6

Ozone damage of rubber and its prevention

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1 Introduction

Among the external factors causing deterioration of rubber products, the most important are oxygen and ozone. Both these gases are present in the atmosphere, although the concentration of the latter is usually very low. While attack by oxygen is relatively slow, that by ozone is very rapid and results in surface cracking if the rubber is under strain. The degree of unsaturation of an elastomer is the most important factor determining its susceptibility to ozone attack. Depending upon the chemical structure of rubbers, the reactivity of the carbon–carbon double bond may differ, and, therefore, susceptibility to ozone attack also shows similar differences among the unsaturated rubbers. As ozone cracking leads to failure of rubber products, it has been a matter of great concern to rubber compounders. Several methods of protection are available and the effectiveness of such methods could be assessed by different methods.

2 Mechanism of Ozone Attack

Ozone attack on unsaturated rubbers is basically similar to ozone attack on model olefins. The mechanism of ozone attack on olefins was originally proposed by Criegee[1] as summarized in Fig. 1. The initial step in the mechanism involves nucleophilic attack of a resonance form of ozone on the olefin to form a product (III) which is a cyclic ozonide and which rapidly undergoes rearrangement by heterolytic cleavage of the oxygen–oxygen bond to form a zwitterion (V) and an aldehyde or ketone (VI). The zwitterion (V) is the key intermediate in the process. This can stabilize by four separate processes as illustrated in Fig. 1.

If the initial olefin structure in Fig. 1 is regarded as that present in an unsaturated polymer, the mechanism can be applied to the ozone attack of rubber. Substitution on the olefin would be expected to follow the general rules for nucleophilic attack: (1) electron donating groups such as alkyl groups would increase the nucleophilic tendency of the olefin

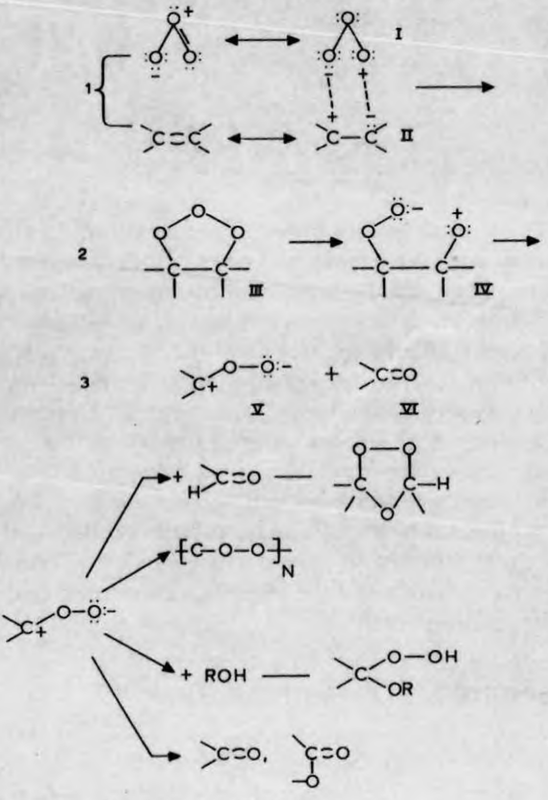


Figure 1. Mechanism of ozonation of olefins.

and increase reaction rates and (2) electron withdrawing groups such as halogens would decrease the nucleophilic tendency of the olefin and decrease reaction rates. Thus, it is expected that chloroprene rubber (CR) would be less reactive to ozone compared to natural rubber (NR) or butadiene rubber (BR). This type of behaviour is actually observed and CR is considered ozone-resistant and finds use in many applications where long-term ozone resistance is required.

The fact that ozone attack on olefins occurs very rapidly implies that the attack of ozone on unsaturated rubber occurs at the exposed surfaces and the interior of the rubber would be attacked only after all the surface olefins had been consumed. Thus ozone attack on unsaturated rubber is primarily a surface effect.

Experimental support to the mechanism described in Fig. 1 is available from the study by Allison and Stanley[2] who reported a decrease in the molecular weight of unsaturated polymers when ozonized in solution and a decrease in the concentration of double bonds during the ozonization of styrene–butadiene rubber (SBR) in solution. Use of infrared spectroscopy to study the products of ozonization of unsaturated polymers showed that ozonides, carbonyl compounds and hydroxy compounds were formed.[3,4] Thus ozonation of unsaturated rubbers appears to follow the mechanism proposed in Fig. 1.

3 Ozone Crack Growth

The mechanics of ozone crack growth in rubber and the protective action of chemical antiozonants have been reviewed by Lewis.[5] Using a strip test piece containing an edge or centre cut and deformed in simple extension (the surface of the test piece being protected by grease to prevent the formation of subsidiary cracks) Gent *et al.*[6-8] showed that crack growth does not occur unless the elastic energy available for growth, the tearing energy,[9] exceeds a small but finite value. Above the critical energy, the growth is time-dependent and the rate is independent of the available energy, i.e. it is independent of the strain imposed on the rubber and the crack length. For a number of rubbers including NR and SBR, at temperatures well above the glass transition temperature, the single crack growth rate (γ_0) is proportional to the ozone concentration (q_0) so that

$$\gamma_0 = \alpha_0 \cdot q_0 \qquad (1)$$

where α_0 is a constant, characteristic of the vulcanizate.

Under constant deformation the critical energy required for growth ($T\dot{z}$) is of the order of 100 erg/cm^2 for unprotected vulcanizates of most rubbers. However, under repeated loading $T\dot{z}$ is much lower,[10] so that it is probably a measure of the strength of the ozone-degraded material under the experimental conditions employed, rather than a simple surface energy requirement.

3.1 Dependence of the Cracking Pattern on Tensile Strain

In order to produce cracking in a surface containing no inserted cut a critical strain is required. For unprotected vulcanizates this is of the order of a few per cent strain in simple extension. At this deformation the critical energy $T\dot{z}$ is reached at flaws having an effective length of about 10^{-3} cm. The presence of 'naturally occurring' flaws of this size has been indicated from fatigue measurements.[11] Antiozonants which increase $T\dot{z}$, also increase the critical strain. Above the critical strain, the crack density increases rapidly with increasing strain, but the size of the individual cracks decreases. The increase in crack density is due to the fact that at higher strains cracks will grow from smaller flaws. The decrease in the size of the individual cracks is attributable to elastic interference between adjacent cracks. The depth of the cracks, which is likely to be more significant from the strength point of view, is less readily observed. But this was quantitatively measured by Lake[12] by: (1) direct measurement after cutting through a cross-section of a test piece; (2) by measuring the stress relaxation produced by ozone cracking; and (3) from the reduction in fatigue life caused by exposure to ozone.

The strain in the samples is found to influence the rate of crack growth also. The rate is maximum just above the critical strain and decreases at higher strains. The fatigue method tends to give relatively low results at high strains due to elastic interferences between neighbouring cracks but is still useful in this region in that it gives an indication of the effective crack size from a strength point of view. Thus the rate of ozone crack growth in a surface is in accordance with single crack behaviour in its variation with ozone concentration, but differs in being dependent on strain whereas for a single crack the rate is essentially independent of strain. The rate of ozone attack is also found to increase with increased velocity of the ozone carrying air stream passing over the sample.

