

Effect of Ozone on Rubbers: Countermeasures and Unsolved Problems*

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ABSTRACT

Atmospheric ozone degrades polydiene rubbers by reacting with main chain unsaturation to cause chain scission and a diminished surface strength. When the rubber is exposed above a critical tensile strain, the degradation manifests itself as surface cracking which not only detracts from appearance but can also shorten the service life of a thin-walled product by initiating premature tensile or fatigue failure, by increasing stress relaxation and creep or by providing a pathway for fluid loss or ingress. Such attack may be reduced, or altogether prevented, by adding chemical antiozonants that diffuse to the surface to form a protective layer capable of reducing the rate of crack growth or, more usefully, of increasing the threshold strain above that in the exposed product.

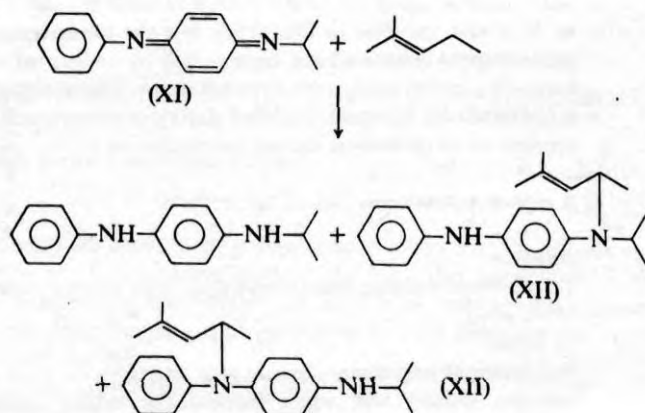
The chemistry, physics and technology of ozone cracking and protection are reviewed with particular reference to natural rubber and to substituted p-phenylenediamine chemical antiozonants. Attention is also drawn to outstanding problems facing the rubber technologist and requiring further research by the chemist. Needs include a non-staining antiozonant capable of protection under dynamic, as well as static, exposure and protective systems exhibiting improved resistance to wasteful loss caused by oxidation, volatilization and surface leaching by water and other fluids.

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afterwards processed into shape by such equipment as an injection-moulding machine, extruder or calender. The required scorch safety is usually dictated by the detailed vulcanizing system in the case of sulphur crosslinking, and delayed-action sulphenamide accelerators are nowadays in widespread use. Dialkyl (and di-cycloalkyl)-*p*-phenylenediamines can reduce this scorch safety and introduce the risk of premature set-up, especially as comparatively high levels (i.e. 3–5 phr) are needed if other protective agents are excluded.

An effective solution to this problem is to add a prevulcanization inhibitor (PVI), several types of which are now commercially available. Such an inhibitor, however, does not restore the loss in crosslink density that also occurs in the presence of both dialkyl and alkyl-phenyl-*p*-phenylenediamines. An entirely novel approach, again developed by MRPRA,¹⁵ stems from the observation that when the quinone diimine reaction product (XI) of a *N,N'*-disubstituted *p*-phenylenediamine is heated in natural rubber most of it is reduced back to the parent *p*-phenylenediamine. Model olefin studies using the *N*-isopropyl-*N'*-phenyl derivative suggest the following reaction pathway.



Such a reaction is conveniently carried out at, or near, vulcanization temperature in the presence of other compounding ingredients. If a thiazole or sulphenamide-accelerated vulcanizing system is used, the quinone diimines do not reduce scorch safety and, in the case of the *N*-alkyl-*N'*-phenyl derivatives, there is a useful PVI effect. An additional

feature is that quinone diimines do not reduce crosslink density; vulcanizate modulus is retained and even slightly increased.

Antiozonant activity is in accord with the level of *p*-phenylenediamine generated *in situ* (typically 60–70% of the quinone diimine concentration). On the evidence of model studies the remaining quinone diimine becomes attached to the rubber chain as mono-*N*-alkenylated *p*-phenylenediamines (XII) and, indeed, some rubber antioxidant activity persists after solvent extraction of the vulcanizate.

Longer life antiozonants?

Objective

To produce a protective system able to confer long time resistance (over several years) and thus requiring an antiozonant resistant to depletion by physical loss or chemical consumption.

Solutions

The exposed rubber surface in need of protection against ozone cracking is also the site at which *p*-phenylenediamine antiozonants are most susceptible to loss by such agencies as heat (volatilization), water and solvents (leaching) and oxygen (direct oxidation and consumption as antioxidant).

