

# Ozonolysis of Model Olefins—Efficiency of Antiozonants

N. M. Huntink,<sup>1</sup> R. N. Datta,<sup>1</sup> A. Talma,<sup>2</sup> J. W. M. Noordermeer<sup>3</sup>

<sup>1</sup>Teijin Twaron, P.O. Box 9600, 6800 TC Arnhem, The Netherlands

<sup>2</sup>Akzo Nobel, P.O. Box 9300, 6800 SB Arnhem, The Netherlands

<sup>3</sup>University of Twente, 7500 AE Enschede, The Netherlands

Received 9 September 2004; accepted 17 May 2005

DOI 10.1002/app.22861

Published online 10 January 2006 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this study, the efficiency of several potential long lasting antiozonants was studied by ozonolysis of model olefins. 2-Methyl-2-pentene was selected as a model for natural rubber (NR) and 5-phenyl-2-hexene as a model for styrene butadiene rubber (SBR). A comparison was made between the efficiency of conventional antiozonants like *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylene diamine (6PPD), *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine (IPPD), and a mixture of diaryl *p*-phenylene diamines (Wingstay 100) and some newly synthesized antiozonants. The stearic acid salt of 6PPD (PPD-C18), 2,4,6-tris(4-(phenylamino)phenyl)-1,3,5-triazinane (ADPAT), and 4-pyrrole diphenylamine (PDPA) showed a higher efficiency than the conventional antiozonants in both NR as well as SBR model system. Special attention was paid to the carboxylic acid salts of 6PPD such as PPD-C18, which has shown good long-term protection of passenger tire sidewall compounds. It was demonstrated that by varying the chain length, C7, C18, and C22, of the carboxylic acid part of the 6PPD salts, the ozone protection

was not influenced under the selected test conditions. The 6PPD salts made from strong acids like succinic acid (SA) and methyl sulfonic acid (MSA) appeared to be less efficient than PPD-C18. It was also investigated whether the reactions between ozone and the double bonds of the model rubber could be measured online by a spectroscopic technique. It was demonstrated that near infrared spectroscopy is a suitable technique to study these reactions. FT Raman looked also a promising technique because of the high response factor of double bonds. However, the addition of *p*-phenylene diamines (PPDAs) to the sample solution resulted in a strong discoloration (dark brown) and therefore in a high fluorescence background signal. This technique can therefore not be used for the evaluation of staining antiozonants. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 853–866, 2006

**Key words:** differential scanning calorimetry (DSC); rubber; synthesis

## INTRODUCTION

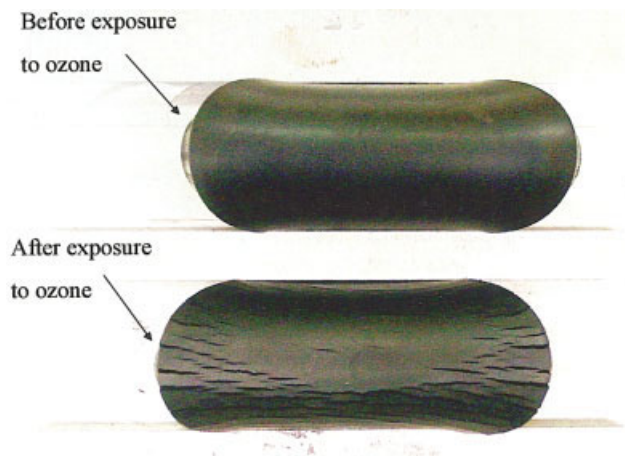
Ozone cracking is an electrophilic reaction and starts with the attack of ozone at a location with a high electron density.<sup>1</sup> In this respect, unsaturated organic compounds like most rubbers are highly reactive with ozone. The reaction of ozone is a bimolecular reaction where one molecule of ozone reacts with one double bond of the rubber to form a primary ozonide. At room temperature, these ozonides cleave as soon as they are formed to give an aldehyde or ketone and a zwitterion. By combination of zwitterions polymeric peroxides can be formed. Because of the retractive forces in stretched rubber, the aldehyde and zwitterion fragments are separated at the molecular-relaxation rate. Therefore, the ozonides and peroxides form at sites remote from the initial cleavage, and the underlying rubber chains are exposed to ozone. These unstable ozonides and polymeric peroxides cleave into a variety of oxygenated products, such as acids,

esters, ketones, and aldehydes, and also expose new rubber chains to the effects of ozone. The net result is that, when rubber chains are cleaved, they retract in the direction of the stress and expose underlying unsaturation. Continuation of this process results in the formation of the characteristic ozone cracks, as demonstrated in Figure 1. The presence of water increases the rate of chain cleavage, which is probably related to the formation of hydroperoxides. The same chemistry occurs on ozonation of rubber, in solution and in the solid state.<sup>2,3</sup>

The reaction of ozone with olefinic compounds is very rapid.<sup>4</sup> Substituents on the double bond that donate electrons increase the rate of reaction while electron-withdrawing substituents slow down the reaction. Thus, the rate of reaction with ozone decreases in the following order: polyisoprene > polybutadiene > polychloroprene.<sup>5</sup> Rubbers can be protected against ozone by using chemical antiozonants and via several physical methods. The chemical antiozonants protect rubber under both static and dynamic conditions, whereas the physical methods are more related towards protection at static conditions.

Chemical antiozonants have been developed to protect rubber against ozone under dynamic conditions.

Correspondence to: N. M. Huntink (Nico.Huntink@Twaron.com).



**Figure 1** Formation of characteristic ozone cracks after exposure to ozone. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

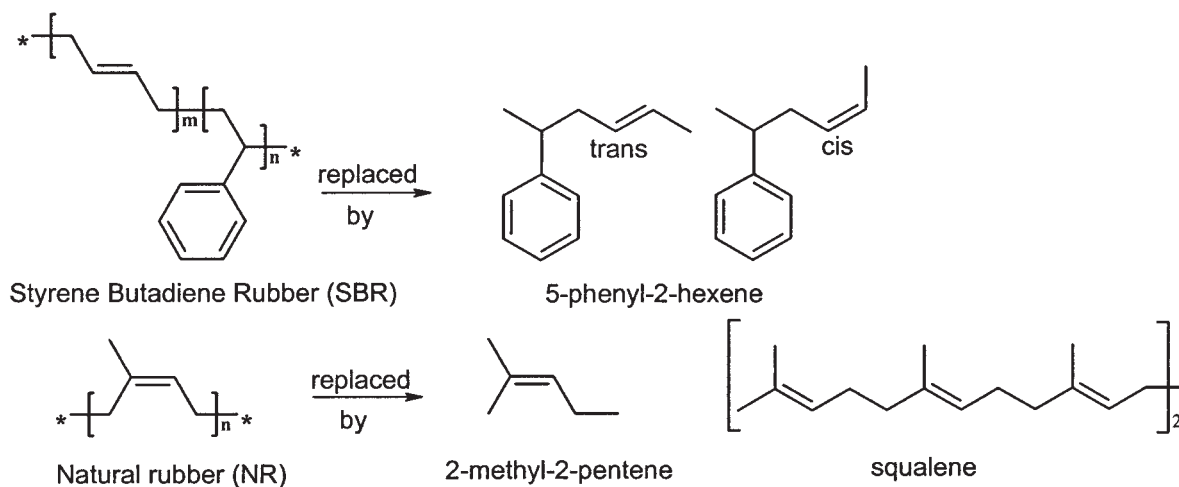
Several mechanisms have been proposed to explain how chemical antiozonants protect rubber. The scavenging mechanism, the protective film mechanism, or a combination of both are nowadays the most accepted mechanisms.<sup>5-14</sup>

Because rubber, whether vulcanized or not, is generally difficult to investigate by standard analytical and spectroscopic techniques, researchers have attempted to overcome this by looking at isolated network constituents: the concept of model-compound vulcanization.<sup>15,16</sup> A low molecular weight model is chosen to represent the reactive unit of the polymeric rubber. This concept has also been chosen for the ozonolysis experiments in this paper. 5-Phenyl-2-hexene was selected as the model for styrene butadiene rubber (SBR). 2-Methyl-2-pentene and squalene were selected as model for natural rubber (NR). The structure of the selected models is shown in Figure 2.