3.2 The Boundary Layer Theory

In the case of a solid body, placed in a moving fluid stream, the boundary layer is defined as the region in which the fluid velocity increases from zero at the solid surface to the free stream velocity. It represents the main barrier to the transport of heat or mass to or from a solid. For a flat sheet situated parallel to the direction of flow of a given fluid the boundary layer thickness, d (Fig. 2) is given, for laminar flow, by

$$d=\eta\left(\frac{x}{v}\right)^{1/2} \tag{2}$$

where v is the free stream velocity of the fluid, x the distance from the leading edge of the sheet and η is a constant which embodies the kinematic viscosity of the fluid. In the true boundary layer the fluid velocity varies continuously with distance from the solid surface, but for the present purpose it is sufficient to consider a simplified boundary layer in which the fluid is regarded as being completely at rest; this simplified boundary layer can be made equivalent to the true one by suitable adjustment of the thickness by means of the constant η in eqn (2).

In the case of ozone attack on rubber a situation is considered in which the ozone concentration at the surface has an unknown value (q) which is less than that in the main gas stream q_0 (Fig. 2(b)). From the simplified boundary layer model, if a steady state situation exists, the concentration gradient across the layer will be constant and equal to $(q_0-q)/d$. Hence the rate of incidence of ozone per unit area of surface will be

$$M=D(q_0-q)/d \tag{3}$$

where D is the diffusion coefficient of ozone in the gas.

It is now assumed that the rate of destruction of ozone at a rubber surface is proportional to the ozone concentration there. Thus the rate of destruction per unit area of stretched surface is taken as

$$m=Rq \tag{4}$$

where R is a destruction coefficient.

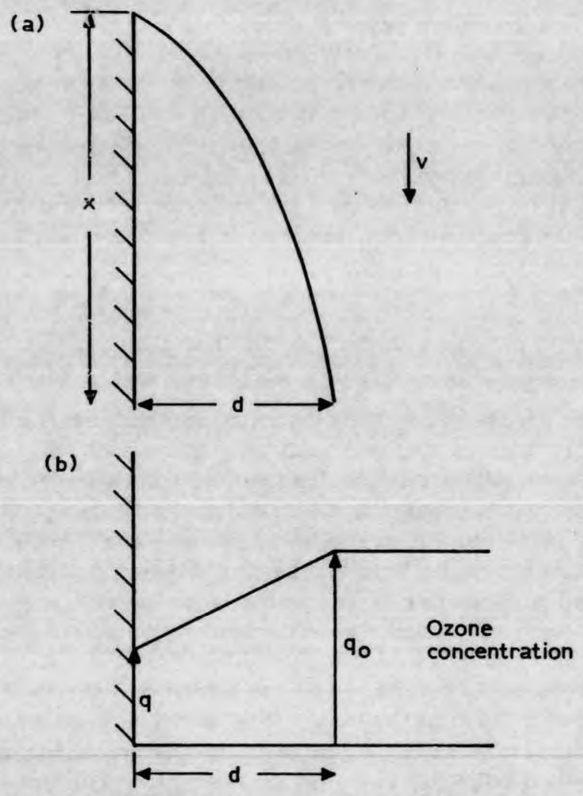


Figure 2. (a) Dependence of the boundary layer thickness *d* on distance *x* from the leading edge of a thin plate (schematic); (b) variation of ozone concentration across the boundary layer (Ref. 12).

At the steady state M and m will be equal so that eqns (3) and (4) yield

$$q/q_0 = 1/(1 + Rd/D) \tag{5}$$

If, following the single crack growth observations as given in eqn (1), the rate of growth in surface (γ) is taken to be proportional to the ozone concentration at that surface, then the above equation can be extended to

$$r/r_0 = q/q_0 = 1/(1 + Rd/D) \tag{6}$$

where r_0 is the rate in the absence of any boundary layer effect, which can be identified with the normal single crack growth rate.

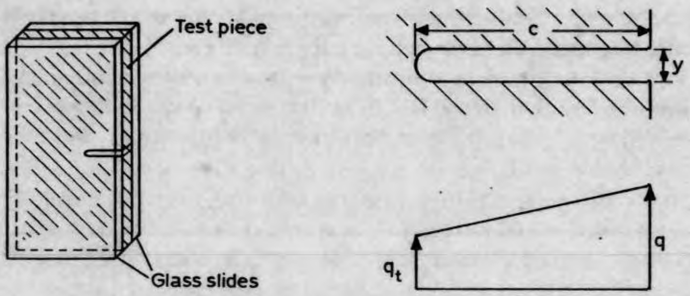
The theory thus suggests that the rate of growth in a surface will in general be lower than the single crack growth rate by an amount which depends on the magnitude of the term Rd/D in eqn (6).

It is well known that the attack of ozone on rubber proceeds much more slowly under liquids than it does in air. The results of Zuev and Malofeevskaya[13] indicate that for a given ozone concentration the rate of attack in air is faster than that in water by a factor which varies between $0{\cdot}4 \times 10^4$ and $1{\cdot}6 \times 10^4$ for different elastomers. The boundary layer-diffusion theory suggests a possible explanation for this large difference in that a boundary layer will exist adjacent to a rubber surface under a liquid in the same way as in a gas. The thickness of the boundary layer is not likely to differ greatly in the two media but the diffusion coefficient of ozone will be markedly different and this will affect the rate of attack. For carbon dioxide, which is of similar molecular size to ozone, the ratio of the diffusion coefficients in air and water is about 10^4 and is thus very similar to the ratio of the rates of attack. It therefore appears that diffusion control may be the major factor which retards the attack under liquids.

3.3 Growth of Deep Cracks

Surface ozone cracks usually do not extend across the full width of the specimen. The gas within a crack will be essentially at rest, so that the transport of ozone from the crack mouth to the growing tip must occur by diffusion. Thus there may be a concentration gradient within a crack and the concentration at the tip, which governs the rate of growth, may be lower than that at the surface.

The growth of deep, enclosed cracks under well-defined conditions, was studied by Lake[12] using tensile strip test pieces with glass slides placed close to the major surfaces (Fig. 3(a)). One or more cracks were allowed to grow from the edge of each test piece so that the crack length could readily be observed as a function of time. This arrangement thus resembles that used for normal single crack growth measurements except that the access of ozone to the tip from the sides of the crack is prevented. The results of the study indicated that an enclosed crack grows at a rate which is initially the same as the normal single crack growth rate but which progressively decreases as the crack length increases. Similar behaviour is observed for different thicknesses of test



(a) (b)

Figure 3. Enclosed cracks: (a) experimental arrangement for single crack growth measurements with glass at the sides of the test piece; (b) simplified model assumed for the theory with constant height of the crack opening (y) and a linear concentration gradient (Ref. 12).

piece, suggesting that the effect is not simply due to constraints arising from friction between the rubber and the glass.

