

Effect of Different Paraffin Waxes and Antiozonant on the Processing and Mechanical Properties of Natural Rubber

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Three commercial paraffin waxes (carbon numbers 20-40) and one alkyl-aryl-p-phenylenediamine antiozonant were mixed individually with natural rubber to produce rubber compounds. The compounds contained a precipitated amorphous white silica nanofiller the surface of which was pre-treated with bis(3-triethoxysilylpropyl-)tetrasulphane (TESPT). The rubber compounds were cured via the tetrasulphane groups of TESPT by adding a sulphenamide accelerator and zinc oxide. The viscosity, cure properties, hardness, tensile strength, elongation at break, stored energy density at break, Young's modulus, modulus at different strain amplitudes, tear strength and cyclic fatigue life of the rubber vulcanisates were measured. The viscosity, scorch time and rate of cure increased, but the optimum cure time decreased when the waxes and antiozonant were added to the rubber. The highest tensile strength, stored energy density at break, modulus at different strain amplitudes and the longest cyclic fatigue life were measured for the vulcanisate with the antiozonant. The rubber vulcanisate containing one of the waxes had the highest tear strength.

Keywords: natural rubber; paraffin waxes, antiozonant; processing properties; mechanical properties; glycol; swelling

Unsaturated hydrocarbon elastomers such as natural rubber (NR) are used in a wide range of industrial applications. For example NR is used to manufacture tyres, anti-vibration management systems and hydraulic engine mountings because it is a resilient polymer with high tear and gum strength and long flex life. However, the backbone of NR has chemically active double bonds, which makes it prone to environmental ageing by ozone¹. The degradation resulting from ozone is

called ozonation. This process is accelerated by heat and adversely affects the durability, performance and service life of the rubber^{1,2}. Unprotected NR absorbs ozone while in a relaxed state and ozonides are formed by the attack of double bonds on the surface layers. These compounds prevent further absorption so that only the surface layer is affected. However, when rubber is in tension, ozone is absorbed continuously and surface cracks are formed. When strain on the rubber exceeds

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a critical value, *i.e.* 5-6%, cracks grow at a constant rate dependent on the ozone concentration³. The chemicals which are used to suppress or delay these processes are called antiozonants.

Paraffin waxes which are predominantly mixtures of paraffin hydrocarbons and alkanes with the generic formula $C_n H_{2n+2}$ migrate through the rubber to the surface and form a thin, inert film, which acts as a barrier to the ozone gas. In this formula, "n" is the carbon number and ranges from 18 to about 50. Typical waxes used for rubber contain $n=25$ to 30 having molecular weight between 350 to 420 and melting point in the range of 38°C to 74°C³. At temperatures which most rubber products are cured, *i.e.* 140°C to 240°C, petroleum waxes dissolve fully in the rubber. As rubber cools down after vulcanisation below the wax melting point, a super-saturated solution of wax forms in the rubber³. The concentration gradient between the inside and outside of the compound causes a continuous migration of the wax to the external surface until a balance is achieved. When this occurs, a thin film of the wax will have formed on the surface and will act as a physical barrier to ozone attack³. The wax film is thin, flexible and non-crystalline but it does not protect against ozone attack under dynamic conditions such as engine mountings. The film ruptures because it is inextensible and leaves the rubber unprotected. Antiozonants, for instance phenylenediamines are often added to compensate for this deficiency^{4,5}. These chemicals provide a chemical barrier against ozone attack, which is effective under both dynamic and static conditions.

The aim of this study was to measure effect of three commercial paraffin waxes and one alkyl-aryl-*p*-phenylenediamine antiozonant individually on the viscosity, cure properties, hardness, tensile strength, elongation at break, stored energy density at break, tear strength,

Young's modulus, modulus at different strain amplitudes and cyclic fatigue life of natural rubber crosslinked and reinforced with a silanised silica nanofiller. In hydraulic engine mounts or hydromounts, natural rubber is in permanent contact with glycol fluid and temperatures can reach 130°C under the bonnet. To assess effect of high temperature glycol liquid on the rubber filled with the paraffin waxes and antiozonant, swelling tests were carried out at 100°C for 8 days.