The choice of an appropriate model compound is determined by the specific properties of the models and by the purpose of the experiments. An elementary disadvantage of low molecular weight models such as 2-methyl-2-pentene or 5-phenyl-2-hexene is that they are monofunctional, i.e., they contain only one double bond. Polyfunctional models such as squalene can display reactivity for which more than one double bond is required. Unfortunately, all the double bonds in squalene are trans-configured and not cis-configured as in NR.

The first part of this paper focuses on the determination of the efficiency of different antiozonants by competitive experiments in  $\text{CH}_2\text{Cl}_2$ . 2-Methyl-2-pentene and 5-phenyl-2-hexene (cis and trans) are selected as models for NR and SBR, respectively. The efficiency of some of the newly synthesized antiozonants is determined and compared with that of conventional antiozonants like *N*-(1,3 dimethylbutyl)-*N'*-phenyl-*p*-phenylene diamine (6PPD), *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine (IPPD), and diaryl *p*-phenylene diamines (Wingstay 100). Only the initial reaction of the antiozonant with ozone is rapid; the resulting ozonized products always react much more slowly. Thus, the number of moles of ozone absorbed by a compound is not necessarily an indication of the effectiveness of the antiozonant. It is only the rate of reaction that is important. The kinetics of the reaction between ozone and the model compound is studied in the presence and the absence of those antiozonants. The kinetics are followed via determination of the concentration of antiozonant and model compound by GC analysis, before and after treatment with ozone, for several time intervals.

The loss of antiozonants, either in a chemical or physical manner, appears to be the limiting factor in providing long-term protection of rubber products.



**Figure 2** Structure of the model compounds used for NR and SBR.

TABLE I  
Abbreviation, Chemical Name, Structure of the Tested Antiozonants

Abbrev.	Chemical name	Structure
QDI	Benzamine, <i>N</i> -(4-(1,3-dimethylbutyl)imino)-2,5-cyclohexadiene-1-ylidene	
6PPD	<i>N</i> -(1,3-dimethylbutyl)- <i>N'</i> -phenyl- <i>p</i> -phenylenediamine	
77PD	<i>N,N</i> -Bis(1,4-dimethylpentyl)- <i>p</i> -phenylenediamine	
IPPD	<i>N</i> -Isopropyl- <i>N</i> -phenyl- <i>p</i> -phenylenediamine	
Wingstay 100	Mixture of diaryl <i>p</i> -phenylene diamines	
PPD-HA	PPD-salt of heptanoic acid	
PPD-C18	PPD-salt of stearic acid	
PPD-SA	PPD-salt of succinic acid	
PDPA	4-Pyrole-diphenylamine	
ADPAT	2,4,6-Tris(4-(phenylamino)phenyl)-1,3,5-triazino	
ADPA-DTBF	2,6-Di- <i>tert</i> -butyl-4[(4-phenylamino-phenylimino)-methyl]-phenol	
PPD-MSA	PPD-salt of methyl sulfonic acid	

That is why for new antiozonants not only the efficiency of the antiozonants must be evaluated, but one also has to carefully investigate other properties that influence their protective functions in a different manner. For instance, the antiozonant's mobility, its ability to migrate, is one of the parameters determining the efficiency of antiozonant action.

It is also investigated whether the reaction between ozone and the model rubber compound can be followed online, by a spectroscopic technique. Both FT Raman and near infrared (NIR) spectroscopy are used for this purpose. These techniques are capable of monitoring the decrease of double bonds and can therefore probably also be used for monitoring rubbers or model rubbers, like squalene, having multiple double

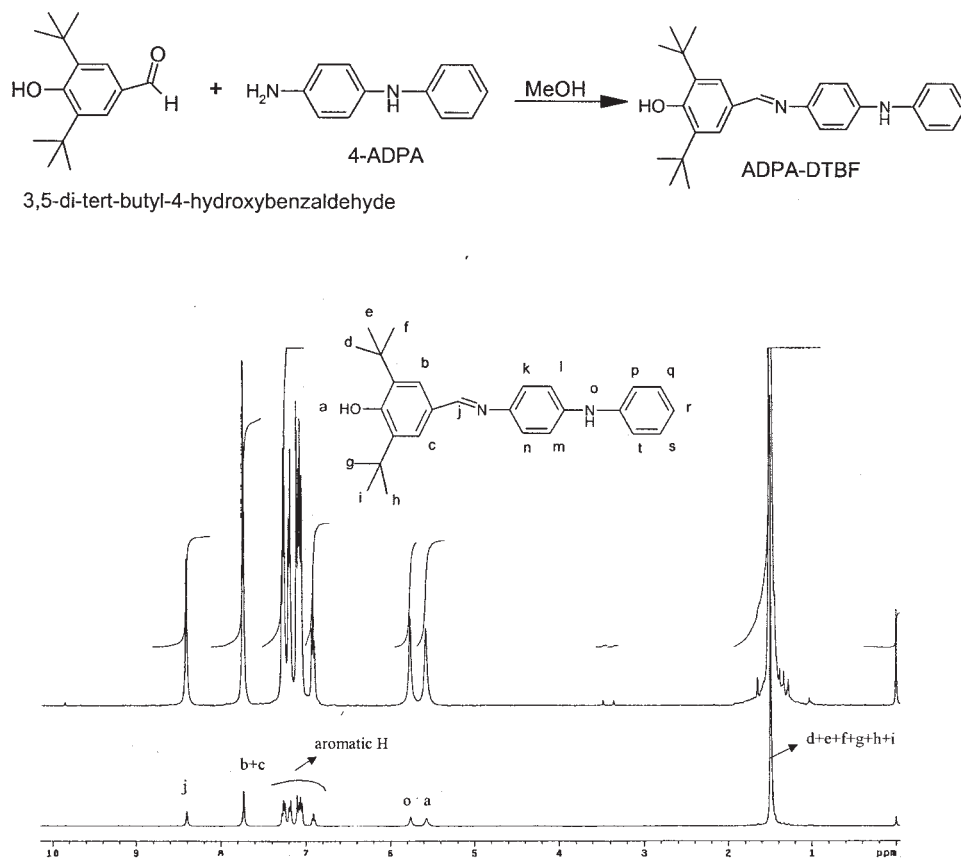
bonds. FT Raman is the preferred spectroscopic technique because it is very sensitive for symmetric vibrations and is noninvasive. These results are described in the Appendix.

## EXPERIMENTAL

### Materials

Materials used for synthesis of tested antiozonants

For the syntheses the following chemicals were used: methanol (J.T. Baker, assay min. 99.8%; CAS no. 67-56-1), ethanol (J.T. Baker, assay min. 99.9%; CAS no. 64-17-5), toluene (J.T. Baker, assay min. 99.5%; CAS



**Figure 3** <sup>1</sup>H NMR spectrum of ADPA-DTBF determined in deuterated chloroform.  $\delta$ : 1.49 (d + e + f + g + h + i); 5.58 (a, OH); 5.77 (o); 6.88–7.30 (aromatic H); 7.75 (b + c); 8.41 (j).

no. 108–88-3), dichloromethane (J.T. Baker, assay min. 99.5%; CAS no. 75–09-2), formaldehyde (Janssen; 37 wt % solution in water; CAS no. 50–00-0), stearic acid (J.T. Baker; CAS no. 57–11-4), succinic acid (Janssen, assay min. 99%; CAS no. 110–15-6), methane sulfonic acid (Across, assay min. 99%; CAS no. 75–75-2), 2,5-hexane dione (Janssen, assay min. 97%; CAS no. 110–13-4), 3,5-di-*t*-butyl-4-hydroxy benzaldehyde (Janssen, assay min. 97%; CAS no. 68–12-2), 2,6-di-*t*-butylphenol (Janssen, assay min. 99%; CAS no. 128–39-2), 4-amino diphenylamine (Janssen, assay min. 99%; CAS no. 101–54-2), formalin (Jansen, assay min. 98%; CAS no. 50–00-0), and *p*-toluenesulfonic acid (Jansen, assay min. 99%; CAS no. 6192–52-5).