A major part of the ozone consumption within a crack is likely to occur at the tip where fresh rubber is continuously being exposed. If it is assumed that ozone is consumed only at the tip and that a quasi steady state condition exists, then for an essentially parallel-sided crack the concentration gradient will be linear (Fig. 3(b)). Hence the rate of incidence of ozone at the tip per unit width of crack, will be given by

$$M_1 = YD(q - qt)/C \tag{7}$$

where q is the ozone concentration at the crack mouth, qt that at the tip, C the crack length, Y its height and D the diffusion coefficient of ozone in the gas within the crack.

The consumption rate of ozone per unit width of the crack (m_1) is assumed to be proportional to qt, so that

$$m_1 = R_1 qt \tag{8}$$

where R_1 is the consumption coefficient for unit width of a single crack.

At the steady state M_1 and m_1 will be equal and from eqns (7) and (8)

$$qt/q = 1/(1 + R_1 C/YD)$$

which, on taking the rate of growth to be proportional to the ozone concentration at the tip, yields

$$r_1/r = qt/q = 1/(1 + R_1 C/yD) \tag{9}$$

where r_1 is the rate of growth when the crack has attained a length C and r is the initial rate of growth when $C = 0$.

When the boundary layer effect is negligible, $q = q_0$, the concentration of ozone in the main gas stream, and $r = r_0$, the normal single crack growth rate, which is constant. On putting $rt = \mathrm{d}c/\mathrm{d}t$ in eqn (9) and integrating, the crack length C can readily be obtained in terms of time t, if the height of the opening of the crack (y) remains constant. Under these circumstances eqn (9) yields, for a crack starting from the edge ($C = 0$ at $t = 0$),

$$C = yD[(1 + 2\,r_0 R_1 t/yD)^{1/2} - 1]/R_1 \tag{10}$$

The experimentally measured value of R_1 is about $0{\cdot}01\ \mathrm{cm}^2\,\mathrm{s}^{-1}$. This could be related to the ozone consumption coefficient per unit area of stretched surface (R) by

$$R_1 = R/l \tag{11}$$

where l is the total length of the cracks that are growing in unit area of surface. At fairly low strains, when the individual cracks can be distinguished, l can be readily determined experimentally. From such measurements, a value of R/l of about $0{\cdot}015\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ is obtained. In view of the various uncertainties, this is in satisfactory agreement with the value deduced from R_1.

The effect of this second diffusion mechanism is to cause a progressive slowing down of the growth when a crack becomes fairly long; in the case of cracking in a stretched surface this would be additive to any boundary layer effect. The constant rate of growth observed for small cracks suggests that for these, the major factor accounting for the variation in rate with strain is the boundary layer effect. However, bearing in mind the complex dependence of the cracking pattern on strain and time of exposure to ozone, which may well affect the amount by which a crack opens, some contribution from the mechanism of diffusion down the crack cannot be ruled out.

3.4 Cracking under Dynamic Conditions

The effect of ozone exposure on the fatigue life of rubber can be predicted by assuming that the rate of ozone crack growth is equal to the single crack growth rate r_0 and is independent of strain.[14] This is in contrast with ozone cracking under constant load where, as has been discussed earlier, the rate is found to decrease with increasing strain.

This difference in behaviour is consistent with the boundary theory in that under dynamic conditions much smaller effects of the boundary layer would be expected; this is because the fairly rapid movement of the test piece and the continual stretching and relaxing of the rubber surface are likely to cause considerable turbulence. Hence the single crack growth characteristics would be expected to apply essentially to fatigue failure.

4 Surface Studies

Owing to experimental problems, the vast majority of information gathered about ozone attack and antiozonant protection has not been from direct analysis of the reactions occurring on the rubber surface, but from other analytical methods such as solution studies, model compound studies and ozone absorption studies. However, with the rapid development of analytical tools capable of surface analysis, more accurate information can now be gathered about ozone attack and antiozonant protection. Andries and Diem[15] used a surface infrared technique, attenuated total reflectance (ATR) spectroscopy to study the ozonolysis of raw elastomers. They reported that ozone attack on synthetic polyisoprene and polybutadiene produced a thin layer of ozonides (band at 1100 cm^{-1}), but that ozone attack on NR produced a thick surface layer of ozonides (1100 cm^{-1}) and carbonyl compounds (1735 cm^{-1}) which continued to develop into the bulk of the rubber with long exposure. They showed that the extensive and complex ozone attack on NR is due to the presence of the acetone extractables in NR. These extractables consist of fatty acids, esters, steroles, lipids, resins and antioxidants. When the acetone extractables are removed from NR, the resulting ATR spectra, after ozone exposure, are identical to those of polyisoprene and polybutadiene. Andries *et al.*[16] used ATR to study the ozone attack and antiozonant protection of clay-filled NR vulcanizates. They found that when an NR compound containing *N*, *N*′-dioctyl-*p*-phenylenediamine is ozonized, a film is seen with an ATR spectrum essentially identical to that of ozonized liquid antiozonant.

In a later study, Andries *et al.*[17] extended the previous ATR studies of NR compounds containing carbon black. Carbon black absorbs IR radiation and thus makes ATR analysis difficult. However, ATR techniques have been modified to make surface analysis of carbon black loaded stocks feasible. Both cured and uncured carbon black loaded

NR stocks were examined, with and without *N*,*N*′-dioctyl-*p*-phenylenediamine. Scanning electron microscopy (SEM) was also used by the authors to relate the surface morphology to the surface chemical composition as identified by ATR. On ozonization of raw NR or NR containing carbon black, a thick layer builds up consisting of ozonides and carbonyl compounds. It is suggested that this layer is composed principally of the reaction products of ozone with unsaturated fatty acids and unsaturated fatty acid esters found in NR. On ozonization of cured and uncured carbon black loaded NR compounds containing curatives, the NR is attacked causing a decrease of rubber on the surface and a corresponding increase in the surface concentration of carbon black. The thick ozonide/carbonyl layer did not form, probably due to the coordination of the fatty acids and esters with ZnO which were added with the curatives. On ozonization of carbon black-loaded NR compounds containing *N*,*N*′-dioctyl-*p*-phenylenediamine antiozonant, a continuous film is seen by SEM which has an ATR spectrum essentially identical to ozonized antiozonant. There is no evidence of ozonized NR products or of complex reaction products between antiozonant and ozonized NR. These results are consistent with a dual scavenger and protective layer mechanism for antiozonant protection.