EXPERIMENTAL

Materials

The raw elastomer used was standard Malaysian natural rubber grade L (SMRL). The reinforcing filler was Coupsil 8113, which was supplied by Evonik Industries AG of Germany. Coupsil 8113 is a precipitated amorphous white silica filler (type Ultrasil VN3), the surface of which had been pre-treated with bis(3-triethoxysilylpropyl)-tetrasulphane (TESPT), also known as Si69 coupling agent, to chemically bond silica to rubber. It has 11.3% by weight silane, 2.5% by weight sulphur (included in TESPT), a 175 m²/g surface area (measured by N₂ adsorption) and a 20–54 nm particle size.

In addition to the raw rubber and filler, the other ingredients were N-cyclohexyl-2-benzothiazole sulphenamide which is a fast-curing delayed action accelerator with a melting point of 103°C (Santocure CBS, Flexsys, Belgium), zinc oxide as an activator (Harcros Durham Chemicals, Durham, UK), and N-(1,3-dimethylbutyl)-N'-phenyl-*p*-phenylene-diamine (Santoflex 13) as an antiozonant with a melting point of 45°C (6PPD, Brussels, Belgium). Three commercial paraffin waxes were also used. They were: 52/54H with a melting point of 53°C and carbon number 21 to 39 (Honeywell,

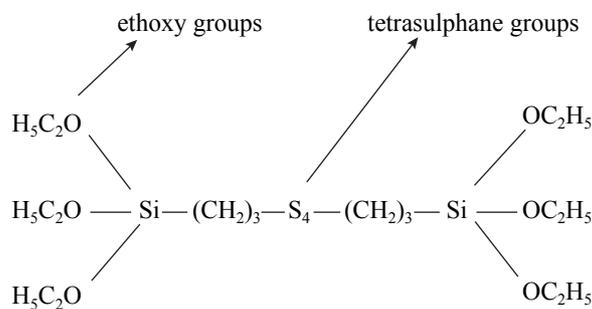
Speciality Wax and Additives SA, Belgium), Okerin 1900H with a melting point of 63°C and carbon number 20 to 30 (Honeywell, Speciality Wax & Additives SA, Belgium) and Controzon R.B.H with a melting point of 56°C and carbon number 21 to 40 (D.O.G. Deutsche Oelfabrik, Germany). The solid 52/54H and Controzon R.B.H waxes were white, Okerin 1900H yellow and antiozonant was dark brown in colour. The liquid medium used for the high temperature swelling tests was glycol with a pH value of 9.5, density of 1.09 g/cm³, boiling range of 185-195°C, and was fully transparent to white light (Glykosafe 610-00, BASF SE, Germany). The melting temperatures of ZnO and silanised silica were above 1000°C. The cure system consisted of CBS and ZnO, which were added to fully crosslink the rubber *via* the tetrasulphane groups in TESPT (*Scheme 1*).

Mixing Procedure and Preparation of Rubber Compounds

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small laboratory mixer with counter rotating rotors. The Banbury rotors and the mixing chamber

were set at 80°C (above the melting points of the waxes and antiozonant) and the rotor speed was set at 45 r.p.m. The volume of the mixing chamber was 78 cm³ and it was 60% full during mixing. Polylab Monitor 4.17 software was used for controlling the mixing condition and storing data.

For preparing the rubber compounds, a total mixing time of 18 min was used, which was long enough to fully disperse the silica particles in the rubber⁶. The filler and rubber were mixed together for 10 min at 80°C and then the waxes and antiozonant were added and mixed for another 5 minutes. The chamber temperature was reduced to 40°C before CBS and ZnO were added and mixing continued for another 3 minutes. The temperature of the rubber compound was kept below 50°C to avoid premature crosslinking in the rubber during the mixing of the chemical curatives. The control compound, which had silanised silica, CBS, ZnO, and no wax or antiozonant was made in the same way. In total, five rubber compounds were made (*Table 1*). The procedures for measuring the right amounts of CBS and ZnO for curing the rubber compounds have been described previously⁶.



Bis(3-triethoxysilylpropyl)-tetrasulphane (TESPT) or Si69 coupling agent.