#### Materials used for ozonolysis experiments

2-Methyl-2-pentene (Janssen, assay min. 99%; CAS no. 625–27-4), squalene (Janssen, assay 98%; CAS no. 111–02-4), dichloromethane (J.T. Baker, assay min. 99.5%; CAS no. 75–09-2), 5-phenyl-2-hexene (synthesis see below), potassium iodide (Janssen, assay min. 99.5%; CAS no. 7758–05-6), sodium hydroxide (Janssen, assay min. 98%; CAS no. 1310–73-2), *n*-decane (Aldrich, assay min. 99%; CAS no. 124–

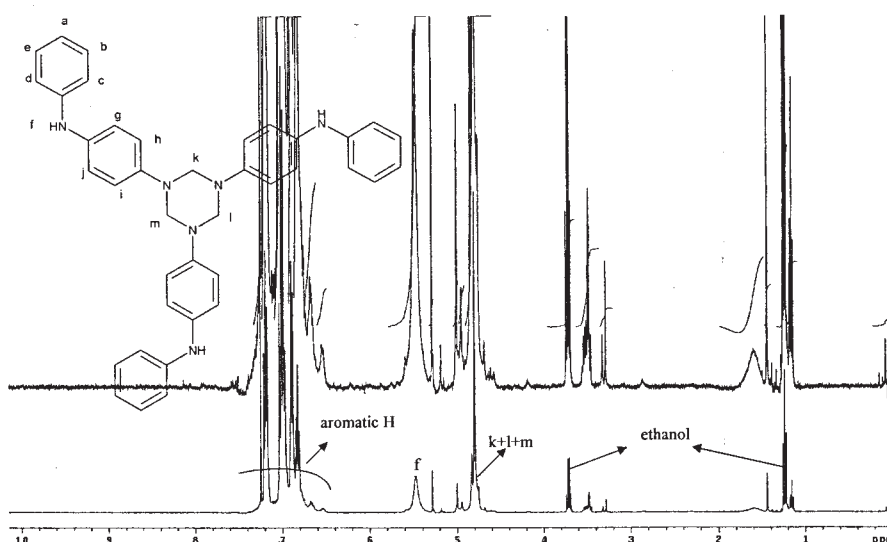
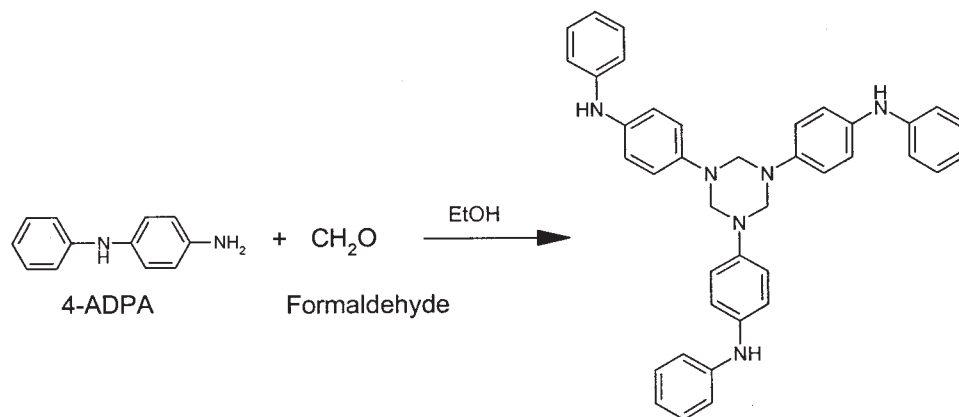
18-5), and calcium chloride (Janssen, assay min. 96%; CAS no. 10043–52-4).

#### Materials used for 5-phenyl-2-hexene (sbr model) synthesis

Ethyl-triphenyl phosphonium bromide (Aldrich, assay min. 99%; CAS no. 1530–32-1), *n*-butyllithium (Acros, 2.5M solution in hexane; CAS no. 109–72-8), 3-phenylbutyraldehyde (Aldrich, assay 97%; CAS no. 16,251–77-7), anhydrous diethylether (J.T. Baker, assay min 99%; CAS no. 60–29-7), magnesium sulfate, dried (Janssen, assay min. 99%; CAS no. 7487–88-9).

#### Tested antiozonants

The chemical name, structure and abbreviation of the tested antiozonants are described in Table I. The following commercial antiozonants were tested: 6PPD (Flexsys, assay 95%; CAS no. 793–24-8), 77PD (Flexsys, assay 93%; CAS no. 3081–14-9), IPPD (Flexsys, assay 95%; CAS no. 101–72-4), 6QDI (Flexsys, assay 90%; CAS no. 52,870–46-9), and Wingstay 100 (Goodyear, mixture of diaryl-*p*-phenylene diamines; CAS no. 68,953–84-4).



**Figure 4**  $^1\text{H}$  NMR spectrum of ADPAT determined in deuterated chloroform.  $\delta$ : 5.79 (k + l + m); 5.48 (f); 6.52–7.43 (aromatic H).

## Synthesis

### Synthesis of the tested antiozoanants

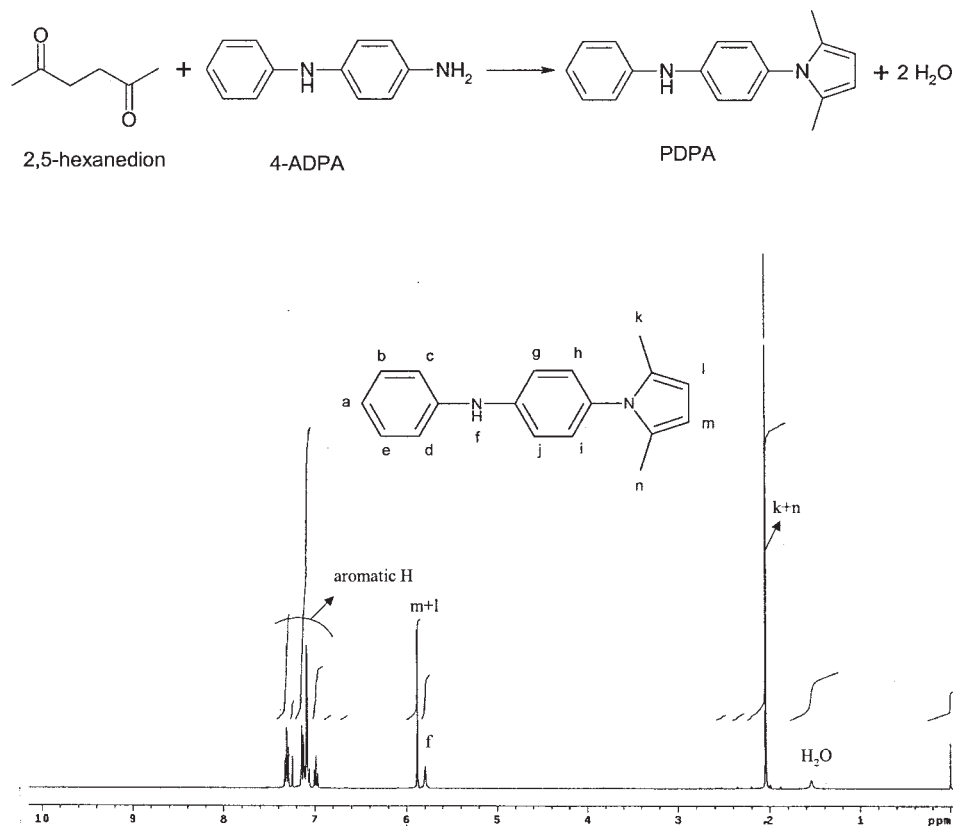
*Salts of 6PPD and carboxylic acids:* PPD-C18 (stearic acid), PPD-C7 (heptanic acid), PPD-SA (succinic acid), and PPD-MSA (methyl sulfonic acid) were synthesized by melting PPD and an equimolar amount of the corresponding acid under continuous stirring for 120 min or by refluxing in methanol for 2 h. Crystallization of the reaction products resulted in a yield between 95% and 100%. Identification was done by DSC. The presence of only one melting peak indicated that the salts were completely formed.

*ADPA-DTBF (2,6-di-tert-butyl-4-(4-(phenylamino)phenyliminomethyl)phenol):* ADPA-DTBF was synthesized by reaction of 3,5-di-tert-butyl-4-hydroxybenzaldehyde and 4-ADPA.<sup>7</sup> 4-ADPA (10.08 g, 54.7mM), 3,5-di-tert-butyl-4-hydroxybenzaldehyde, and 75 mL methanol were refluxed for 1 h in a 250-mL round bottom flask. The reaction product was cooled overnight to room temperature and dried on a rotavapor. The yield was 72%. The product was analyzed by  $^1\text{H}$  NMR and

DSC (sharp melting point at 149°C, whereas the aldehyde melts at 188°C). The purity (98%) was estimated by  $^1\text{H}$  NMR (see Fig. 3).

