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Ozone Cracking and Protection of Elastomers at High and Low Temperatures

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Ozone attack on elastomers varying in their glass transition temperatures (θ_G) by some 50°C was studied over a range of temperatures from about −20°C to +70°C. If the ambient temperature is low, the rate of crack growth due to ozone may be reduced by the high internal viscosity of the material. However, diffusion of chemical antiozonants or waxes which confer protection by forming a layer on the elastomer surface, is also slowed down. It appears more difficult to obtain good protection at low temperatures. High ambient temperatures do not greatly increase the rate of ozone crack growth and might be expected to improve antiozonant and wax protection for elastomers of high θ_G as a result of increased rates of diffusion. This was observed to some extent.

Ozone can cause cracking in vulcanised elastomers subject to constant or repeated loading. The ozone concentration in the outdoor atmosphere at ground level is typically about 1 p.p.h.m. (part per hundred million of air by volume) although levels an order of magnitude or so higher have been observed for limited periods in polluted areas. Indoors, or in enclosed spaces, ozone levels may be an order of magnitude lower unless there are electrical or other discharges, when much higher levels may result. The recommended ambient temperature for standard ozone tests is now 40°C. This is far above operating temperatures for many uses of elastomers, although it may be too low, intermittently, for articles subject to direct sunlight, particularly in tropical regions.

The effects of ozone concentration and ambient temperature on the basic ozone cracking process are well understood, as is the effect of the glass transition temperature of the elastomer[1,2,3]. However, when protective agents – chemical antiozonants or waxes – are present, these effects are much less well understood. High or low temperatures, in particular, have been relatively little studied and this paper describes work that is in progress to try to remedy this. The protective systems examined include chemical antiozonants or waxes alone and wax/antiozonant combinations, used in elastomers of various glass transition temperatures in tests over a wide range of ozone concentrations.

THEORIES FOR LAYER FORMATION

Chemical Antiozonants

When a chemical antiozonant is present in an elastomer, layer formation occurs only on exposure to ozone and is believed to be primarily the result of direct reaction between the antiozonant and ozone. In earlier work it was shown for natural rubber that under some circumstances, the rate of layer formation was consistent with control by diffusion of antiozonant across the already-formed layer to react with ozone at its outer surface[4] *(Figure 1a)*. Under these circumstances, assuming the layer to be formed entirely of reacted antiozonant and the concentration of unreacted material within it to be small, the mass per unit area

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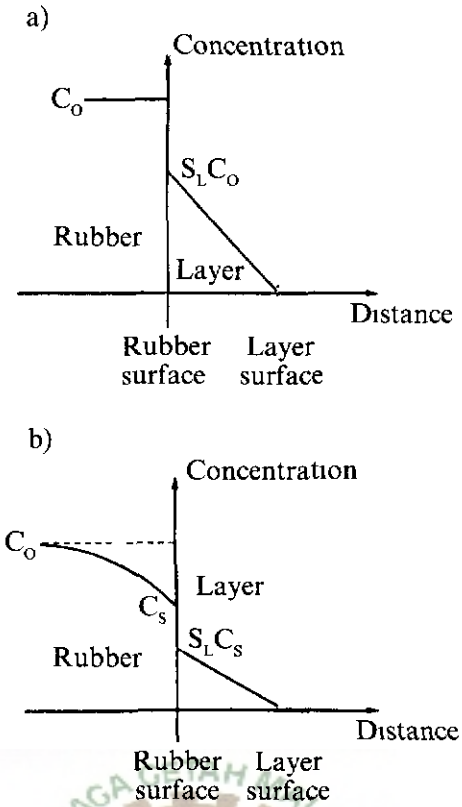

Figure 1 Diffusion models for antiozonant layer formation a) rate governed by diffusion of antiozonant within the layer only, b) rate governed by both diffusion in the layer and in the rubber

M_L, of layer formed after time t is given by

$$M_L = \sqrt{2\rho_L D_L S_L C_o t} \qquad 1$$

where C_o is the concentration of antiozonant in the bulk of the rubber

P_L the density of the layer material

D_L the diffusion coefficient

S_L the solubility, relative to that in the rubber, of the antiozonant in the layer

If the product of the latter two quantities is put as

$$P_L = S_L D_L \qquad 2$$

P_L is in essence the relative permeability of the layer material to the antiozonant

Consistent with *Equation 1*, the rate of layer formation on natural rubber was observed to be independent of ozone concentration over a range from about 25 p.p.h.m. to 750 p.p.h.m. although it increased at higher concentrations

In deriving *Equation 1*, it is assumed that the concentration of (unreacted) antiozonant in the layer is small. Under these circumstances the concentration gradient in the layer will be essentially linear (cf *Figure 1a*). If, in addition to diffusion across the layer, diffusion within the rubber is also important, a similar equation to *Equation 1* applies with C_o replaced C_s, the concentration at the rubber surface, which is lower than C_o *(Figure 1b)*. C_s is a function of C_o and the relative permeabilities of the rubber

and the layer to the antiozonant, and with the assumptions made is given by

$$\frac{C_s}{C_o} = 1 + \varepsilon - \sqrt{(1+\varepsilon)^2 - 1} \qquad \ldots 3$$

where

$$\varepsilon = \frac{\pi}{4}\frac{\rho_L D_L S_L}{D C_o} \qquad \ldots 4$$

and D is the diffusion coefficient of the antiozonant in the rubber.