SEM was used by Mathew[18] to study the ozone cracking pattern in NR and an NR/EPDM blend. It was found that the cracking pattern is almost identical in both unfilled NR and the blend. However, the carbon black filled vulcanizates showed differences in the cracking behaviour. In the case of the filled NR vulcanizates the cracks were found to propagate straight without much deviation. However, in the case of the filled NR/EPDM vulcanizate, the crack density was found to be less and the cracks longer. It was also concluded that the ozone resistant EPDM zones in the blend prevented the cracks from proceeding straight. This explanation was first put forward by Andrews[19] in the case of NR/EPR blends. Further microscopic work on ozone cracking was presented by Ban *et al.*[20] in the case of blends of EPDM with NR and BR. These authors suggest that the size of the dispersed EPDM particles in the compounds studied by them may be too small to restrain the spread of ozone cracking by Andrews' mechanism. Some of the SEM results presented by them suggest the presence of some brittle and crystalline material within the ozone cracks. Microtomed thin sections have been prepared and a polyvinyl alcohol replica has also been used to pull some of this material from the crack for further examination, which indicated that the exudate within the crack is wax. It appears that as the ozone crack develops, wax is desorbed from the compound to the new free surface where it can form an ozone inert, low ozone permeability layer. Crack growth may then occur as the wax is separated from the crack wall due to stress concentrations, such as those due to undispersed carbon black agglomerates in the compound. New crack branches may then arise as ozone attacks freshly exposed rubber surface. It may be that EPDM particles can act as 'micro-reservoirs' for wax along the locus of the ozone crack. As the crack passes, EPDM particles may rupture, or wax gets desorbed from the particles to the free new surface to lay down an inert protectant layer and prevent further penetration of ozone to the crack tip.

5 Protection Against Ozone Damage

There is no universal protective system capable of protecting rubbers against ozone damage under all conditions. All practical systems have their shortcomings. However, by proper design of both formulation and products, ozone cracking can be substantially reduced or often eliminated altogether. The most important methods of protection involve the use of petroleum waxes, flexible coatings, chemical anti-ozonants and blending with ozone inert rubbers. The selection of a protective system for a particular vulcanizate depends on the service conditions to which it is exposed, i.e. the strain imposed upon the vulcanizate, whether it is dynamic or static, the temperature and the concentration of ozone in the atmosphere.

5.1 Petroleum Waxes

Petroleum waxes can be broadly classified into two types: paraffinic and microcrystalline. The former generally exhibits lower molecular weight, lower melting point, higher concentration of linear or straight chain hydrocarbons and greater crystallinity compared with the microcrystalline waxes. Table 1 summarizes the difference between the two types of waxes. It is generally agreed that waxes added to rubber are capable of migrating to the surface by a mechanism described by Nah and Thomas,[21] thereby providing protection against ozone attack by the formation of an impervious barrier. The ability of a wax to migrate to the surface, or bloom, depends upon the specific type of wax, the rubber composition and the time and temperature before and during exposure

Table 1. Wax composition.

	Paraffinic	Micro-crystalline
Average molecular weight	350–420	490–800
% Normal paraffin	High	Low
% Isoparaffin and naphthenes	Low	High
Melting point range (°C)	38–75	57–100
Typical carbon chain length	C-26	C-60

From Ref. 22.

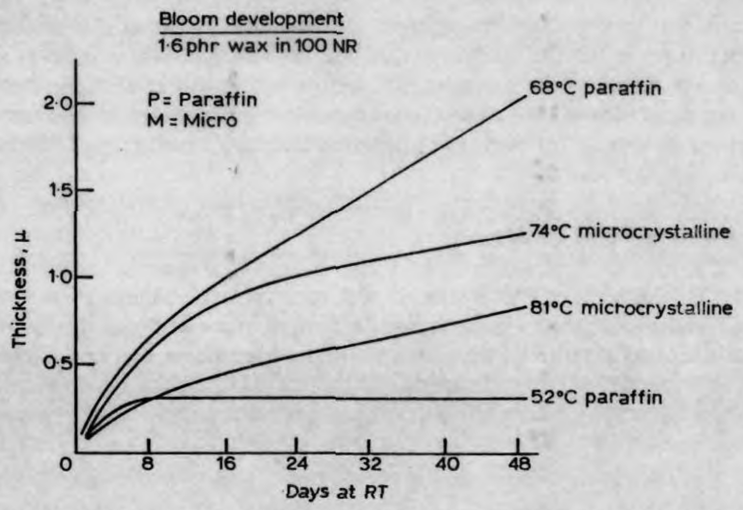


Figure 4. Effect of wax melting point on rate of bloom in natural rubber (Ref. 22).

to ozone. All these parameters influence the solubility/mobility characteristics of each specific wax. The factors which influence the rate of bloom of a variety of petroleum waxes have been discussed by Dimauro *et al.*[22]

5.2 Rate of Blooming of Wax

The rate of development of wax bloom in the case of two grades each of paraffinic and microcrystalline waxes is given in Fig. 4. It shows the rapid initial formation of the wax bloom, followed by a reduction in the rate of blooming after 8–10 days' exposure. It may be noted that the paraffinic wax with a melting point of 52°C plateaus after the first week, an indication of its higher solubility, hence lower mobility in the rubber. If all the wax in the bulk of these samples had migrated to the surface, the film thickness would be 16 μm. Assuming a solubility level of about 0·8 phr, this value would be reduced to 7·7 μm, still higher than the observed values. Apparently, the 48 day exposure was insufficient to reach the theoretical equilibrium thickness.

Figure 5 schematically shows how the combination of mobility and solubility determines the extent of the wax bloom at any given temperature. If the temperature is altered, the balance is upset. At higher temperatures solubility increases and the thickness of the wax layer is decreased. Conversely, lowering the temperature will at first increase the extent of bloom due to lower wax solubility. However, as the temperature decreases further, wax migration decreases and rate of bloom to the surface is reduced.

5.3 Melting Point of Wax

Table 2, which gives the extent of bloom versus the melting point of waxes, shows that the extent of paraffinic wax bloom will pass through a maximum and eventually decrease as the melting point increases. This

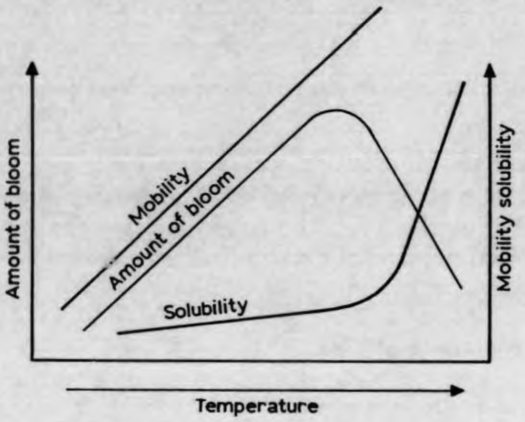


Figure 5. Wax bloom as a function of mobility and solubility (Ref. 22).

Table 2. Hot versus cold ozone protection of paraffinic waxes.

Ozone concentration (pphm)	25	25
Temperature (°C)	17	30
Preconditioned at 25°C (days)	0	3
5 Phr paraffinic wax, m.p. (°C)		
44–47	NC	C
46–50	NC	C
50–54	NC	NC
57–61	NC	NC
65–69	C	NC

From Ref. 22.
NC denotes specimens not cracked.
C denotes specimens cracked.

demonstrates the balance between wax migration and solubility as a function of melting point in determining the extent of bloom. The higher melting microcrystalline waxes show a general decrease in bloom with increasing melting points, since the mobility in rubber is lower.