*ADPAT (2,4,6-tris(4-(phenylamino)phenyl)-1,3,5-triazine):* ADPAT was synthesized by a reaction of 4-ADPA and formaldehyde in ethanol. 4-ADPA (15.51 g, 84.2mM) and catalyst 2,6-di-tert-butylphenol (0.5 g, 2.4mM) were dissolved in 75 mL ethanol in a 250-mL round bottom flask. The reaction mixture was heated till 70°C. Formaline (6.83 g, 84.2mM; 37%) was added to the reaction mixture after 20 min. The temperature was increased till reflux temperature (90–95°C). Mixture was refluxed for 1 h and cooled to room temperature overnight. The reaction product was filtered and dried on a rotavapor. The dried product was dissolved in dichloromethane and washed with water. The organic layer was dried on a rotavapor. The yield was 78%. The reaction product was characterized by  $^1\text{H}$  NMR. The purity (94%) was estimated by  $^1\text{H}$  NMR (see Fig. 4).

*PDPA (4-pyrrole-diphenylamine):* PDPA was synthesized by reaction of 2,5-hexanedione and 4-ADPA,



**Figure 5** <sup>1</sup>H NMR spectrum of PDPA determined in deuterated chloroform.  $\delta$ : 2.04 (k + n); 5.80 (f); 6.89 (m + l); 6.98–7.38 (aromatic H).

using *p*-toluene sulfonic acid as a catalyst. 2,5-hexanedione (25 g, 0.219M), 4-ADPA (40.5 g, 0.219M), *p*-toluene sulfonic acid (0.2 g), and toluene (250 mL) were refluxed in a 1000-mL three-necked flask equipped with a Dean Stark framework. The reaction product was dried on a rotavapor. The dried product was dissolved in chloromethane and washed with water. The organic layer was dried on a rotavapor. The yield was 66%. The product was characterized by <sup>1</sup>H NMR and IR spectroscopy. The purity (>99%) was estimated by <sup>1</sup>H NMR (see Fig. 5).

#### Synthesis of 5-phenyl-2-hexene (model for sbr)

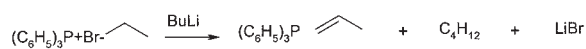
The SBR model 5-phenyl-2-hexene was synthesized in two steps via a Wittig reaction, as demonstrated in Figure 6.<sup>17</sup> It is very important that the reactor and the glassware used during the synthesis do not contain any traces of water.

Triphenyl phosphonium bromide (25 g, 67.4mM) is added into a 1000-mL three-necked round bottom flask, which is flushed with nitrogen to eliminate traces of water. Then 250 mL anhydrous diethylether is added, while stirring the solution. Afterwards, 40 mL butyllithium is added dropwise via a dropping funnel for 60 min. The reactor is cooled with ice dur-

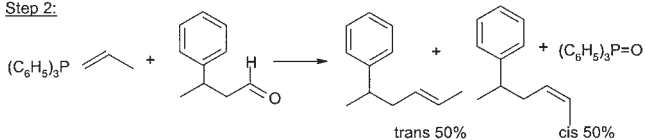
ing the addition of butyllithium. The solution, which becomes orange colored, is stirred for 4 h at room temperature. Then 15 mL 3-phenylbutyraldehyde is added dropwise for 60 min. The reactor is again cooled with ice during the addition of 3-phenylbutyraldehyde. A white powder precipitates.

The reaction mixture is refluxed overnight at  $T = 40^{\circ}\text{C}$ . The reaction product is cooled down to room temperature, filtered, washed with anhydrous diethylether, and dried on a rotavapor. The reaction product is washed three times with 100 mL water and subsequently dried over magnesium sulfate. The final product

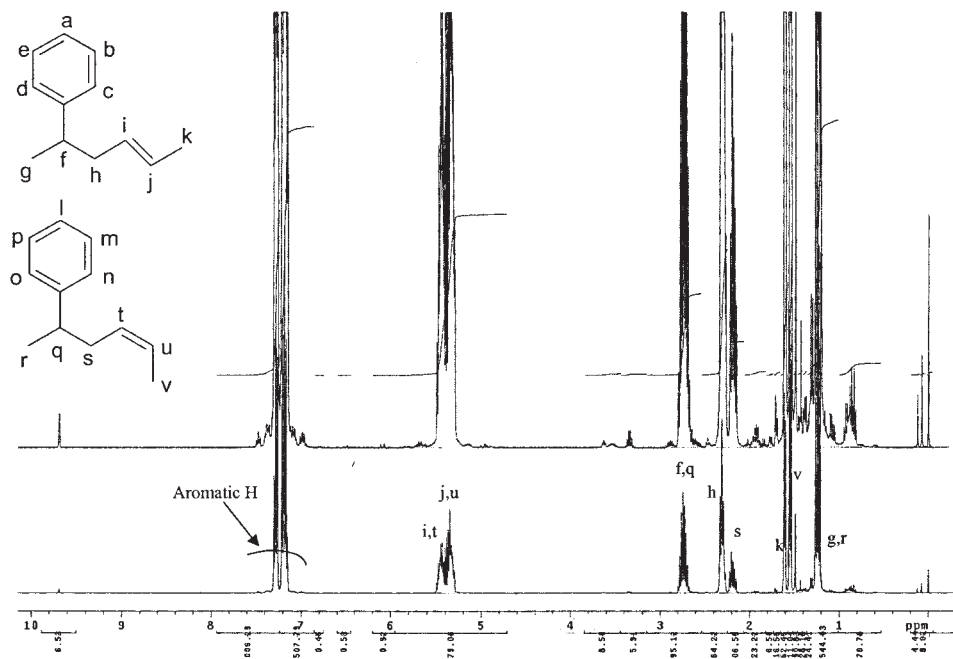
#### Step 1:



#### Step 2:



**Figure 6** Reaction mechanism for the synthesis of 5-phenyl-2-hexene.



**Figure 7**  $^1\text{H}$  NMR spectrum of 5-phenyl-2-hexene determined in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR:  $\delta$  7.1–7.3 (aromatic H);  $\delta$  5.3–5.5 (i, t, j, u);  $\delta$  2.73 (f, q);  $\delta$  2.32 (h);  $\delta$  2.21 (s);  $\delta$  1.61 (k);  $\delta$  1.55 (v);  $\delta$  1.25 (g, r).

is purified by vacuum Kugelrohr distillation; its boiling point is  $230^\circ\text{C}$  at 8 mbar. The product was identified using  $^1\text{H}$  NMR (see Fig. 7). The purity was 98%.

**Ozonolysis**

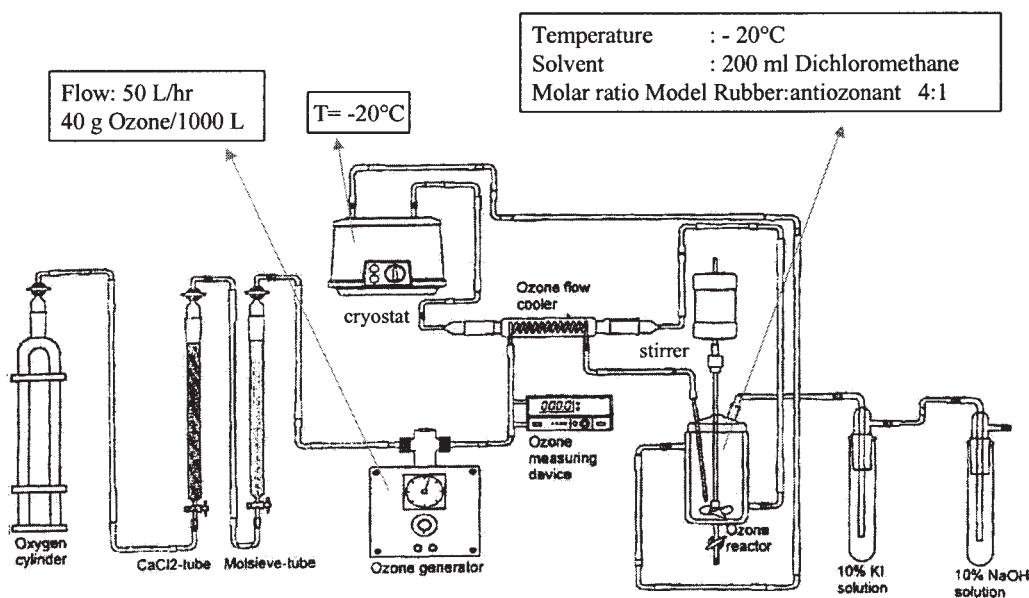
**Equipment**

Experiments were done in the equipment shown in Figures 8 and 9. The ozone generator was used under

