis has been made that crosslinks that are capable of lowering the stress peaks (slipping model) give a favorable network with respect to strength properties.

The lower migration rate of 6PPD-C18 and thus the higher amount of antiozonant available can explain the improved resistance against ozone obtained for the vulcanizate containing the mixture of 6PPD and 6PPD-C18 after dynamic ageing.

Conclusions

The dynamic ageing procedure described in this paper (a combination of dynamic flexing and heat ageing) showed a good correlation with outdoor ageing. The described procedure was developed in order to demonstrate long-term protection against ozone. It was clearly demonstrated that physical and dynamic properties are better retained in the presence of a combination of Santoflex 6PPD and Santoflex 6PPD-C18 compared to conventional antiozonant, such as Santoflex IPPD and Santoflex 6PPD. It is obvious that the described combination of antiozonants provide longer lasting and better appearance of tire black sidewalls.

A lower migration rate for the development product Santoflex 6PPD-C18 was observed compared to that of the conventional antiozonants IPPD and 6PPD. The lower migration rate could be explained by the fact that the 6PPD-C18 complex is active as a slow release agent for 6PPD. The stearic acid part of the complex is not migrating.

![Figure 7. The effect of different antiozonants on the tensile strength.](image1)

![Figure 8. The effect of different antiozonants on resistance against ozone.](image2)

![Figure 9. Effect of different antiozonants on fatigue properties.](image3)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>05</th>
<th>06</th>
<th>07</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged</td>
<td>BLANK</td>
<td>PPD</td>
<td>PPD/PPD-C18</td>
</tr>
<tr>
<td>Total</td>
<td>4.98</td>
<td>5.05</td>
<td>5.10</td>
</tr>
<tr>
<td>Poly-S</td>
<td>3.92</td>
<td>4.05</td>
<td>4.10</td>
</tr>
<tr>
<td>Di-S</td>
<td>0.83</td>
<td>0.74</td>
<td>0.75</td>
</tr>
<tr>
<td>Mono-S</td>
<td>0.23</td>
<td>0.26</td>
<td>0.25</td>
</tr>
<tr>
<td>Dynamic ageing</td>
<td>4.70</td>
<td>5.20</td>
<td>5.25</td>
</tr>
<tr>
<td>Total</td>
<td>2.51</td>
<td>2.70</td>
<td>3.62</td>
</tr>
<tr>
<td>Poly-S</td>
<td>0.60</td>
<td>0.52</td>
<td>0.70</td>
</tr>
<tr>
<td>Di-S</td>
<td>1.59</td>
<td>1.98</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Table 3. Effect of different antiozonants on the crosslink density distribution [2Mc⁻¹·10E5 gm mole/gram].
Acknowledgments
We would like to thank Flexsys for allowing publishing this paper. Furthermore, also thanks are due to Dr. S. Datta and Mr. W. Maslow for the analytical support and Mr. G. Hogeboom for the support in the application laboratory.

References

The authors
Dr. R. N. Datta is Market Development Manager and Mr. N. M. Huntink is Application Research Manager of Flexsys BV, Technology Center, The Netherlands

Corresponding adress:
Mr. N. M. Huntink
Flexsys BV
Technology Center
Zutphenseweg 10
NL-7418 AJ Deventer
E-mail: Nico.M.Huntink@Flexsys.com