5.4 Effect of Temperature of Exposure

As the rate of wax bloom is dependent upon a balance between its solubility and mobility, it is not surprising that the exposure temperature is one of the most significant factors controlling the effectiveness of wax. Paraffinic wax is found to bloom more rapidly and to a greater extent at 20°C than at 40°C, whereas the microcrystalline wax shows the opposite. In the case of uncured compounds the same trends are also observed. However, the absolute amounts of wax bloom were much lower since the wax is more soluble in the uncured rubber. Since the majority of the wax remains dissolved in the uncured rubber, this explains how a wax can protect a cured vulcanizate while not significantly interfering with the uncured adhesion to other substrates.

5.5 Wax Concentration

The influence of concentration of wax bloom in rubber is straightforward for both paraffinic and microcrystalline waxes. The extent of bloom increases with wax concentration, provided the solubility limit of wax in rubber is exceeded.

5.6 Effect of Wax Type on Ozone Protection

Lewis[23] compared the extent of ozone cracking resistance in natural rubber provided by a series of paraffinic waxes at both 17° and 30°C, and the results are given in Table 3. At 17°C all the paraffinic waxes, except the highest melting one, provide ozone protection. Apparently, its mobility is too low at 17°C to migrate to the rubber surface sufficiently to provide the necessary physical barrier. The reverse is true at 30°C. The two lowest melting waxes are ineffective due to their high solubility at this temperature. Hence the degree of protection is consistent with those parameters which influence wax bloom development. The relationship between ozone resistance and optimum migration rate has been further demonstrated by Angert *et al.*[24] Obviously, a wax which protects well under the standard 40°C ozone cabinet conditions will not necessarily be the best choice for ambient exposure, where temperatures can vary from −30 to 50°C. It may be noted that the blended wax with the wide range of migration temperature, provides the best overall protection.

5.7 Effect of Process Oils and Fillers on Wax Bloom

Extender oils may promote or reduce wax blooming, depending upon the type of oil, concentration and temperature. Aromatic oils tend to retard blooming while paraffinic or naphthenic oils can increase or decrease blooming depending upon exposure temperature. In the case of a highly black loaded NR compound containing 40 phr of paraffinic

Table 3. Stress–relaxation ozone test.

Protectant (2·5 phr)	Hours to 90% retention of 100% modulus		
	Static	Dynamic	Total
None	13	15	28
Proprietary blended wax[a]	20	2	22
N-(1,3 dimethylbutyl)-*N*-phenyl-*p*-phenylenediamine	55	95	150
Both of the above	160	65	225+

From Ref. 22.
[a] Sunolite 240.

oil, at 30°C, the oil allows the wax to diffuse more easily to the surface. At 40°C the wax is more soluble in the oil and, therefore, less wax diffuses to the surface.

Fillers are also found to influence wax bloom.[24] The higher the activity of the filler, the greater the bloom. Whiting, however, was found to depress the rate of blooming.

5.8 Effect of Wax under Dynamic Conditions

Wax film, being brittle, cracks under dynamic conditions and, therefore, may not protect rubber from ozone attack. Table 3 compares both static and dynamic performance using the stress relaxation ozone test.

These results suggest that wax can be detrimental to dynamic ozone resistance. Apparently, localized stresses can be induced in the rubber by wax. These stresses can lead to premature failure under dynamic testing conditions. In order to ensure balanced protection under both static and dynamic conditions, a chemical antidegradant could be used in combination with a blended wax. It is also believed that a blooming wax can function as a carrier for the chemical antidegradant from the bulk of the rubber to the surface, where its presence is most required.

5.9 Flexible Coatings

It is desirable to paint rubber products for aesthetic reasons. For example, rubber is now quite widely used in rubber bumpers, overriders, rubber bumper covers and rubbing strips in conjunction with other anti-impact or energy absorbing devices. Rubber bumpers and other automotive components have quite large areas and it has now become very important to match their colour with that of the car body. The requirements of the car industry are for flexible, abrasion and corrosion-resistant surfaces. Polyurethane paints are the most promising to meet these requirements and give flexible surface with 160–180% elongation at break.

Painting of natural rubber with flexible urethane paints has been described by Cutts and Wheelans.[25] Apart from the improved appearance, the painted rubber surface is found to possess excellent resistance to ozone cracking. To give good protection, however, the paint should completely cover the rubber surface and it is best if the whole sample is given at least two complete coats of paint. Samples with one coat of paint have remained uncracked at 50% extension at an ozone concentration of 25 pphm at 30°C for 136 days. One sample with two coats of paint has remained crackfree at 115% extension at 25 pphm at 30°C for 136 days.

While designing a rubber product meant for paint coating, it must be noted that compounding ingredients, which may spoil the appearance of the painted surface or the adhesion between the paint and the rubber, are avoided. For example, staining antioxidants and antiozonants and aromatic process oils are avoided because they discolour paint. Waxes and compounding ingredients which may bloom, are avoided because they may spoil the adhesion between paint and rubber or they may bloom through the paint in an unsightly manner.

5.10 Chemical Antiozonants

Wax blooms cannot withstand flexing and flexible coatings will be removed by abrasive wear of the surface. Consequently chemical antiozonants are required for dynamic applications such as tyres and beltings. When staining can be tolerated, antiozonants such as *N*-alkyl-*N'*-phenyl and *N*, *N'*-dialkyl-*p*-phenylenediamines are extremely effective. Both types reduce the rate of crack growth under static and dynamic conditions and the *N*, *N'*-dialkyl derivatives also increase the critical strain. An explanation of these effects was advanced by Andrews and Braden[26] on the basis of electron microscopic studies of the surfaces of chemically protected rubbers.

With the *N*-alkyl-*N'*-phenyl-*p*-phenylenediamines, antiozonant activity decreases as the molecular weight of the alkyl group increases, but at the same time solubility increases and the physical state changes from solid to liquid. Of the *N*, *N'*-dialkyl derivatives, *N*, *N'*-di-(1,4-dimethylpentyl)p-phenylenediamine is more effective than the two *N*, *N'*-dioctyl isomers. When examined by the accelerated tests the 1-methylheptyl substituent gives higher activity than its 1-ethyl, 3-methylpentyl isomer. These symmetrical antiozonants are liquid, but the less effective solid *N*, *N'*-dicyclohexyl derivative is also available. They are weaker antidegradants than the *N*-alkyl-*N'*-phenyl-*p*-phenylenediamines and can reduce scorch safety considerably as was shown by Lewis[23] in Table 4.

Critical strain does not increase linearly with the level of *N*, *N'*-dialkyl-*p*-phenelenediamine used, and when added alone at least 2·5 phr is required in natural rubber to provide a useful improvement, although lower levels of these and the *N*-alkyl-*N'*-phenyl derivatives give protection under dynamic conditions and against fatigue cracking.

Table 4. *N, N′* Disubstituted *p*-phenylenediamine antidegradants.