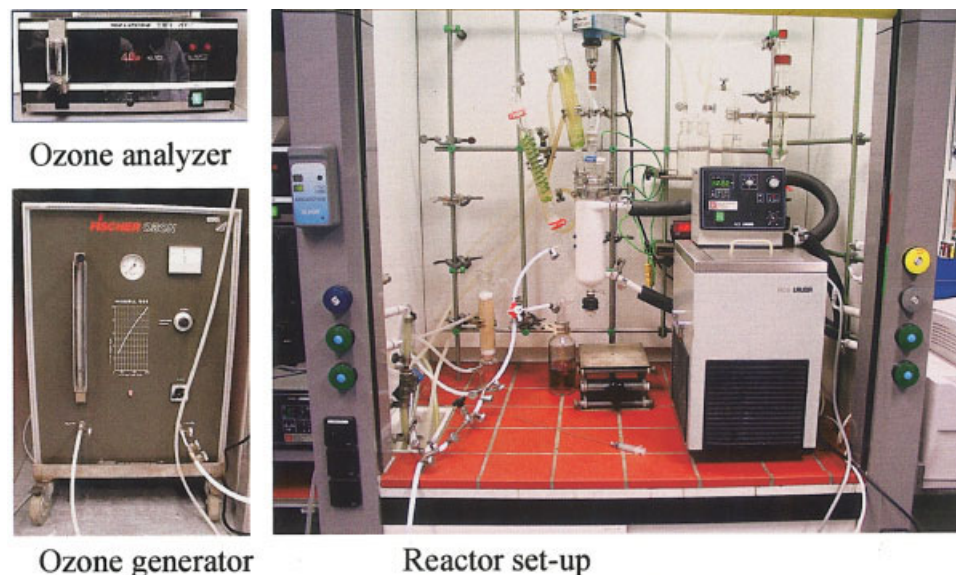
the following conditions: oxygen flow 50 L/h and current 3.2 A, which generate an ozone flow of 40 g/1000 L oxygen. The oxygen was dried through a saturated calcium chloride solution and a molsieve to protect the ozone generator against corrosion.

**Procedure**

Dichloromethane (200 mL) is poured into the reactor. The reactor temperature is stabilized at a temperature



**Figure 8** Diagram of the ozonolysis test equipment.



**Figure 9** Ozonolysis test equipment. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

of  $-20^{\circ}\text{C}$ , before starting the ozonolysis. This relatively low temperature is selected to prevent evaporation of the low molecular weight model rubbers. A solution of the model rubber, 4 g (48mM) 2-methyl-pentene or 1.9 g (12mM) 5-phenyl-2-hexene, 12mM antiozonant for testing of the NR model or 3mM for testing of the SBR model, and 1.7 g (12mM) *n*-decane for testing of the NR model or 0.43 g (3mM) for testing of the SBR model is injected into the reactor.

Ozone is introduced into the reactor when the ozone flow is stabilized at 40 g/L. Samples are taken at several fixed time intervals and analyzed by GC. Samples are taken with a syringe by using a rubber septum. The first sample is taken when the reaction mixture is homogenized, time  $t = 0$ .

#### Characterization of the ozonolysis products

$^1\text{H}$  NMR: The structure and purity of the ozonolysis products were characterized using  $^1\text{H}$  NMR spectroscopy. The products were dissolved in deuterated chloroform (Aldrich, 99.8 % D; Cas no. 865-49-6).  $^1\text{H}$  NMR measurements were performed on a Varian Inova 400 MHz (Varian) model L 700 spectrometer.

GC analysis: Samples gathered during the ozonolysis experiments were analyzed by GC to quantify the amount of remaining model rubber and antiozonant. *n*-Decane was used as an internal standard. Measurements were done under the conditions described (column: Sil 5 CB; column dimensions: 17 m  $\times$  0.32 mm ID; film thickness: 0.4  $\mu\text{m}$ ; injection temp.: split,  $325^{\circ}\text{C}$ ):

	Column	:Sil5CB
	Column dimensions	:17m*0.32mmID
	Film thickness	:0.4 $\mu$
	Injection temp.	:Split,325 $^{\circ}\text{C}$
<u>2 methyl-2-pentene:</u>		
Temp. program	:35 $^{\circ}\text{C}$ (5 min.)	$\xrightarrow{5^{\circ}\text{C}/\text{min.}}$ 80 $^{\circ}\text{C}$ $\xrightarrow{20^{\circ}\text{C}/\text{min.}}$ 320 $^{\circ}\text{C}$ (14 min.)
Detection temp.	:FID,200 $^{\circ}\text{C}$	
<u>5-phenyl2-hexene</u>		
Temp. program	:35 $^{\circ}\text{C}$ (5 min)	$\xrightarrow{20^{\circ}\text{C}/\text{min.}}$ 320 $^{\circ}\text{C}$ (21 min.)
Detection temp.	:FID, 375 $^{\circ}\text{C}$	

GC/MS: Identification of the different peaks was done by FIA-MS using the Platform-II quadrupole ex Mi-

chromass. In positive ESI, components should give  $[\text{M} + \text{H}]^+$  or  $[\text{M} + \text{Na}]^+$  adducts. 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 10/30/60 V; source temperature 60°C). Methanol was used as a carrier solvent.

**FT Raman spectroscopy:** FT Raman measurements were performed on a Kaiser Hololab series 5000 Raman spectrometer. Experiments were done with two different lasers: an external 30-mW, 632.8-nm HeNe laser with filtered probehead, 2.5 in. focal length lens and an internal 250-mW, 785-nm diode laser with filtered probehead, 1 in. focal length lens. Spectra were collected with Holograms V3.1 with settings: accumulation, cosmic ray correction, and dark subtraction.

Data were evaluated using the Galactic Grams 32 V4.04 software, including Quantbasic.

**NIR spectroscopy:** nir measurements were performed on a bomem mb160 nir spectrometer with 3-mm-vial holder. the temperature of the vial holder was 95°C. spectra were collected using the following settings: absorbency mode; resolution 8 cm<sup>-1</sup>; 25 scans; region from 4500 to 10,000 cm<sup>-1</sup>. data were evaluated using the galactic grams 32 v4.04 software, including quantbasic.

## RESULTS AND DISCUSSION

The efficiency of several of the newly synthesized antiozonants was determined and compared with that of the conventional antiozonants like 6PPD, IPPD, and Wingstay 100. The antiozonants were tested in competition experiments with model rubber compounds. It was investigated how fast the tested antiozonant reacts with ozone during ozonolysis, by comparing the decrease of the amount of model rubber to that of the antiozonant. Experiments were performed at model/antiozonant ratios of 4 : 1. Reactions were followed by GC analysis of samples obtained after several fixed time intervals.

Because GC analyses are rather time consuming and because the experiments are disturbed by taking sam-

**TABLE II**  
Remaining Amount of 2-Methyl-2-pentene (model for NR) and 6PPD Antiozonant After 60 Min Ozonolysis

Molar ratio of 2-methyl-2-pentene/6PPD (mole/mole)	Remaining	
	2-methyl-2-pentene (%)	6PPD (%)
4 : 0	25	—
4 : 0.5	42	16
4 : 1	75	31
4 : 2	76	47

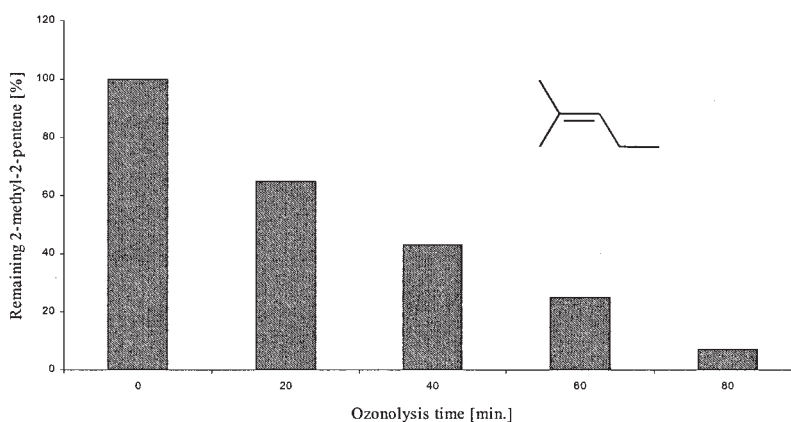
ples, it was investigated whether the reactions between ozone and the double bonds of the model rubber can also be followed online, by a spectroscopic technique. FT Raman and NIR spectroscopy were investigated for this purpose.