Scheme 1

TABLE 1. RECIPE FOR THE RUBBER COMPOUNDS

Formulation (p.h.r.)	Compound number				
	1	2	3	4	5
Natural rubber (SMR L)	100	100	100	100	100
Coupsil 8113	30	30	30	30	30
CBS	4.4	4.4	4.4	4.4	4.4
Zinc oxide	1	1	1	1	1
Paraffin wax 1900H	-	2	-	-	-
Paraffin wax 52/54H	-	-	2	-	-
Paraffin wax Controzon R.B.H	-	-	-	2	-
Santoflex 13	-	-	-	-	2
	Mooney viscosity (MU)				
	53	60	60	61	72
	ODR results at 160°C				
Minimum torque (dN m)	14	18	19	18	20
Maximum torque (dN m)	61	70	69	69	67
Δtorque (dN m)	47	52	50	51	47
Scorch time, t_{s2} (min)	7.3	9.3	10	10	8
Optimum cure time, t_{95} (min)	28	21	21	20	22
Cure rate index (min^{-1})	4.8	8.6	9.1	10	7.1

Finally, when mixing ended, the rubber was recovered from the mixer and milled to a thickness of about 7 mm for further work. The compounds were kept at ambient temperature ($21 \pm 2^\circ\text{C}$) for at least 24 h before their viscosity and cure properties were measured.

Viscosity of the Waxes, Antiozonant and Rubber Compounds

The melt viscosity of the paraffin waxes and antiozonant was measured in a Haake K20 Rheometer (Rheometric Scientific Ltd, Surrey, UK) at 80°C and a shear rate of 444.6 s^{-1} (the highest rate available on the rheometer). The test was conducted for 15 min and the minimum and maximum values of viscosity were recorded in the last 3 min when a steady value was reached. The values were then averaged and summarised in

Table 2. The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer (Wallace Instruments, Surrey, UK) according to British Standard⁷. The results were expressed in Mooney Units (MU).

Cure Properties of the Rubber Compounds

The scorch time, t_{s2} , which is the time for the onset of cure, and the optimum cure time, t_{95} , which is the time for the completion of cure, were determined from the cure traces generated at $160 \pm 2^\circ\text{C}$ by an oscillating disc rheometer curemeter (Monsanto, Swindon, UK)⁸. The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using the method described previously⁹. The rheometer tests ran for up to 1 h and 30 minutes. Δtorque which is the difference between the

TABLE 2. VISCOSITY OF THE PARAFFIN WAXES AND ANTIOZONANT MEASURED AT 80°C

	1900H	52/54H	Controzon R.B.H	antiozonant
Viscosity (mPa.s)*	5.5	1.7	1.5	11.8

*mPa.s = milli Pascal second

maximum and minimum torque values on the cure trace of the rubber and indicates crosslink density changes¹⁰ was calculated from these traces.

Test Pieces and Test Procedure

The rubber compounds were cured in a compression mould with a pressure of 11 MPa. Pieces of rubber, each approximately 140 g in weight, were cut from the milled sheet. Each piece was placed in the centre of the mould to enable it to flow in all the directions when pressure was applied and prevent anisotropy from forming in the cured rubbers.

For determining the tensile properties, tear strength, Young's modulus and modulus at different strain amplitudes, sheets of rubber 23 cm by 23 cm by approximately 2.4 mm thick were cured at $160 \pm 2^\circ\text{C}$, from which various samples for further tests were cut. For measuring the hardness of the rubber, cylindrical samples 16 mm in diameter and 8 mm in height were also cured.

Hardness and Cohesive Tear Strength of the Rubber Vulcanisates

The hardness of the rubber vulcanisates was measured in a Shore A Durometer hardness tester (The Shore Instrument and MFG, Co., New York) at ambient temperature (20°C) over a 15 s interval after which a reading was taken.

This was repeated at three different positions on each sample and the median of the three readings was calculated¹¹.

The tear tests were performed at an angle of 180° , at ambient temperature (20°C) and at a constant cross-head speed of 100 mm/min¹². For each rubber, five test pieces were fractured and the average tearing force was used to calculate tearing energy, T, for the rubbers¹³. The median values of the tearing energies were subsequently noted.

Tensile Properties, Young's Modulus and Modulus at Different Strain Amplitudes

The tensile stress, elongation at break and stored energy density at break of the rubbers were determined in uniaxial tension using standard dumbbell test pieces. The tests were performed at 20°C and at a cross-head speed of 100 mm/min¹⁴. The median of the three values were subsequently noted.