Waxes

The mechanism of layer formation by waxes is quite different from that by chemical antiozonants. Waxes are relatively inert and blooming occurs when the amount of wax incorporated in the rubber exceeds the solubility. This is possible because the melting points of the waxes used are generally within the range from about 45°C to 70°C. Thus at processing temperatures, which are normally well above the upper limit, the waxes are liquid, with relatively high solubility, whereas at operating temperatures they are crystalline solids with much lower solubility. Blooming is not simply due to super-saturation, however, but is believed to involve stress-induced diffusion due to the elastic forces acting on crystals formed inside the rubber[5]. Quantitative solution for the rate of layer formation involves, although it is not sensitive to, the distribution of crystals in the rubber. The dependence of the mass of wax layer per unit area of surface (M_w) on time (t) can be approximated by

$$M = \sqrt{\frac{F\,(C_W - S_W)\,D_W S_W G t}{\theta}} \qquad \ldots 5$$

where D_w is the diffusion coefficient

S_w the solubility of the wax in the rubber

C_w the concentration of wax incorporated,

G the shear modulus of the rubber

θ the absolute temperature

F is a function involving the wax distribution and other parameters.

Thus the rate of protective layer formation with a wax is not influenced by the ozone concentration but it is generally sensitive to temperature. This is not so much because θ appears in *Equation 5* (this small effect would in fact be balanced by the dependence of G on θ according to the statistical theory of rubber elasticity) but because of the variation of D_w and S_w with temperature. In practice, most waxes used are blends of components having different molecular weights and melting points, often over quite a wide range. (Apart from providing more consistent blooming behaviour over a range of temperatures, the bloom obtained by this means provides better protection, as pure waxes tend to give large crystals that form a very uneven bloom[6].)

EXPERIMENTAL PROCEDURE

Ozone tests were carried out using a commercially-available test cabinet[7] for concentrations within the range 50 – 200 p.p.h.m. while an apparatus similar to that described by Farlie[1] was used for concentrations of about 10^4 to 10^5 p.p.h.m. In this apparatus, ozone was generated from cylinder oxygen using an ultra-violet discharge. Intermediate concentrations from about 10^2 to 10^3 p.p.h.m. were obtained by diluting the ozonised oxygen from the 'high' concentration apparatus with a suitable flow of air. Tests in the commercial cabinet were carried out at various temperatures with a range from about 8°C to 70°C. Tests in the laboratory apparatus were carried out at about 23°C or −17°C.

Ozone cracking tests on surfaces were carried out using strip or dumbbell test-pieces held at an essentially constant strain which was normally within the range 10% to 100%. The test-pieces were examined inter-

mittently during the course of exposure to ozone to determine whether or not cracking had occurred. In some cases, an estimate of the rate of crack growth was made by measuring the crack length (in a direction perpendicular to a major surface) at the end of a test.

Measurements of the rate of growth of a single crack by ozone were made using a test-piece in the form of a strip containing an initiating edge cut, as described by Braden and Gent[1]. Protection, by a coating of inert grease or other means, was used to prevent formation of subsidiary cracks.

The elastomers used were natural rubber (NR, glass transition temperature, θ_G *ca* $-67°C$), epoxidised natural rubber with about 50% epoxidation (ENR 50, θ_G *ca* $-21°C$) and two acrylonitrile-butadiene copolymers (34% acrylonitrile, NBR 34, θ_G *ca* $-27°C$, or 38% acrylonitrile, NBR 38, θ_G *ca* $-23°C$). Accelerated sulphur-vulcanisates of each elastomer were prepared in the form of 2 mm thick sheets from which test-pieces were die-stamped. The sheets were stored at *ca* 0°C to minimise ageing and blooming effects. When a chemical antiozonant alone was incorporated, nearly all the experiments described were carried out with di(methylethylpentyl) paraphenylenediamine (DOPPD – 'UOP88', Universal Oil Products, Illinois) which was used at levels from 2 p.h.r. to 20 p.h.r. (parts per hundred of rubber by weight). Various wax/antiozonant combinations were also employed, generally with 6 p.h.r. wax and 3 p.h.r. antiozonant.

Diffusion coefficients of the antiozonant were estimated from transfer measurements in which a test-piece containing DOPPD was pressed into contact with a test-piece of a similar vulcanisate containing, initially, no DOPPD *(Figure 2)*. The amount of antiozonant that had diffused after various times was estimated from the weight changes of the test-pieces, enabling the diffusion coefficient to be calculated according to standard diffusion theory[8].