The rubber industry has pursued the problem on four fronts.

The first, already referred to, involves the partial replacement by the less active diaryl-*p*-phenylenediamines and/or the use of higher molecular mass antiozonants, the most notable example of which in recent years has been the steadily growing replacement of IPPD by the less volatile, less water-extractable and more rubber-soluble, *N*-(hexyl)-*N'*-phenyl-*p*-phenylenediamine. Both the latter antiozonants are only sparingly soluble in water, but water is usually available in plentiful supply outdoors and the solubility of alkyl-phenyl and dialkyl-*p*-phenylenediamines can increase markedly under slightly acidified conditions.¹⁶

The second approach, applicable only where bulk permits, is to have a reservoir of antiozonant available within the thickness of the product or, as has been suggested for tyre treads, within the underlying carcass area. The reservoir effect, which is simply an increase in available free antiozonant per unit surface exposed area, is considered a major reason why leaching by rainfall is less critical in a tyre than in a thin-walled windscreen wiper blade.

INTRODUCTION

By far the most damaging effect atmospheric ozone has on rubbers is the degradation of a stretched surface in such a way that a pattern of cracks forms (Fig. 1). Unlike sunlight crazing, which is random, ozone cracks grow perpendicularly to the direction of strain, and outdoors, in the absence of protection, they can appear within a few days at a typical ambient ozone concentration of 1–3 parts per hundred million parts (pphm) of air. In many cases this cracking is no more than superficial, without adverse effect on properties of the product. It assumes much greater importance when an unwanted crack triggers off more catastrophic tear or fatigue failure, allows escape of a sealed fluid, increases stress relaxation or creep through a reduction in cross-sectional area, exposes components beneath a protective rubber surface and, not least, spoils the appearance of the product. Rubbers susceptible to ozone

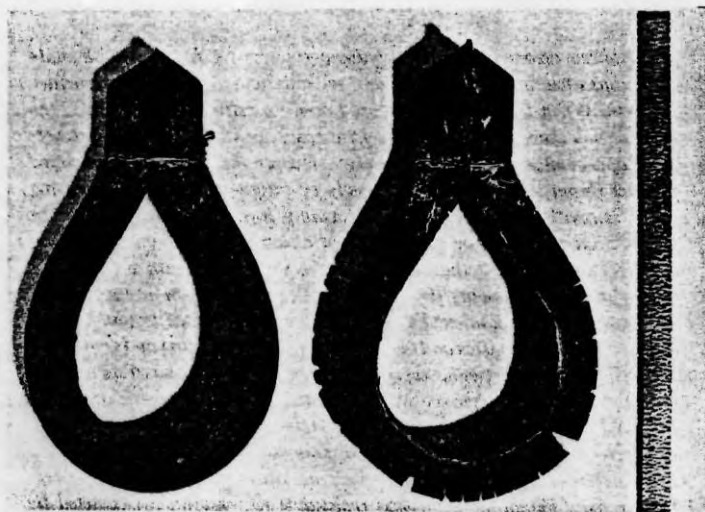
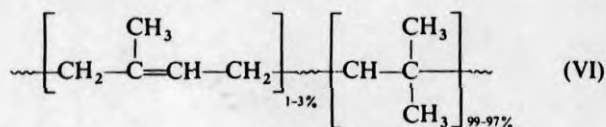
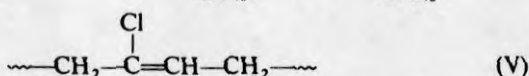
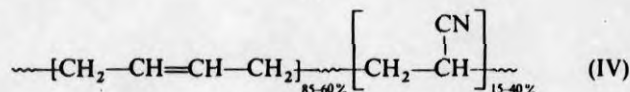
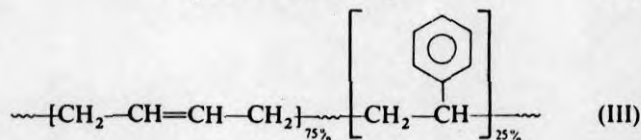
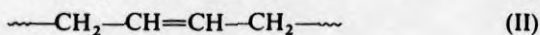
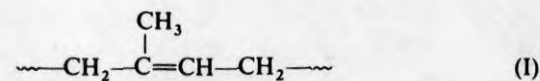