### Optimization of test conditions

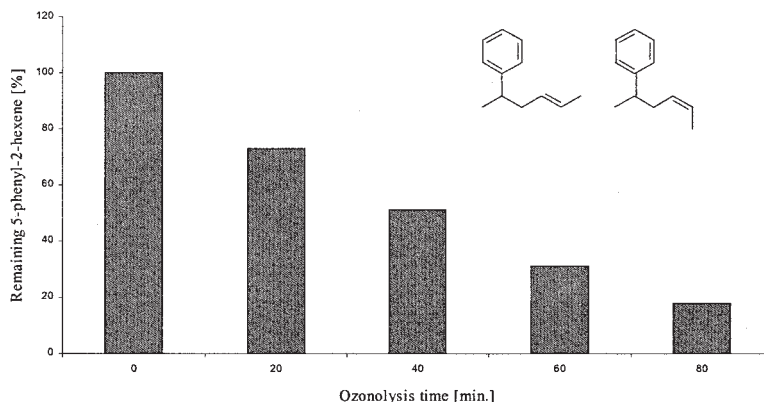
Before testing the efficiency of different antiozonants, test conditions had to be optimized. Four experiments were done to find out which 2-methyl-2-pentene/6PPD ratio (4 : 0, 4 : 0.5, 4 : 1, or 4 : 2) is the most suitable for testing the antiozonant efficiency. The results for 60 min. ozonolysis are shown in Table II. As can be seen from these results, a good protection of the model rubber was obtained in the presence of 6PPD. A much lower amount of 2-methyl-2-pentene did react with ozone when 6PPD was present. Testing at the ratios 4 : 1 and 4 : 2 resulted in approximately the same protection of the model rubber, indicating that the 4 : 1 ratio is close to an optimum. This ratio was therefore selected to test the different antiozonants.

### Rate of ozonolysis of model rubbers in absence of antiozonants

The SBR model 5-phenyl-2-hexene was tested at a 4 times lower concentration compared with the NR



**Figure 10** Ozonolysis of the NR model 2-methyl-2-pentene in absence of antiozonant.



**Figure 11** Ozonolysis of the SBR model 5-phenyl-2-hexene in absence of antiozonant.

model 2-methyl-2-pentene, because the SBR model is not commercially available and because the synthesis of this product was rather time consuming. This explains the approximately 4 times faster disappearance of the SBR model compared with that of the NR model, as can be seen from Figures 10 and 11. For this reason, samples were taken every 20 min during the 2-methyl-2-pentene experiments and every 5 min during the 5-phenyl-2-hexene experiments.

Reaction rates between 2-methyl-2-pentene and 5-phenyl-2-hexene with ozone can be concluded to be the same, when tested in the absence of antiozonants, because there is no competition and because all the ozone that is passed into the reactor does react. The latter can be derived from the fact that no discoloration of the KI solution behind the ozone reactor was observed during the ozonolysis experiments.

Ozonolysis of 5-phenyl-2-hexene showed that there is a small difference between reactivity of the cis and the trans form. The cis form appeared to be slightly more reactive. The trans form is supposed to be more reactive, according to Baily.<sup>3</sup> However, Huisgen showed that the cis form can also be more reactive, when tested in the liquid form.<sup>18</sup> No conclusion could be drawn to explain these differences. No differences between reactivity of the cis and the trans form were made during the ozonolysis experiments described in this paper. The sum of both the cis and the trans form is reported as the estimated amount of 5-phenyl-2-hexene.

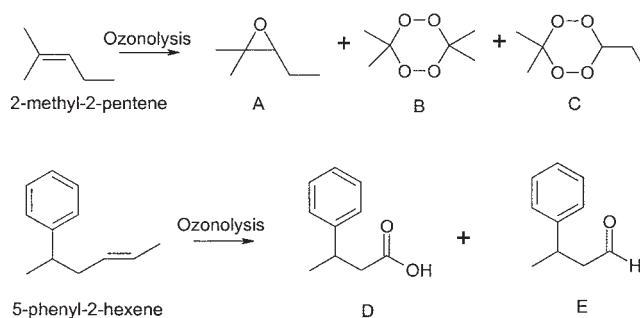
Measurements were performed at low temperatures ( $-20^{\circ}\text{C}$ ) to minimize evaporation of the model rubbers during ozonolysis, especially for the low boiling NR model: the boiling point of 2-methyl-2-pentene is  $67^{\circ}\text{C}$ . However, even at this low temperature, approximately 7% of the NR model evaporated during 80 min of ozonolysis. This was estimated by passing oxygen into the reactor instead of ozone, at the same flow as used during the ozonolysis experiments. All results tabulated in this paper are therefore corrected

for this value. The SBR model did not evaporate during the experiment with oxygen.

Several experiments were performed in duplicate to estimate the reproducibility of the test. Differences found between duplicate values were approximately 3% for the NR model and 4% for the SBR model. The reaction products formed by ozonolysis of the model rubbers were characterized by GC/MS. The products that were formed are shown in Figure 12.

#### Rate of ozonolysis of model rubbers in presence of antiozonants

It is known that antiozonants like 6PPD also have antioxidant activity. Therefore, it was first investigated whether 6PPD does react with oxygen under the applied ozonolysis test conditions. A mixture of 2-methyl-2-pentene and 6PPD (4 : 1) was tested by passing oxygen instead of ozone through the reactor. The reaction was stopped after 80 min and the reaction products were analyzed by GC. It showed that disappearance of 6PPD was negligible during this test, indicating that the reaction between antiozonant and



**Figure 12** Reaction products formed by ozonolysis of 2-methyl-2-pentene and 5-phenyl-2-hexene: A, 3-ethyl-2,2-dimethyloxirane; B, 3,3,6,6-tetramethyl-1,2,4,5-tetroxane; C, 3,3-dimethyl-6-ethyl-1,2,4,5-tetroxane; D, 3-methyl-3-phenyl propanoic acid; E, 3-methyl-3-phenyl propanal.

**TABLE III**  
**Remaining Amount of Model Rubber and Antiozonant**  
**Obtained After 60 Min Ozonolysis of 2-Methyl-2-**  
**pentene and 15 Min of 5-Phenyl-2-hexene<sup>a</sup>**

Tested product	Remaining amount (%)			
	2-methyl-2-pentene (NR-model)		5-phenyl-2-hexene (SBR-model)	
	Model	Antiozonant	Model	Antiozonant
Control	25	—	27	—
6PPD	75	31	82	42
IPPD	72	33	80	39
77PD	75	27	84	42
Wingstay 100	69	36	77	31
6QDI	49	75	58	64
PPD-C18	83	30	89	40
PPD-C7	81	13	ND	ND
PPD-C22	81	38	ND	ND
PPD-SA	63	30	ND	ND
PPD-MSA	61	16	ND	ND
ADPA-DTBF	66	-	ND	ND
ADPAT	87	79	93	71
PDPA	81	37	85	48

ADPA-DTBF could not be analyzed by GC.

The concentration of 5-phenyl-2-hexene and the corresponding amount of antiozonant are 4 times lower than that of 2-methyl-2-pentene.

<sup>a</sup> The ratio model : 6PPD = 4 : 1.

oxygen is very slow at the applied test temperature ( $-20^{\circ}\text{C}$ ), and can therefore be neglected during the ozonolysis experiments.