The weight of reacted antiozonant layer formed after exposure to ozone was determined from the weight change after removal of the layer from the surface of the rubber. The layer could be removed by scraping with a blade, swabbing with tissue containing a suitable solvent or repeated application of adhesive tape. The latter method was mostly used for the chemical antiozonant layer, whereas scraping was found to be best for

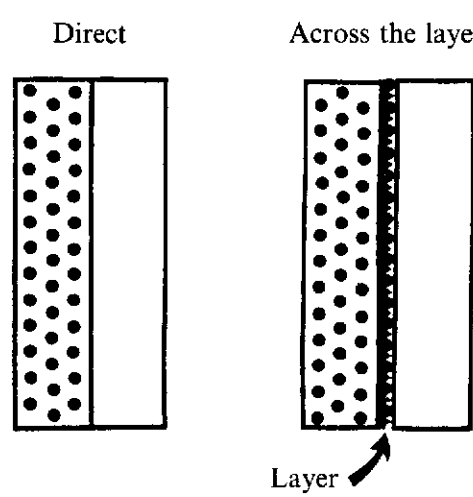

Figure 2. Arrangements for transfer measurements: direct; across the layer.

wax layers. In experiments with waxes, the elastomer sheets were vulcanised between aluminium foil or polyester sheets to minimise blooming during storage. Test-pieces for bloom formation measurements were kept at a constant temperature of either 20°C or 40°C for a fixed period. The weight of the bloom was then determined from the weight change after its removal.

Preliminary experiments to estimate the permeability of the antiozonant layer material to the (unreacted) antiozonant have been carried out by forming a layer on the surface of a test-piece by exposure to ozone and then carrying out a transfer measurement through the layer to a control test-piece pressed into contact *(Figure 2)*. In this case, the permeability was estimated by assuming the layer to act as a membrane[8]. Only a single time could be used in each experiment as the layer was disrupted when the test-pieces were separated.

RESULTS

Earlier work has indicated that two basic parameters govern the growth of a single, isolated crack by ozone: i) a threshold energy below which the crack will not grow; and, ii) the rate at which the crack grows when the threshold is equalled or exceeded[1]. For cracking in surfaces, a threshold strain corresponds to the attainment of the threshold energy at the largest flaws that are present in the surface. In the present work, the single crack growth rate and the threshold strain are being used to assess the ozone resistance of the various elastomers and protective systems studied.

Single Crack Growth Studies

Earlier work has shown that the rate of ozone crack growth is essentially proportional to the ozone concentration, provided that the test temperature is not too close to the glass transition temperature of the elastomer[1,2,3,9]. *Figure 3* shows single crack results for different elastomers without added protective agent and including various amounts of DOPPD at room temperature for high ozone concentrations of about 10^4 p.p.h.m. or 10^5 p.p.h.m. The rates of growth in the unprotected NR, ENR 50 and NBR 34 vulcanisates are very similar and are reduced to a similar extent by the incorporation of DOPPD. Consistent with earlier observations[1,9], NBR 38 shows somewhat lower rates of growth for the unprotected vulcanisate but rather smaller reductions when DOPPD is added. Bearing in mind the variability, the results for both protected and unprotected vulcanisates are broadly consistent with a rate that is essentially proportional to the ozone concentration. Observations at much lower ozone concentrations and different temperatures, made during the course of threshold strain experiments, also appear consistent with this.

Threshold Effects

Certain protective agents have the ability effectively to increase the threshold energy or threshold strain. By contrast with the reduction in rate of growth, these increases tend to be strongly influenced by ozone concentration. *Figure 4* shows results for NBR 34 vulcanisates containing 0, 5 or 10 p.h.r. DOPPD, at ozone concentrations ranging from 100 p.p.h.m. to 1500 p.p.h.m. The exposure strain is plotted against the time at which cracks were first observed (τ_1), on logarithmic scales. In order to allow results for different ozone concentrations readily to be compared, τ_1 is multiplied by the ozone concentration (this will superimpose results where the rate of crack growth is proportional to the ozone concentration and τ_1 is determined mainly by the rate). As can be seen this superimposition works quite well for the results for the nitrile vulcanisates in *Figure 4* bearing in mind particularly that considerable scatter in the results at shorter times arises because the test-pieces were inspected only intermittently). The displacement of the curves for different DOPPD levels is broadly consistent with the differences in rate of growth observed in *Figure 3*. These results show