The modulus of the vulcanisates at 50%, 100%, 200% and 300% strain amplitudes and Young's modulus were measured in uniaxial tension using standard dumbbell test-pieces. The tests were carried out at ambient temperature (20°C) at a cross-head speed of 100 mm/min¹⁴. Lloyd Nexygen 4.5.1 computer software was used to store and process the data. The tear strength, tensile properties and modulus of the rubber vulcanisates were measured using a Lloyd testing machine LR50K (Hampshire, UK).

Cyclic Fatigue Life of the Rubber Vulcanisates

The cyclic fatigue life (the number of cycles to failure), N , of the vulcanisates was measured in uniaxial tension in a Hampden dynamic testing machine (Northampton, UK), with standard dumbbell test pieces. The test-pieces were die stamped from the sheets of cured rubber. The tests were performed at a constant maximum deflection of 100% and a test frequency of 1.6 Hz. The test temperature was $21 \pm 2^\circ\text{C}$ and the strain on each test piece was relaxed to zero at the end of each cycle. For each rubber vulcanisate, 8 test-pieces were cycled to failure and median of the values was noted¹⁵.

Swelling Tests in High Temperature Glycol Liquid

Samples of rubber approximately 900 mm² in area and 2.5 mm thick and each weighing 2.56 g were placed individually in 27 mL of

glycol in labelled bottles (*Figure 1*) and kept in an oven at 100°C for 8 days. The bottles were removed from the oven and stored at ambient temperature (21°C) for another 24 hours. The samples were then taken from the glycol, thoroughly blotted to remove excess surface liquid and weighed. The percentage swelling of the rubber samples was calculated using *Equation 1* and is summarised in *Table 3*.

$$\% \text{ swelling} = \frac{\text{Swollen weight} - \text{Original dry weight}}{\text{Original dry weight}} \times 100 \quad \dots 1$$

RESULTS AND DISCUSSION

Effect of the Waxes and Antiozonant on the Viscosity, Cure Behaviour and Mechanical Properties of the Rubber Compound

When the waxes were mixed with the rubber, the viscosity increased by 15% to



Figure 1. Showing a sample of rubber in clear glycol liquid before it was placed in an oven at 100°C for 8 days. Sample shown is rubber mixed with 52/54H wax.

TABLE 3. HARDNESS, TENSILE PROPERTIES, YOUNG'S MODULUS, MODULUS AT DIFFERENT STRAIN AMPLITUDES, TEAR STRENGTH, CYCLIC FATIGUE LIFE AND SWELLING BEHAVIOUR OF THE RUBBER VULCANISATES

Properties	Compound number				
	1	2	3	4	5
Hardness (Shore A)	51	52	52	53	53
Tensile strength (MPa)	37	39	37	39	42
Elongation at break (%)	1143	1113	1149	1133	1152
Stored energy density at break (MJ/m ³)	143	142	141	150	164
Tear strength (kJ/m ²)	26	26	29	41	31
Range of values (kJ/m ²)	22-29	25-39	27-38	35-51	27-42
Young's modulus (MPa)	2.0	2.2	2.1	2.1	2.2
Modulus at different strain amplitudes (MPa)					
50%	0.78	0.81	0.83	0.83	0.88
100%	0.68	0.76	0.74	0.74	0.77
200%	0.86	1.04	0.95	0.87	1.03
300 %	1.30	1.53	1.33	1.45	1.62
Cyclic fatigue life (kc)	74	116.3	79.4	94.3	179.7
Range of values (kc)	61-92	99-144	72-106	72-107	133-237
% swelling at 100°C	1.6	0.8	0.8	1.6	0

60–61 MU (*Table 1*). The addition of the antiozonant had an even greater influence on the viscosity, raising it by 36% to 72 MU. It was noted that the melt viscosity of the antiozonant was nearly 86% higher than that of the waxes (*Table 2*) which explains the higher viscosity of compound 5. Interestingly, the viscosity of compounds 2–4 was the same in spite of the waxes having different viscosities.

Rubber viscosity is influenced by various factors such as mixing time¹⁶, mixing temperature¹⁷, filler type, filler loading^{18,19} and chemical curatives²⁰. This study has shown that the addition of small amounts of waxes and antiozonant, *i.e.* 2 p.h.r., also has a noticeable effect on viscosity with an increase in the viscosity.