Heveacrumb SMR5, 100; zinc oxide, 5; stearic acid, 2; HAF black, 45; process oil, 5; CBS, 0·5; sulphur, 2·5; cure, 40 min (140°C)

Type of *NN′* disubstituted *p*-phenylenediamine at 2 phr	Mooney scorch 120°C ML (1 + 5) (min)	Tensile strength retention after air oven ageing for 3 days at 100°C (%)	De Mattia flex crack resistance Grade C (kHz)	Ozone resistance at 25 pphm ozone and 30°C	
				Critical strain (%)	Time to first crack, dynamic exposure (h)
No additive	26	16	65	3	0·5
N-isopropyl *N′*-phenyl (IPPD)	20·5	44	255	5	18
N-(1,3-dimethylbutyl) *N′*-phenyl	23	45	150	5	9
N-(1-methylyheptyl) *N′*-phenyl	22	42	205	3	6
NN′-di(1,4,dimethylpentyl) (DHPPD)	14	32	175	12	18
NN′-di(1-ethyl-3-methyl-pentyl) (DOPPD)	20	30	140	10	14
NN′-di(1-methylheptyl) (DMHPD)	17	43	195	12	22
NN′-dicyclohexyl	12	39	165	5	6

From Ref. 23.

The amount of antiozonant added may be reduced considerably if it is used with a small loading of wax. Provided that a wax bloom is present, blends of this type raise critical strain considerably and are more effective than higher levels of antiozonant and wax used separately. The mechanism of protection is not fully understood, but the antiozonant may be reducing the critical bloom thickness of the wax, while it is significant that the *N*-alkyl-*N′*-phenyl-*p*-phenylenediamines are more effective than the *N*, *N′*-dialkyl derivatives, in spite of their inferior static protection when used alone. This distinction is most marked in the presence of low melting paraffin waxes with which the *N*, *N′*-dialkyl-*p*-phenylenediamines frequently give no improvement at all. Unless there are intermittent periods of static exposure, wax is detrimental to the dynamic ozone resistance conferred by antiozonants, although the loss is less pronounced with *N*-alkyl-*N′*-phenyl-*p*-phenylenediamines.

Less effective than the *p*-phenylenediamine antiozonants is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline. This is highly staining and only reduces the rate of crack growth. It does not protect against static cracking unless blended with waxes.

5.11 Mechanism of Action of Chemical Antiozonants

The mechanism of protection by chemical antiozonants is still a matter being debated. It is increasingly accepted that *p*-phenylenediamines diffuse to the exposed surface once a concentration gradient is established by consumption of antiozonant through reaction with ozone or ozonized products. However, it is not certain which reactions are primarily responsible for crack prevention or retardation. Four theories have been proposed, two suggesting the key reaction involves the ozonolysis-reaction products of rubber and the other two favouring direct ozonation of the *p*-phenylenediamine. These theories have been recently reviewed by Lewis.[5]

The first theory suggests that the antiozonant reacts with ozonized rubber in such a way as to prevent chain scission or to couple broken chains terminated by active groups such as aldehydes.[27,28] The presence of reaction products between *p*-phenylenediamines and previously ozonized olefins and the detection of bound nitrogen in the rubber after solvent extraction support this theory. This might explain in part why antiozonant activity varies among rubber types in which antiozonants have broadly similar diffusion characteristics; SBR, for example, is more responsive than natural rubber. However, this theory does not adequately account for enhancement in threshold strain because statistically some chain scission would be expected. Also as per this theory ozone resistance can fall if a previously exposed surface is wiped with a solvent.

The second theory says that the antiozonant reacts with the zwitterion or ozonized rubber to form a stress free, low molecular mass film capable of repair upon rupture.[29] According to this theory, cracking can not occur because the antiozonant modified degraded surface undergoes stress relaxation. However, this theory also fails to explain all the observations on ozone cracking.

The third theory suggests that the antiozonant scavenges ozone before it can attack the rubber.[30] The fact that *p*-phenylenediamines in solution react with ozone more quickly than do olefins and the development of cracks after long-term exposure when the free antiozonant reservoir has been exhausted, support this theory. It also explains the extended delay in crack initiation and the reduction in rate of crack growth. However, it is found that there are more effective scavengers than *p*-phenylenediamines, which are not antiozonants. It is also observed that crack-free protection is still conferred when the antiozonant reservoir has been depleted to such an extent that its diffusion rate to the surface is much smaller than the rate of incidence of ozone.

According to the fourth theory, the antiozonant reacts with ozone to form a stress-free protective film which prevents the ozone from reacting with the rubber surface.[12] Observation of a film less extensible than the underlying rubber and the conditioning effect whereby a dialkyl-*p*-phenylenediamine-protected rubber previously exposed to a low ozone concentration can withstand a higher ozone concentration, whereas a fresh sample or a previously exposed one wiped with solvent will crack, are evidence to the theory. However, the theory does not explain some dependence of antiozonant activity on rubber type.

5.12 Blending with Ozone Resistant Rubber

In the case of products where staining, discoloration and surface blooms are unacceptable and where ozone resistance under static and dynamic conditions is required, a portion of the rubber could be replaced with an ozone resistant rubber like polychloroprene (CR), ethylene propylene copolymers (EPM) and terpolymers (EPDM) and chlorobutyl. These blends are used in white sidewalls, sponge products and high quality weatherseals. But at the levels necessary for a substantial improvement in ozone resistance some sacrifice of processibility and vulcanizate properties may have to be tolerated.

It must be remembered that blends of such rubbers with general purpose rubbers are not homogeneous, as they do not go into solid solution. Usually the rubbers remain as separate phases. Growing microscopic cracks in the unsaturated rubber phase are prevented from further propagation when they encounter zones of ozone-resistant rubber.[19,31] The level of protection improves as more inert rubber is included.

The zones of the resistant rubber in the blend will only be effective if they remain intact under the stress at the tip of the growing crack. In the absence of vulcanization or at low crosslink densities, these areas may yield under high stress and so allow crack growth to continue. This is probably the explanation for the higher ozone resistance and fatigue life of peroxide cured NR/EPM blends, compared with those vulcanized by a sulphur system. In the latter case only the natural rubber is capable of vulcanization.

It is found that the overall performance of blends will be influenced strongly by the relative rates of vulcanization of the rubbers used. All the ozone inert rubbers are slower curing than natural rubber. In some cases the differences in cure rates is so large that unless a proper choice of vulcanizing system is made, most of the crosslinks will be formed in the NR phase only. For this reason, slow guanidine accelerated sulphur systems give better ozone resistance to natural rubber/chlorobutyl blends than do thiuram disulphides and many other systems when measurements are made at similar stiffness[23] (Table 5).

The mechanism of improvement in ozone resistance by an ozone inert rubber like EPM has been studied by Andrews.[19] According to this study a growing crack in the reactive phase must, sooner or later, encounter an inert particle and come to a halt, further propagation being possible only by the crack circumventing the particle or jumping over it. Except for very small particles circumvention is unlikely since it would involve the crack propagating parallel to the applied stress, i.e. in a direction involving a minimum release of elastic stored energy. The alternative possibility of the crack jumping or bridging the particle leaving the latter unsevered, has actually been observed in the electron micrographs and clearly occurs when the presence of the crack projects a sufficient concentration of stress to the far side of the particle to initiate a new crack there (Fig. 6). The probability of such a jump increases with the length of the crack and also with the overall stress level in the specimen. The length of the cracks in the reactive phase will,

Table 5. Influence of vulcanizing system on the ozone resistance of natural rubber/chlorobutyl blends.