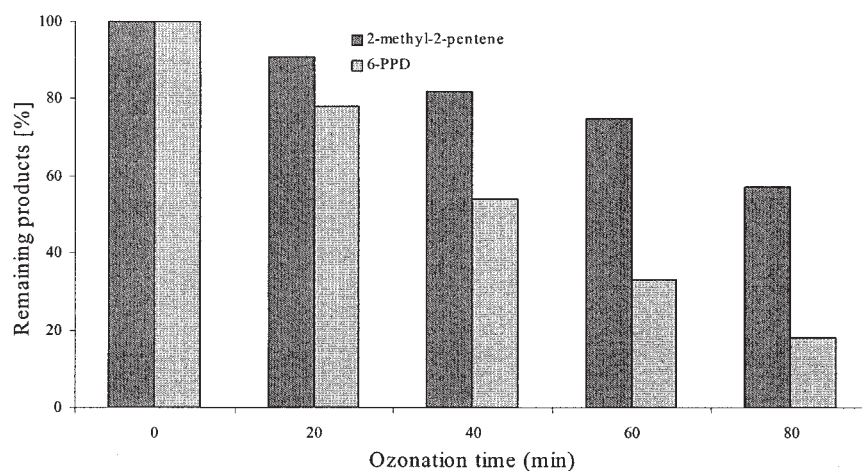
Several conventional and new antiozonants were tested in the presence of 2-methyl-2-pentene and 5-phenyl-2-hexene model rubbers. The amount of remaining antiozonant and model rubber is reported after 60 min reaction for 2-methyl-2-pentene and after 15 min reaction for 5-phenyl-2-hexene, to make a comparison between both systems and between the different antiozonants possible. The results are reported in

Table III for both models and the various antiozonants tested. The results obtained for 6PPD tested in the presence of the 2-methyl-2-pentene are shown in Figure 13, as an example.

It is clear from these results that 2-methyl-2-pentene is slightly more reactive than 5-phenyl-2-hexene, which can be explained by a higher electron density of the double bond of 2-methyl-2-pentene compared with that of the double bond of 5-phenyl-2-hexene. The latter is disubstituted instead of the trisubstituted 2-methyl-2-pentene. Both the methyl and the phenyl group are electron donating groups. However, the phenyl group in 5-phenyl-2-hexene is further away from the double bond compared to the methyl group in 2-methyl-2-pentene and therefore has less influence on the electron density of the double bond.

The product 6QDI shows a worse efficiency compared with 6PPD. This can be explained by the fact that it is one of the reaction products formed by ozonolysis of 6PPD, as shown in Figure 14, and therefore has lost part of its reactivity already.

From all the tested new antiozonants, the products PPD-C18, ADPAT, and PDPA show improved efficiency compared with the conventional antiozonants 6PPD and IPPD. The improved efficiency observed for ADPAT can be explained by a high amine functionality of this molecule. The improved efficiency observed for PPD-C18 and PDPA corresponds with the improved antiozonant properties in a typical passenger tire sidewall compound.<sup>19</sup> It is most likely related to the higher reactivity of one of the nitrogen atoms in these molecules and/or because of a better solubility than 6PPD. Unfortunately, many reaction products are formed during the ozonolysis experiments, which makes it very difficult and time consuming to draw conclusions based on the individual products.



**Figure 13** Results obtained for the ozonolysis of 2-methyl-2-pentene in the presence of 6PPD; ratio model : 6PPD = 4 : 1.

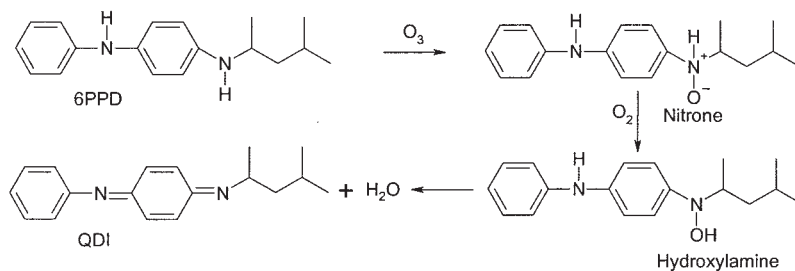


Figure 14 Formation of characteristic ozone cracks after exposure to ozone.

On the basis of performance, the stearic acid salt of 6PPD (PPD-C18) seems to be one of the most attractive products to be developed as long-lasting antiozonant. It shows, besides a decreased migration rate, also improved antiozonant efficiency compared to 6PPD.<sup>19</sup> The 6PPD-salts of other organic acids were therefore studied in some more detail. A comparison was made between 6PPD-salts prepared from different carboxylic acids, having various alkyl chain lengths, C7, C18, and C22, and different  $pK_a$  values: stearic acid with  $pK_a = 5$ , succinic acid with  $pK_a = 4.16$ – $5.61$  and methyl sulfonic acid with  $pK_a = -2$ . The results are given in Table III. It is clear from these results, that the alkyl chain length hardly shows any effect on the remaining amount of model rubber. However, it seems that the efficiency of 6PPD salts prepared from strong acids like SA and MSA is lower. This may be related to a lower solubility of these products in dichloromethane, but was not further investigated.

## CONCLUSIONS

The efficiency of several potential long-lasting antiozonants was studied by ozonolysis of model rubbers in the presence and absence of those products. 2-Methyl-2-pentene was used as model for NR and 5-phenyl-2-hexene was used as model for SBR. The NR model appeared to be slightly more reactive than the SBR model because of a higher electron density of the double bonds in the NR model.

ADPAT, PDPA, and the carboxylic acid salts of 6PPD (PPD-C7, PPD-C18, and PPD-C22) showed increased reactivity with ozone compared to the conventional antiozonants like 6PPD and IPPD. The increased reactivity of ADPAT can be explained by the relatively high amount of amine units in one molecule. The increased efficiency observed for PDPA and the carboxylic acid salts of 6PPD is most likely related to an enhanced reactivity of one of the nitrogen atoms present in these molecules or because of a better solubility in dichloromethane.

The alkyl chain length of the carboxylic acid (C7, C18, and C22) used to prepare the 6PPD salts has hardly any effect on the antiozonant efficiency. The

$pK_a$  value of the carboxylic acids used to prepare the 6PPD salts seemed to be more important. 6PPD salts prepared from strong acids (SA, MSA) appeared to be less efficient than PPD-C18.

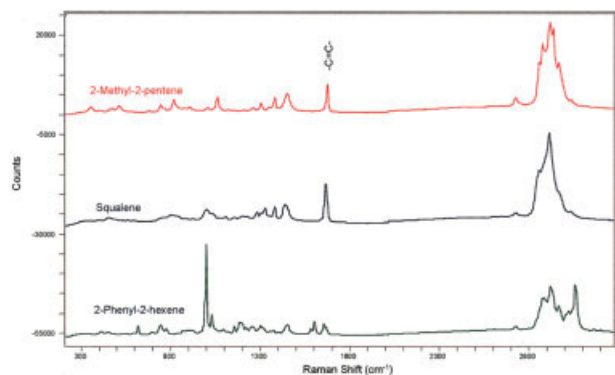
It can be concluded from the results described in the Appendix that NIR spectroscopy is a suitable technique for online detection of the ozonolysis. A linear calibration curve was obtained for the concentration of squalene plotted against the absorption at  $5277\text{ cm}^{-1}$ .

Although FT Raman spectroscopy showed a higher sensitivity for double bonds compared to NIR spectroscopy, this technique was not suitable to analyze samples containing staining antiozonants like 6PPD and IPPD. A high fluorescence background signal was observed in the presence of those products. Replacement of the excitation source (632.6 nm) by a laser having a higher excitation wavelength (785 nm) resulted in a reduced fluorescence background signal but it was still too high to detect double bonds under the applied concentration levels used for the ozonolysis experiments.

## APPENDIX: ONLINE DETECTION OF OZONOLYSIS BY SPECTROSCOPIC TECHNIQUES

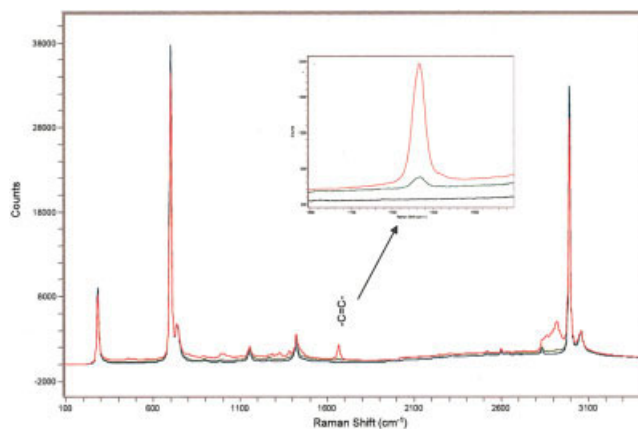
FT Raman spectroscopy and NIR spectroscopy were applied as spectroscopic techniques for online detection of the ozonolysis. These techniques are capable of monitoring the decrease of double bonds and can probably also be used for monitoring rubbers or model rubbers, like squalene, having multiple double bonds.