The addition of the waxes and antiozonant retarded the onset of cure increasing the

scorch time by 37%. However, the optimum cure time decreased by approximately 29% and the cure rate index rose by more than 100%. Clearly, both the cure rate and cure time gained significant benefit from the waxes and antiozonant. It is also noteworthy that Δ torque, which indicates crosslink density changes in the rubber, was relatively constant at about 47–52 dNm (*Table 1*).

The waxes and antiozonant affected the mechanical properties of the rubber vulcanisate differently (*Table 3*). For example, the highest tensile strength at 42 MPa, stored energy density at break at 164 MJ/m³, and modulus at different strain amplitudes at 0.88–1.62 MPa were measured for the rubber with the antiozonant. A marginal improvement in the tensile strength of NR was reported when the antiozonant was added² and our results have confirmed this effect.

The cyclic fatigue life, which is of significant importance to applications such as engine mountings where cracks can grow in rubber under repeated stressing also benefitted from the antiozonant and increased by more than 100% to about 180 kc. A similar study by Lederer and Fath⁵ found a rise of about 60% in the cyclic fatigue life of NR with 3 p.h.r. antiozonant (the same type used in this study) and no wax. This study showed that the cyclic fatigue life deteriorated when 1 p.h.r. Sunolite 240 paraffin wax was added with 3 p.h.r. antiozonant. It was also shown that the rubber with 5 p.h.r. of wax and no antiozonant had a much shorter cyclic fatigue life than that of the control rubber although the life improved as the weight ratio of wax/antiozonant was lowered. This was different from our results, which demonstrated the cyclic fatigue life of NR without antiozonant benefitting from the three paraffin waxes.

The rubber with the Controzon R.B.H wax (compound 4) had the highest tearing energy of 41 kJ/m², and this was 58% higher than that of the control compound. The elongation at break was not affected to any significant degree by the inclusion of the waxes and antiozonant in the rubber but the hardness and Young's modulus rose by 4% and 10%, respectively. Clearly, the mechanical properties of the rubber vulcanisate benefitted from the waxes and antiozonant and the waxes had a similar effect on the mechanical properties of the vulcanisate. This could have been due to the similar melting points (53–63°C) and carbon numbers (20–40) of the waxes.

Swelling of the Rubber Vulcanisates in High Temperature Glycol Liquid

As mentioned earlier, natural rubber is in permanent contact with glycol liquid in hydraulic engine mounts and temperatures

under bonnet can reach as high as 130°C. When the bottles were removed from the oven, the liquid in them had different colours. The liquid which contained the wax-filled rubbers was yellowish and the one with the antiozonant-filled rubber brownish in colour (*Figure 2*). This indicated that the waxes and antiozonant had migrated from the rubber into the glycol liquid, contaminating it. Immersion in high temperature glycol liquid affected the compounds differently. For instance, compounds 1 and 4 swelled by 1.6%, compounds 2 and 3 by 0.8%, and compound 5 did not swell at all demonstrating the rubber with the antiozonant had the highest and the one with Controzon R.B.H wax the lowest resistance to swelling in the glycol liquid. It appeared that an optimum resistance to swelling could be achieved for the rubber by using the antiozonant with either 1900H or 52/54H wax.

As stated earlier, phenylenediamine derivatives are used in combination with waxes to achieve overall protection for rubber. The efficiency of most of the antiozonants is increased many times by the addition of waxes especially in blend with paraffin waxes¹. However, this study has shown that at 100°C, both the waxes and antiozonant migrate into the glycol liquid. For NR at ambient temperature, paraffin waxes have been shown to diffuse to rubber surfaces at higher rates than antiozonants and moreover, the rates increased appreciably at high temperatures because the diffusion is temperature-dependent^{21,22}. Choi²³ reported an 85% increase in the migration of phenylenediamines-type antiozonants in some carbon black-filled NR containing wax at 100°C over a 5-day period. It seemed that the overall benefit of the combined paraffin wax/antidegradant protection for NR was likely to diminish even faster at elevated temperatures in glycol liquid. Consequently, this combination is not suitable for the protection of the rubber in a hydromount.