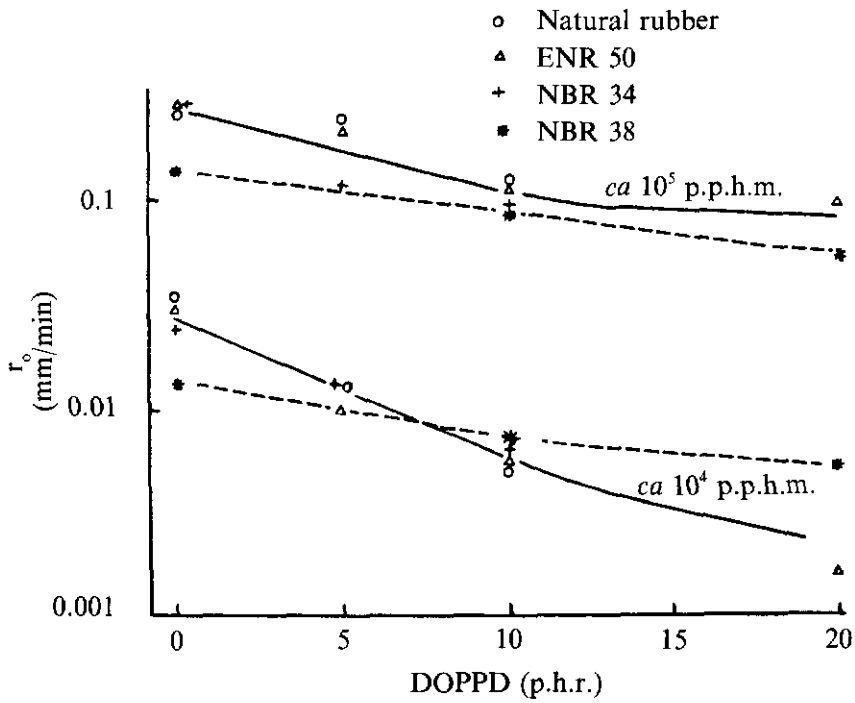

Figure 3. Rate of single crack growth (logarithmic scale) versus antiozonant level at the ozone concentrations indicated on the graph for vulcanisates of natural rubber, ENR 50, NBR 34 and NBR 38. Each point represents an average of about three results.

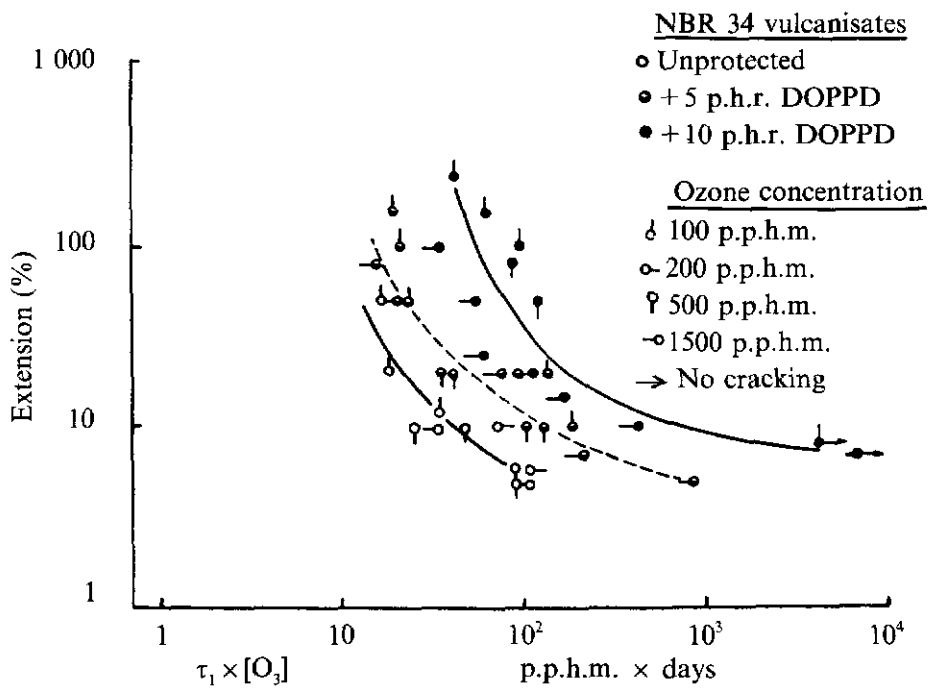

Figure 4. Time to first cracking (τ_1) for NBR 34 vulcanisates. Each point carries a flag to denote the ozone concentration used.

little or no increase in the threshold strain – even with 10 p.h.r. DOPPD the indicated threshold strain is no more than 10% which is only slightly above the level expected for the unprotected vulcanisate.

By contrast, the results for natural rubber in *Figure 5* show evidence of appreciable increase in threshold strain even with only 2.5 p.h.r. DOPPD. The effect is dependent on ozone concentration and is not significant at 1500 p.p.h.m. However, at 100 p.p.h.m. the results show no cracking at a strain of 20% after 1000 p.p.h.m. days – once a time of this order has been survived, the likelihood that cracking will occur subsequently is greatly reduced. Thus a threshold strain in excess of 20% is indicated. An interesting feature of these results is that whereas cracking occurred at 100% strain, no cracks were observed after a much longer time at 150%, indicating a second threshold strain (above which no cracking occurs) in this vicinity. This second threshold is believed to be associated with crystallisation[10]. With 5 p.h.r. DOPPD, no cracking occurred in natural rubber at all strains tested even at an ozone concentration of 1500 p.p.h.m.

With ENR 50, similar behaviour was observed to that with NBR 34. With DOPPD at the 5 p.h.r. level, no significant change in threshold strain was detected, as was the case with 10 p.h.r. at an ozone concentration of 1500 p.p.h.m., although a slight increase was indicated at 100 p.p.h.m. *(Figure 6)*. Even with 20 p.h.r. DOPPD, only a slight increase in threshold was obtained at 1500 p.p.h.m. although cracking was prevented at all strains at 100 p.p.h.m.