The first technique investigated was FT Raman spectroscopy, because this technique is very sensitive for symmetric vibrations and is noninvasive. Figure A1 shows the Raman spectra of 5-phenyl-2-hexene, 2-methyl-2-pentene, and squalene recorded with a Raman system equipped with a HeNe laser. Unfortunately, this technique appeared to be not sensitive enough to detect C=C double bonds in the concentration level as used during the ozonolysis experiments: 2% (m/m) 2-methyl-2-pentene in

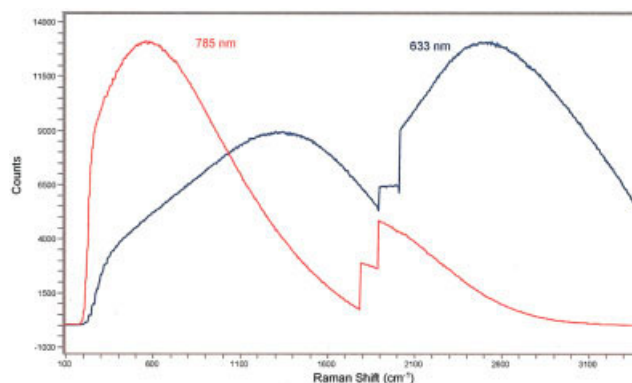


**Figure A1** FT-Raman spectra of pure 2-methyl-2-pentene, 5-phenyl-2-hexene, and squalene. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$\text{CH}_2\text{Cl}_2$ . Increasing the concentration of 2-methyl-2-pentene to raise the detection limit was not possible, because of the limited availability of the 2-methyl-2-pentene. The extinction coefficient for the double bond of 5-phenyl-2-hexene was even lower because of the presence of the aromatic ring in this molecule. Squalene has a much higher response factor compared to 2-methyl-2-pentene and 5-phenyl-2-hexene because of the multiplicity of the double bonds: 6 double bonds in one molecule. As can be seen from Figure A2, a concentration of 1% can easily be detected. The vibration signals obtained from dichloromethane do not interfere with the signal of the double bonds of squalene. However, as can be seen from Figure A3, a high fluorescence background signal is observed when 6PPD is present in the system. Addition of 6PPD resulted in a strong discoloration (black to brown) of the reaction mixture. It is known that FT Raman spectroscopy is difficult



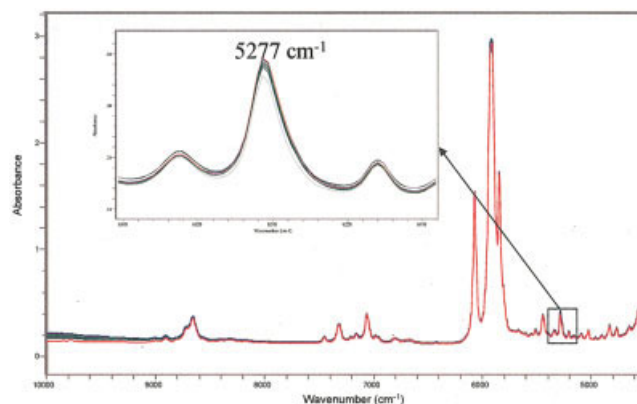
**Figure A2** FT-Raman spectra of squalene: 0%, 1%, and 10% (m/m) in dichloromethane. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



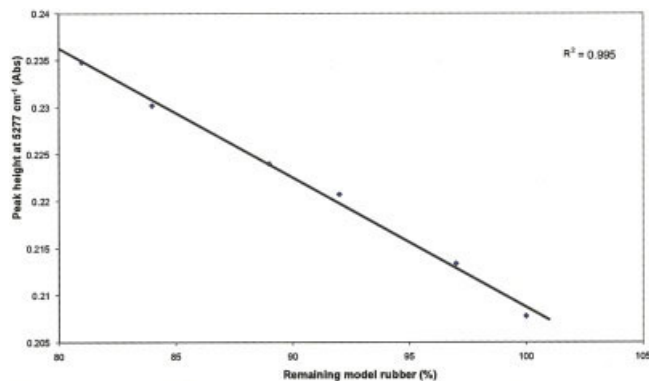
**Figure A3** FT-Raman spectra of 2% (m/m) squalene and 0.5% (m/m) 6PPD in dichloromethane. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

to apply for the analysis of dark colored products. It was further investigated whether the amount of fluorescence could be reduced by replacing the excitation source (632.6 nm) by a laser having a higher excitation wavelength (785 nm). However, as can be seen from the results plotted in Figure A3, the fluorescence background is reduced but still too high to detect the double bonds of squalene. It must be concluded from these results that FT Raman spectroscopy is not a suitable spectroscopic technique to monitor decrease of double bonds of model compounds for online detection of ozonolysis in the presence of staining colored antiozonants.

Subsequently, the application of NIR-spectroscopy as online detection method for ozonolysis was evaluated for squalene in the presence of 6PPD. Although much weaker as with FT Raman spectroscopy, the  $\text{C}=\text{C}$  double bonds are supposed to vibrate also in the NIR. An example of a NIR spectrum of one of these experiments is shown in Figure



**Figure A4** NIR spectra of 2% (m/m) squalene and 0.5% (m/m) 6PPD in dichloromethane after ozonolysis. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure A5** Calibration curve for quantification of squalene by NIR spectroscopy. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

A4. Unfortunately, no specific C = C absorption band could be observed in the NIR spectrum. However, a good linear relation was found between the absorption band at  $5277\text{ cm}^{-1}$  and the concentration of the remaining amount of squalene (see Figure A5). The absorption band at  $5277\text{ cm}^{-1}$  is most probably related to a reaction product of the double bonds of squalene with ozone but was not further investigated. This technique seems therefore to be most suitable for online detection of ozonolysis. Unfortunately, this route could not be applied for screening different antiozonants, because of time limitation and no longer availability of the test equipment. Results were included in this paper for future reference.

The writers gratefully acknowledge Flexsys for allowing to publish this paper. The assistance of G. van 't Slot, O. Coulier and B. Olde Hanter was invaluable.

## References

- Saito, Y. *Int Polym Sci Technol* 1995, 22, 47.
- Bruck, D.; Konigshofen, H.; Ruetz, L. *Rubber Chem Technol* 1985, 58, 728.
- Bailey, P. S. *Ozonation in organic chemistry*; Vol. 39.1. 1978, p 25.
- Razumovskii, S. D.; Batashova, L. S. *Rubber Chem Technol* 1970, 43, 1340.
- Razumovskii, S. D.; Podmasteriev, V. V.; Zaikov, G. E. *Polym Degrad Stab* 1988, 20, 37.
- Braden, M. J. *J Appl Polym Sci* 1962, 6, 86.
- Engels, H. W.; Hammer, H.; Brück, D.; Redetzky, W. *Rubber Chem Technol* 1989, 62, 609.
- Ambelang, J. C.; Kline, R. H.; Lorenz, O. M.; Parks, C. R.; Wadelin, C. *Rubber Chem Technol* 1963, 36, 1497.
- Hofmann, W. *Rubber Technology Handbook*; Hanser Publishers, 1989; p 273.
- Andries, J. C.; Rhee, C. K.; Smith, R. W.; Ross, D. B.; Diem, H. E. *Rubber Chem Technol* 1979, 52, 823.
- Latimer, R. P.; Hooser, E. R.; Layer, R. W.; Rhee, C. K. *Rubber Chem Technol* 1980, 53, 1170.
- Latimer, R. P.; Hooser, E. R.; Layer, R. W.; Rhee, C. K. *Rubber Chem Technol* 1983, 56, 431.
- Hong, S. W.; Lin, C.-Y. *Rubber World* August 2000; p. 36.
- Hong, S. W.; Greene, P. K.; Lin, C.-Y. In *ACS Rubber Division 155th Conference, Chicago, IL, 13–16 April 1999*; paper no. 65.
- Hahn, J.; Runk, M.; Schollmeyer, M.; Theimer, U.; Walter, E. *Kautschuk Gummi Kunststoffe* 1998, 51, 206.
- Nieuwenhuizen, P. J.; Haasnoot, J. G.; Reedijk, J. *Kautschuk Gummi Kunststoffe* 2000, 53, 144.
- Baumgarten, H. E. *Organic Synth* 1973, 5, 751.
- Huisgen, R. *Angew Chem Int Ed* 1963, 2, 633.
- Huntink, N. M.; Datta, R. N.; Talma, A. G. *Kautsch Gummi Kunstst* 2003, 55, 310.