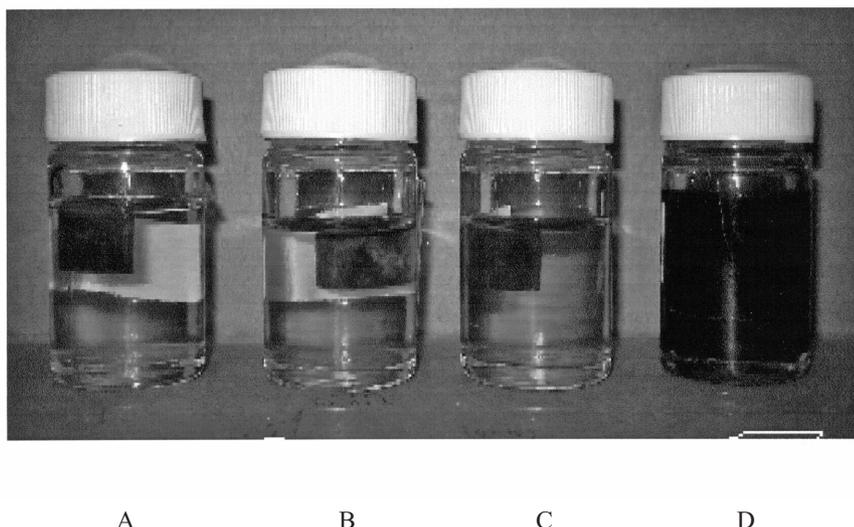


Figure 2. Showing a sample of rubber in clear glycol liquid after removal from oven at 100°C for 8 days. Compound 2: rubber with 1900H wax (A); Compound 3: rubber with 52/54H wax (B); Compound 4: rubber with controzen R. B. H wax (C); Compound 5: rubber with 6PPD (D).

Another way to protect rubber against ozone is to add an ozone resistant polymer such as ethylene-propylene diene rubber (EPDM), halobutyl, polyethylene and polyvinyl acetate to the rubber²⁴. There are also several substituted p-Phenylenediamine the diffusion coefficient of which in different rubbers at different temperatures have been measured. It was found that the diffusion coefficient increased with increasing temperature and with decreased compatibility with the rubber. The low diffusion coefficient observed for (N-(1-phenylethyl)-N'-phenyl-p-phenylenediamine) compared to that of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine was explained by an increased molecular weight and/or increased compatibility with the rubbers. For the former, a diffusion coefficient of $1.66 \times 10^{-7} \text{ cm}^2/\text{s}$ and for the latter $2.34 \times 10^{-7} \text{ cm}^2/\text{s}$ in NR at 85°C (the highest temperature used in the tests) was measured²⁵. There are several new types of long-lasting

antiozonants (5–15 years, depending on the service condition), which have been developed over the last twenty years. They include attachment of hydrocarbon chains to conventional antiozonants in order to increase the molecular weight and compatibility with elastomers, polymeric or oligomeric antiozonants, and binding of several functional groups onto a single platform²⁵. In fact, in recent years, there has been a move from low molecular weight products to higher molecular weight products. A new class of antiozonants have been developed, which are chemically bound to the elastomer chain. While the extraction resistance of the bound antiozonants was significantly improved, performance suffered greatly. Because degradation processes may occur in localised portions of the bulk of the elastomer, mobility of the antiozonants has a major influence on antiozonants activity²⁵. As this study has shown commercial paraffin waxes

and antiozonants do not perform well at high temperatures in hydromounts and therefore they must be replaced with more effective stabilisers.

CONCLUSIONS

From this study, it was concluded that:

- The viscosity, scorch time and rate of cure increased and the optimum cure time decreased when the waxes and antiozonant were added to the rubber. The highest viscosity was measured for the rubber with the antiozonant and this correlated well with the viscosity of the antiozonant, which was almost 86% higher than that of the paraffin waxes.
- The viscosity of the rubber compounds containing the waxes was constant in spite of the waxes having different viscosities.
- The highest tensile strength, stored energy density at break, and modulus at different strain amplitudes and the longest cyclic fatigue life were measured for the rubber with the antiozonant. The rubber containing the Controzon R.B.H wax had the highest tear strength.
- The waxes and antiozonant diffused into the glycol liquid after immersion at 100°C for 8 days. This would have deprived the rubber of protection against ozone.

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