Antiozonant Diffusion

The above results show that while DOPPD can confer a similar reduction in rate of growth in nitrile or epoxidised natural rubber to that in natural rubber, its ability to increase the threshold condition is much less. Since the latter ability is known to be associated with the formation of a protective

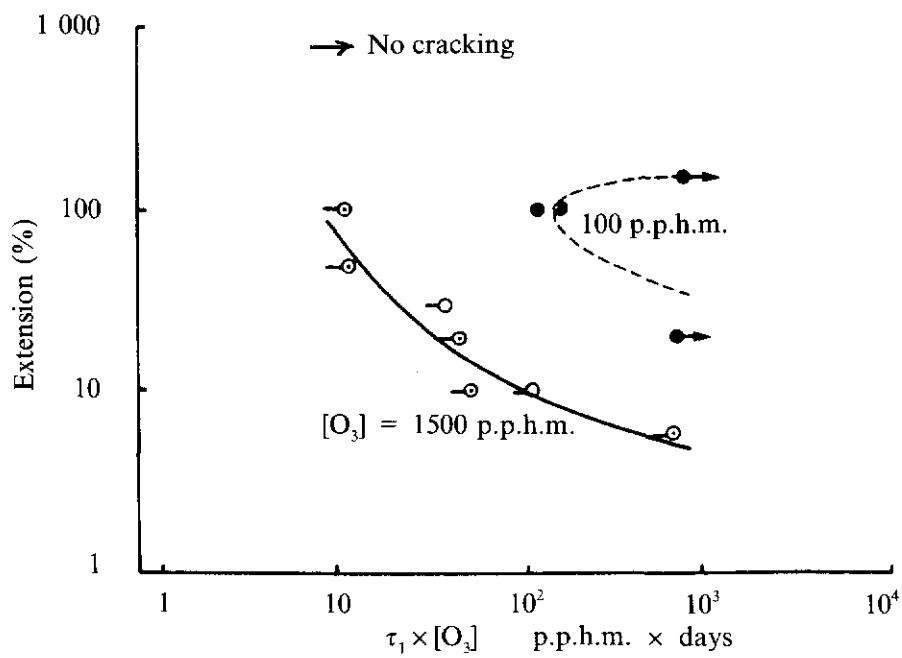

Figure 5. Time to first cracking (τ_1) for an NR vulcanisate containing 2.5 p.h.r. DOPPD at the ozone concentrations indicated on the graph.

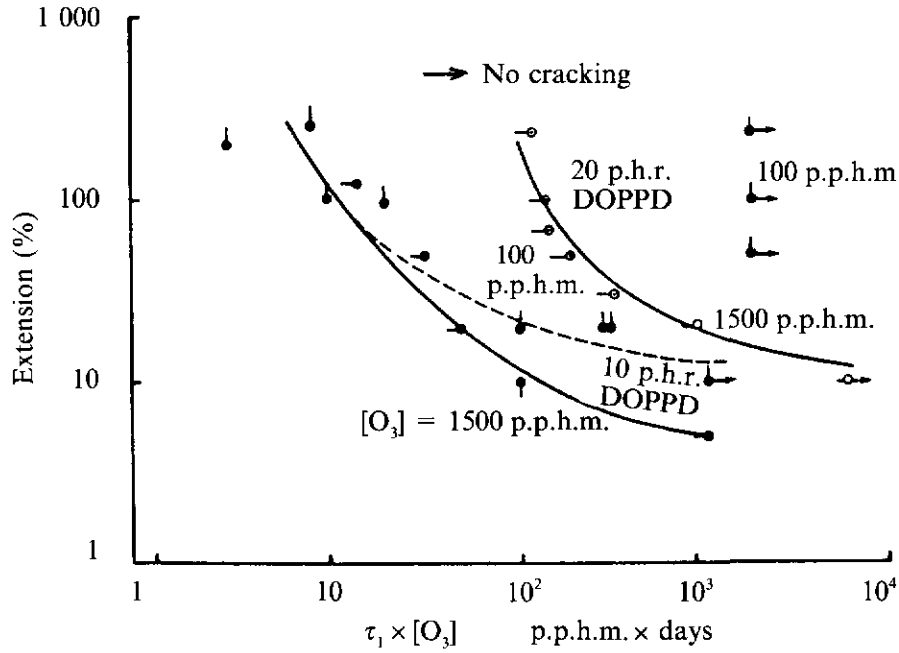

Figure 6. Time to first cracking for ENR 50 vulcanisates containing the levels of antiozonant and at the ozone concentrations indicated on the graph.

layer on the surface of the elastomer by the antiozonant following reaction with ozone[4], which must involve diffusion, it is tempting to conclude that the poorer protection of NBR and ENR is associated with slower diffusion of the antiozonant in these elastomers, which would be expected because of their higher internal viscosities. Studies of the diffusion of DOPPD in the different elastomers were made by transfer measurements, as described earlier. Results are shown in *Table 1*. At 23°C (the temperature of the earlier ozone cracking experiments), the diffusion coefficient of DOPPD in NBR 34 or ENR 50 is only about 1% of that in NR. At elevated temperatures, the diffusion coefficient of DOPPD increases for all the elastomers, although the increase is greater for the high glass transition temperature materials *(Table 1)*. Of interest is 40°C since it is the recommended temperature for standard ozone tests (although of limited relevance for practical purposes), while at 70°C the diffusion coefficient in ENR 50 or NBR 34 is similar to that in NR at 23°C.