RSS1, 50; chlorobutyl (HT 10–66), 50; zinc oxide, 5; stearic acid, 1; antioxidant, 2; HAF black, 50; vulcanizing system as given. Cure, 30 mins (153°C)

Vulcanizing system (phr)	Relaxed modulus at 100% strain (MN m^{-2})	Critical strain (%) after	
		3 days at 25 pphm ozone and 30°C	36 weeks atmospheric exposure
TMTD, 2	1·79	<20	<20
SDEC, 3	1·87	<20	<20
TPG, 3; sulphur, 1	1·74	35	35
DOTG, 1,2; sulphur, 1·5	1·70	25	30

From Ref. 23.
SDEC = selenium diethyldithiocarbamate; TPG = triphenylguanidine; DOTG = di-*o*-tolyguanidine.

however, be governed by the density of unreactive particles, the presence of which will therefore diminish the probability of jumps. Thus, the basis of Andrews' theory is the assumption that crack jumping is the basic process involved in the production of macroscopic ozone cracks in elastomer blends containing both a reactive and an unreactive phase. Attention is focused on the initial encounter of a crack with unreactive material; if a jump occurs it is assumed that the lengthened crack will jump all other obstacles and develop into a macroscopic crack. This assumption is completely valid if all particles have the same breadth and is probably reasonable in practice if the small volume proportion of very small particles is neglected. The elastic moduli of the two phases are assumed to be identical.

Using scanning electron microscopy on the ozone cracked surfaces of a NR/EPDM blend, Mathew[18] has also shown crack deviation by the zones of ozone inert rubber (Fig. 7). In more recent work by Mathew *et al.*[32] the beneficial effect of EPM rubber in improving ozone resistance of NR was further confirmed. A blend ratio in the range of 80:20 to 70:30 NR:EPM was used to give adequate protection. Addition of HAF black improved ozone resistance of the blends further. It was also observed that blending of black masterbatches was beneficial only when

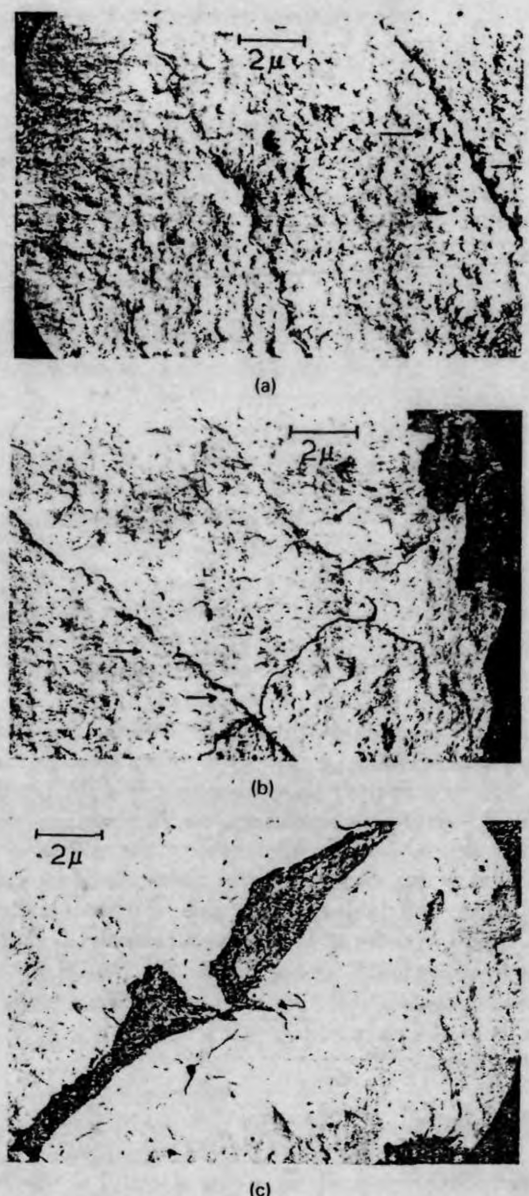


Figure 6. (a), (b) Electron micrographs showing ozone cracks in a 75/25 peroxide cured NR/EPM blend, showing unsevered EPM zones bridged by cracks; (c) ozone crack profile in a 75/25 sulphur cured NR/EPM blend showing crack jumping. Replicated at 10% strain (Ref. 19).

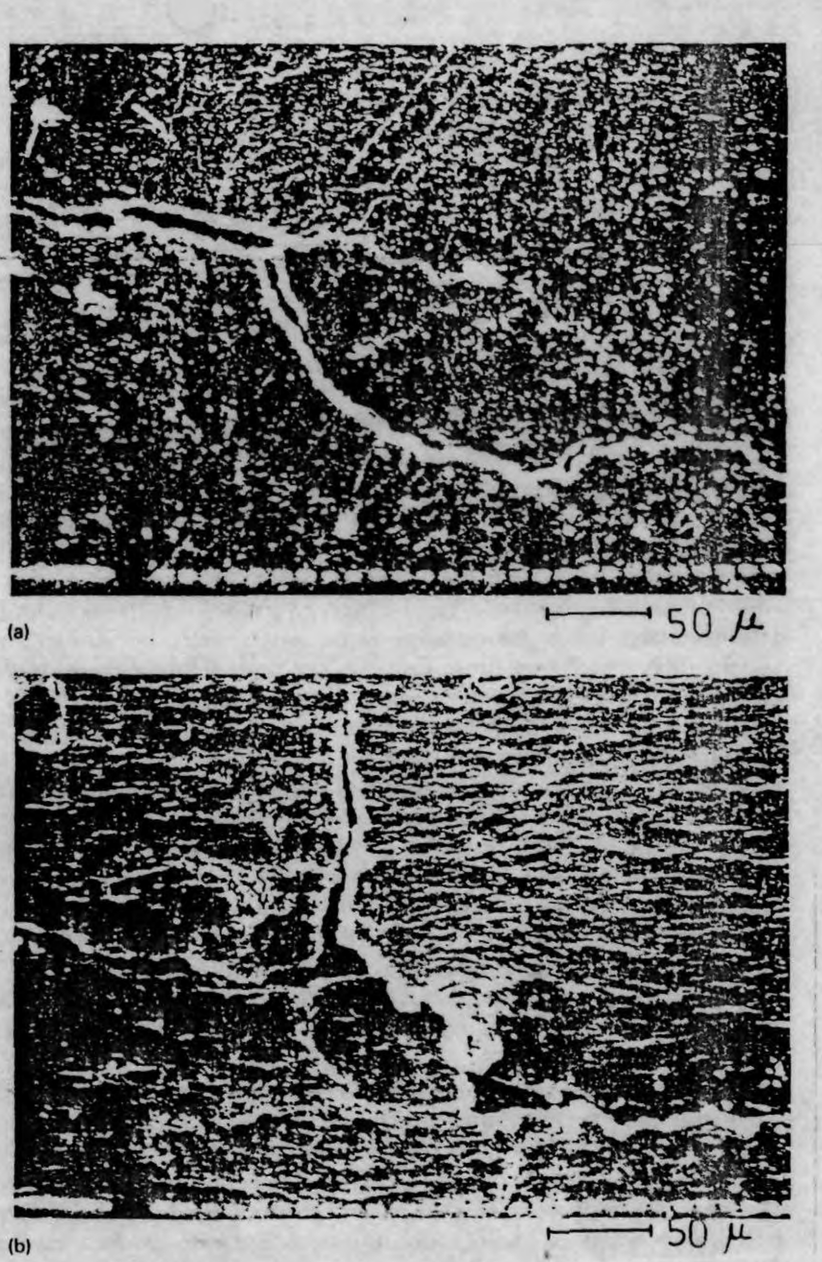


Figure 7. SEM showing crack deviation in HAF black filled NR/EPDM blend; (a) blending of polymers followed by the addition of black; (b) blending polymer-black masterbatches (Ref. 18).

the proportion of EPM was more than 30 phr. Addition of china clay was found to reduce ozone resistance of both NR and the blends.