TABLE 1. EFFECT OF TEMPERATURE ON DIFFUSION COEFFICIENTS (10 p.h.r. DOPPD)

Temperature (°C)	Diffusion coefficient (cm^2/s) in a vulcanisate of		
	NR (θ_G *ca* −69°C)	ENR 50 (θ_G *ca* −24°C)	NBR 34 (θ_G *ca* −28°C)
−17	6.0×10^{-11}	*ca* 10^{-14}?	–
23	4.6×10^{-9}	5.1×10^{-11}	4.9×10^{-11}
40	2.4×10^{-8}	6.2×10^{-10}	7.2×10^{-10}
70	1.1×10^{-7}	8.8×10^{-9}	9.7×10^{-9}

Ozone Cracking Experiments at Elevated Temperatures

Results of ozone cracking tests at 40°C are shown in *Table 2*. With 5 p.h.r. or 10 p.h.r. DOPPD, the threshold strain for vulcanisates of ENR 50 or NBR 34 is higher at 40°C than at 20°C but is still well below that for NR with 5 p.h.r. DOPPD at 20°C. However, the diffusion coefficients, although increased by more than an order of magnitude at 40°C, are appreciably lower than that for NR at 20°C *(Table 1)*. Initial cracking test results at 70°C, (where the diffusion coefficients are slightly higher than for NR at 20°C) indicate the protection of ENR 50 or NBR 34 still to be inferior to that of NR at 20°C, although various difficulties have been encountered with these tests and further experiments are in progress.

Rather similar behaviour was observed with wax or wax/antiozonant protective systems for which some results are also shown in *Table 2*. For NR, all of the protective systems gave threshold strains in excess of 100% except for the paraffin wax alone at 40°C. For ENR 50 or NBR 34, by contrast, only the antiozonant/lower melting point wax combinations gave significant protection at 20°C, whereas most of the systems gave considerably better protection at 40°C.

With waxes, temperature affects the blooming rate through both the diffusion coefficient and the solubility in the rubber, which increases rapidly as the melting point of the wax is approached. These parameters also enter directly into the blooming equation (cf *Equation 5*) whereas in the case of DOPPD, the diffusion coefficient of the antiozonant in the rubber only enters somewhat indirectly into the equation for layer formation *(Equation 1) via Equations 3* and *4*. Thus a rather stronger effect of temperature on protective action might be expected for protective systems involving waxes compared with those involving a chemical antiozonant alone. The results in *Table 2* appear consistent with this.

Cracking Experiments at Low Temperatures

Experiments at 8°C and 50 p.p.h.m. ozone showed little or no protective action of a wax/antiozonant system in NBR 34 or

TABLE 2. COMPARISON OF THRESHOLD STRAINS AT 20°C AND 40°C

Protective system	Threshold strain (%) for an ozone concentration of 50 p.p.h.m. at the test temperature indicated for vulcanisates of					
	NR		ENR 50		NBR 34	
	20°C	40°C	20°C	40°C	20°C	40°C
5 p.h.r. DOPPD	> 100	> 100	< 10	*ca* 15	< 10	*ca* 15
10 p.h.r. DOPPD	–	–	*ca* 15	*ca* 50	*ca* 50	> 100
3 p.h.r. 6PPD + 6 p.h.r. Wax A	> 100	> 100	*ca* 10	*ca* 30	*ca* 10	*ca* 50
3 p.h.r. IPPD + 6 p.h.r. Wax B	> 100	> 100	*ca* 10	> 100	*ca* 30	*ca* 100
3 p.h.r. IPPD + 6 p.h.r. Wax C	–	–	*ca* 50	> 100	–	–
6 p.h.r. Wax C	> 100	*ca* 10	< 10	*ca* 10	*ca* 10	*ca* 10

6PPD is a di(methyl butyl) phenyl substituted ppd (Santoflex 13)
IPPD is an isopropyl phenyl substituted ppd (Nonox ZA)
Wax A was Antilux 600 (quoted melting point range 62°C to 65°C)
Wax B was Antilux 500 (quoted MP range 56°C to 60°C)
Wax C was a paraffin wax (MP range 48°C to 50°C)
+ Failure sometimes occurred by mechanical crack growth in NBR 34 at 40°C

TABLE 3. THRESHOLD STRAINS AT 8°C

Protective system	Threshold strain (%) for an ozone concentration of 50 p.p.h.m. at 8°C for vulcanisates of		
	NR	ENR 50	NBR 34
10 p.h.r. DOPPD	> 100%	*ca* 50%	*ca* 50%
3 p.h.r. IPPD + 6 Wax B	> 100%	–	–
3 p.h.r. IPPD + 6 Wax C	> 100%	*ca* 10%	*ca* 10%

Waxes B and C are as in *Table 2*.

ENR 50 even with the lowest melting point wax *(Table 3)*. With 10 p.h.r. DOPPD, however, protection of either elastomer was similar to that obtained at 20°C. Thus the 8°C results are consistent with the expected temperature effects for the two systems, as discussed above. Reasonable protection of NR was obtained with either system. The rate of crack growth in the high glass transition temperature elastomers was noticeably slower at 8°C, as expected on visco-elastic grounds[2,3].

Experiments at −17°C were carried out at a high ozone concentration of about 10^5 p.p.h.m. In order to prevent cracking in natural rubber at this concentration at room temperature, about 15 p.h.r. of DOPPD is required[11]; similar protection was obtained at 10^5 p.p.h.m. at −17°C with 20 p.h.r. DOPPD.

Protective Layer Formation

Measurements of the rates of layer formation for the different elastomers correlate with threshold strain observations for either DOPPD or wax/chemical anti-ozonant protective systems. *Figure 7* shows results for vulcanisates containing 10 p.h.r. DOPPD after exposure to 200 p.p.h.m. of ozone at 40°C. The rate of layer formation for NR is some four times that for the other materials, paralleling the much better protection obtained in NR, while NBR 34 has a slightly higher rate than ENR 50, again in accord with the relatively small differences in the threshold strain for these materials *(Table 2)*. Similar layer formation behaviour with a wax/antiozonant system is illustrated in *Table 4*. In this case, test-pieces

TABLE 4. EFFECT OF TEMPERATURE ON LAYER FORMATION WITH A WAX/ ANTIOZONANT[a] PROTECTIVE SYSTEM

Elastomer	Mass/unit area of layer (mg/cm^2) after 7 months ($\sqrt{t} = 70h^{1/2}$) at	
	20°C	40°C
NR	0.88	1.16
ENR 50	0.02	0.39
NBR 34	0.05	0.84

[a]3 p.h.r 6PPD and 6 p.h.r. Antilux 600

were stored in the absence of ozone at either 20°C or 40°C. As can be seen, the rates of layer formation are again higher for NR than for the other elastomers, with the differences being much greater at 20°C than at 40°C (as expected from the diffusion mechanism discussed earlier). NBR 34 again shows somewhat faster layer formation than ENR 50. These features parallel the differences in threshold strain illustrated in *Table 2*.

Figure 8 compares layer formation results at −17°C with those at room temperature for an NR vulcanisate containing 10 p.h.r. DOPPD. As can be seen the rates of layer formation at the two temperatures are virtually identical. The diffusion coefficient of DOPPD in NR at −17°C is very similar to that in ENR 50 or NBR 34 at 23°C

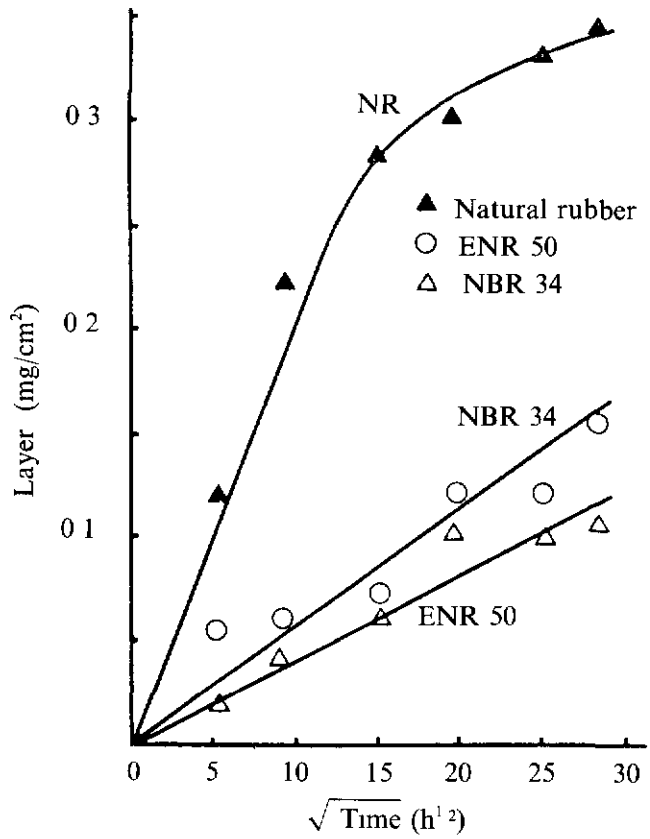

Figure 7 Dependence of the mass of antiozonant layer formed on the square root of the time of exposure to an ozone concentration of 200 p p h m at 40 C for vulcanisates of natural rubber, ENR 50 and NBR 34

(cf *Table 1*) Thus it appears that factors other than slow diffusion of the antiozonant in the elastomer must be involved in the much lower rates of layer formation with the chemical antiozonant alone in ENR 50 and NBR 34 at 23°C

One factor that may be relevant is the partitioning of the antiozonant between the elastomer and the layer material – S_L in *Equation 1* Swelling and other measurements indicate the solubility of the (unreacted) antiozonant in the elastomers to vary according to NR < NBR 34 < ENR 50 Thus partitioning of the unreacted antiozonant into the layer may tend to decrease in the same order, leading to a corresponding decrease in the rate of layer formation (cf *Equation 1*) A check on this can be made by transfer measurements across the layer *(Figure 2)* to obtain the permeability of the layer material to the unreacted antiozonant (P_L in *Equation 2*) Earlier measurements[4] indicated a value for P_L of about 7×10^{-13} cm²/s for the layer on natural rubber If it is assumed that the layer material is the same irrespective of the elastomer (as is possible if it is comprised primarily of reacted antiozonant) then differences in P_L for different elastomers would correspond to differences in S_L (cf *Equation 2*) These experiments are difficult to carry out, partly because the