6 External Factors Affecting Ozone Cracking

6.1 Atmospheric Ozone Concentration

The average ozone concentration at ground level is between zero and 5 pphm with peaks in spring and early summer.[33] Higher local concentrations can be produced by pollution in areas where there is strong sunlight, poor ventilation and a high concentration of automotive exhaust fumes. The highest recorded example is Los Angeles where concentrations of 25 pphm are not uncommon. High levels (up to 100 pphm) have also been observed around generating stations and arc welding equipments. Concentration of ozone increases with altitude and 10 pphm have been measured in certain mountainous regions, while up to 12 pphm have been observed inside high flying aircraft. However, the levels surrounding many applications of rubber are considerably lower than those found in the normal atmosphere. In the engine compartment of motor vehicles the average is not more than 0·5 pphm and inside the bodywork it is frequently less than 0·1 pphm. In buildings it may be only one tenth or less of that found outdoors. In view of this wide variation, some idea of the average and maximum concentrations likely to be experienced is necessary.

The critical bloom thickness required of waxes increases with ozone concentration, but even at 1000 pphm is still only in the order of 1 μm for most types. At the severities normally found in service, any changes in thickness necessary will be so small that change of wax type is not necessary unless the loading used is very low and unless protection at very high strains is required. Where high concentrations of ozone exist, fast diffusing waxes are recommended in case the bloom is disturbed during exposure.

Unlike waxes, chemical antiozonants such as *N*,*N*′-dialkyl-*p*-phenylenediamine are very sensitive to ozone concentration especially when used for static protection. The resistance imparted by a given amount of DOPPD is lost when a critical ozone concentration is exceeded. However, the improvement given by antiozonants used as rate reducers is less dependent on ozone concentration, and even when tested at 50 000 pphm, 1–2 phr reduces the growth rate of single cracks to a third of that measured in unprotected vulcanizates.

6.2 Temperature

Temperature is found to have significant influence on the ozone resistance of rubber vulcanizates. As the surface and bulk temperatures of rubber products may vary more widely than that of the surrounding air, it is essential that the chemical antiozonant or wax used should remain effective over the range of temperatures encountered during service. For rubbers exposed to direct sunlight, protection may be required from sub zero to over 50°C.

The effectiveness of wax is very sensitive to temperature, which determines the rate and extent of blooming, as discussed earlier. The activity of *p*-phenylene antiozonants is less directly affected by temperature change than that of waxes. Surface diffusion is chemically controlled, taking place as a result of the lowering of concentration at the surface by reaction with ozone, and will not depend on solubility. In addition, any film formed as part of protection is likely to be less soluble in rubber than the original antiozonant and, unlike wax blooms, reabsorption will not occur when the temperature is raised.

Loss of antiozonant by actual reaction with ozone is usually small. Physical loss by volatilization is unlikely at normal temperatures, but consumption of antiozonant during thermal ageing of the rubber particularly in sunlight is possible. It is known that *N*-alkyl-*N'*-phenyl and especially *N*,*N'*-dialkyl-*p*-phenylenediamines are susceptible to oxidation on heating giving products which are no longer antiozonants. The loss increases with the period of ageing, and the ozone protection falls to the level given by the remaining free antiozonant.

Blends of wax and antiozonant remain susceptible to temperature change just like waxes used alone, as is indicated in Table 6. If the surface temperature is high enough to cause reabsorption of the wax bloom, the static protection will fall substantially to that of the antiozonant. As low wax and antiozonant levels are normally used in these systems, it is understandable that only small increases of temperature are necessary to reduce activity.

6.3 Rainfall

Heavy rainfall is likely to wash away wax bloom. The brittle low melting waxes are particularly susceptible and hence more flexible microcrystalline grades should be used at a sufficiently high level where rainfall is a problem.

Table 6. Effect of wax type on the temperature dependence of antiozonant/wax blends

Heveacrumb SMR5, 100; zinc oxide, 5; stearic acid, 2; HAF black, 45; process oil, 5; CBS, 0·5; sulphur, 2·5; cure, 40 min (140°C)

Test conditions	Critical strain (%) given by 2 phr IPPD with 2 phr of paraffin wax, melting point (°C)		
	44–47	50–54	65–69
6 days at 25 pphm ozone and 17°C	>50	>50	>50
6 days at 25 pphm ozone and 30°C	12	>50	>50
3 days at 50 pphm ozone and 40°C	<10	<10	>50

From Ref. 23.

Some of the chemical antiozonants are leached from the rubber surface by water, particularly under slightly acidic conditions. This could lead to early cracking if fresh antiozonant cannot diffuse sufficiently quickly from the bulk of the rubber. IPPD is the most susceptible among the commercial antiozonants. The contribution which leaching may make to product failure is not easy to isolate. It is likely to be most important in thin-walled products used in regions of high localized ozone concentration and where periods of heavy rainfall are followed by dry weather. Thick products may be only slightly affected since a large reservoir of antiozonant will remain to restore surface levels.

If water leaching is thought to occur to an unacceptable level, less water soluble high molecular weight antiozonants should be used. The additional presence of wax, whilst not preventing extraction of antiozonant, may also be desirable where resistance to static ozone cracking is critical, but it will be detrimental to dynamic resistance which depends only on the antiozonant level.

6.4 Storage

The activity of waxes is influenced by the conditions of storage between fabrication and use. Blooming will take place immediately after vulcanization provided supersaturation exists at the temperature of storage. But if the product is unstrained during this period the wax film will break upon subsequent stretching and can not confer protection. As the rate of surface diffusion falls rapidly with the period of blooming, the time required to reform the critical bloom thickness will increase markedly with storage before stretching, and will be even longer when the level of wax in the rubber approaches the solubility point. As the rubber becomes exhausted of wax, protection against ozone cracking will fall, as reflected by a decrease in critical strain. This will be particularly noticeable in thin-walled articles and when low levels of fast diffusing waxes are present. If very long storage periods before service are unavoidable, waxes which have a low diffusion coefficient at the temperature of storage, and which protect with a small critical thickness, should be used.

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