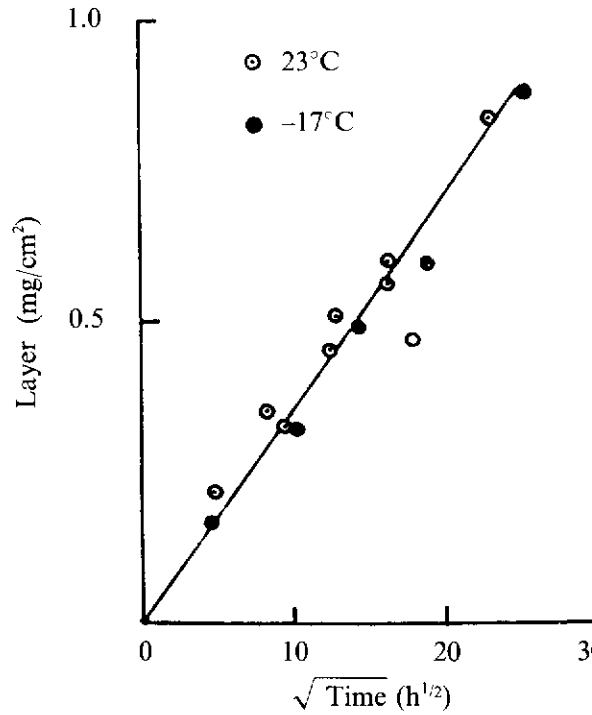

Figure 8. Mass of antiozonant layer formed versus square root of the time of exposure to 10^3 p.p.h.m. ozone for an NR vulcanisate containing 10 p.h.r. DOPPD at 23°C and 17°C.

amount of material transferred is very small. The results are therefore subject to considerable scatter but initial results with ENR 50 do not indicate any major difference in P_L compared with NR.

A further factor that may affect layer formation with DOPPD is the fact that ENR 50 and NBR 34 are more polar materials than NR. The reacted antiozonant layer is also polar in nature, dissolving very readily in polar solvents such as acetone. There may thus be a greater tendency for the layer material to diffuse back into ENR 50 or NBR 34 instead of remaining on the surface to give protection. Evidence indicating this to happen has been obtained with a light-coloured vulcanisate of ENR 50 containing DOPPD. After exposure to ozone the surface of the elastomer remained darker in colour even after removal of the layer material and repeated swabbing with acetone. A cross-section cut perpendicular to the surface showed the dark colour to extend a small distance (*ca* 0.1 mm) below the surface. Furthermore, the extent of the penetration was observed to increase with the passage of time, approximately as the square root of the time that had elapsed from the start of the ozone exposure. These kinetics indicated a diffusion coefficient of about one sixth that of unreacted DOPPD in ENR 50 (cf *Table 1*). Thus it appears that a somewhat higher molecular weight reaction product of DOPPD tends to diffuse back from the layer into ENR 50. Similar behaviour has not been observed with NR but cannot be entirely ruled out as NR vulcanisates are generally darker in colour than those of ENR 50, making any colour change more difficult to detect.

CONCLUSIONS

The work described shows that the test temperature can have marked effects on the ozone resistance of vulcanisates containing chemical antiozonant or wax/antiozonant protective systems The effects are mainly associated with differences in threshold strain rather than rate of crack growth and vary according to the glass transition temperature of the elastomer and the protective system adopted Elastomers with high glass transition temperature, such as epoxidised natural rubber or nitrile rubber are more readily protected at temperatures above room temperature, when the protective agents are more mobile Protection of such materials at lower temperatures is correspondingly more difficult but a dialkyl ppd appears better than wax antiozonant systems, for reasons that can be understood from differences in the diffusion mechanisms Reasonable protection of natural rubber was obtained at 8°C with a wax/antiozonant system and down to −17°C with a dialkyl paraphenylenediamine

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REFERENCES

1 BRADEN, M AND GENT, A N (1960) The Attack of Ozone on Stretched Rubber Vulcanizates I The Rate of Cut Growth *J appl Polym Sci* **3**, 90 and 100

2 GENT, A N AND McGRATH, J E (1965) Effect of Temperature on Ozone Cracking of Rubbers *J Polym Sci A* **3**, 1473

3 GENT, A N AND HIRAKAWA, H J (1967) Effect of Temperature on Ozone Cracking of Butyl Rubbers *J Polym Sci A-2* **5**, 157

4 LAKE, G J (1970) Ozone Cracking and Protection of Rubbers *Rubb Chem Technol* **43**, 1230

5 NAH, S H AND THOMAS, A G (1980) Migration and Blooming of Waxes to the Surface of Rubber Vulcanizates *J Polym Sci Polym Phys Ed* **18**, 511

6 OWEN, P J Private Communication

7 HAMPDEN TEST EQUIPMENT LTD Model No 603

8 CRANK, J (1975) *The Mathematics of Diffusion* Oxford Clarendon

9 BRADEN, M AND GENT, A N (1962) The Attack of Ozone on Stretched Rubber Vulcanizates Part 3 Action of Antiozonants *J appl Polym Sci*, **6**, 449

10 LAKE, G J The Determination of Threshold Strain of Rubber in Ozone Resistance Tests *Polymer Testing* in the press

11 LAKE G J (1973) Relation entre essais de laboratoire et duree de vie du caoutchouc en service *Rev Gen Caoutch* **50**, 287