Fig. 1. Ozone cracking in natural rubber. Left to right—looped triangular test piece (max. strain, *ca* 25%) stored in a cupboard for several years; a duplicate test piece exposed to ozonized air; a strip test piece (tensile strain, 20%) also exposed to ozonized air. Each of these samples contains a protective system unsuited to the conditions of exposure used (see text).

attack are those having main chain unsaturation. The handful of diene-based rubbers in this category account for over 90% of annual elastomer consumption. Most in need of protection are the general-purpose materials of natural rubber and its synthetic counterpart polyisoprene (I), polybutadiene (II) and the copolymers of butadiene and styrene (SBR—III). Also lacking ozone resistance are the oil-resistant copolymers of butadiene and acrylonitrile (nitrile rubber—IV). Some inherent stability is shown by polychloroprene (V) and much more by the predominantly saturated copolymer of isobutene and isoprene (butyl rubber—VI), but these, too, sometimes need the benefit of extra protection.



The rubber industry has devised various protective measures, some of them very effective, but all with shortcomings. Because of the rubbers involved there is a sizeable market for antiozonants, which are used at higher concentrations than other antidegradants normally are. Additional demands come from the hurdle of having to meet a specification, perhaps unrelated to service conditions, and the concern some end-users have that cracking, however unimportant, *might* just occur. One recent

forecast suggests that, whereas the EEC consumption of rubber chemicals will increase by 29% between 1982 and 1988, that of antidegradants, including antiozonants, will rise by 40%.

The purpose of this paper, which is intended for a non-specialist readership, is to review the methods available for combating ozone attack, highlight recent advances and identify the outstanding problems concerning both stabilization and testing.

OZONE ATTACK

A brief account of the generally accepted mechanism of ozone attack is instructive because cracking is a physico-chemical phenomenon, with its severity depending on the mechanical conditions of exposure (see Fig. 2), as well as the reactivity of the base polymer. For a more detailed treatment attention is drawn to a recent review by Razumovskii and Zaikov.¹

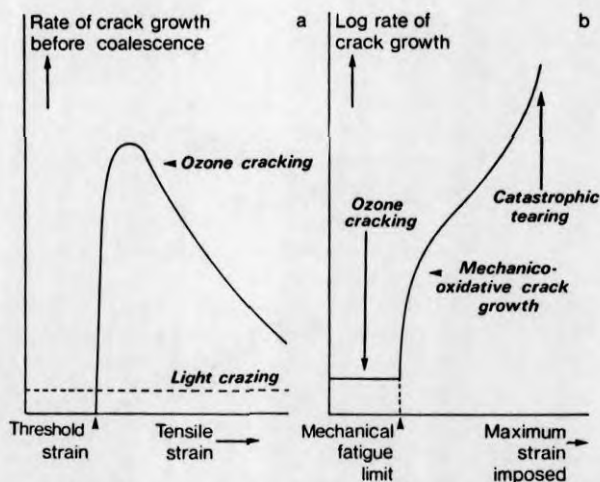
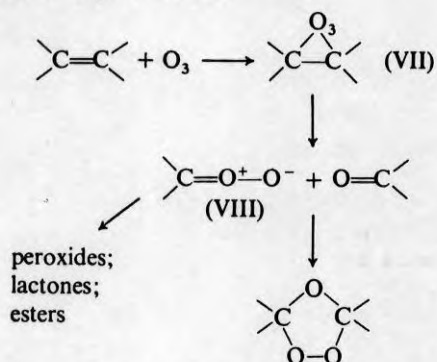


Fig. 2. Strain dependence of ozone cracking. (a) Static strain exposure. Note that, unlike ozone cracking, light crazing occurs independently of extension and is comparatively shallow. (b) Dynamic strain exposure. Note that ozone attack is the only cause of crack growth below the mechanical fatigue limit of the rubber. For a soft natural rubber vulcanizate the fatigue limit is typically *ca.* 70% extension.

Chemistry

The ozonolysis of unsaturated rubbers has been shown to be complex, not least in natural rubber where naturally occurring non-rubber constituents can also participate, but there is some agreement with the Criegee mechanism² depicted below.



The key reactions are the initial addition of ozone across a main chain double bond to form the unstable molozonide (VII) and the subsequent chain scission caused by rearrangement of the intermediate zwitterion (VIII). In unstretched solid rubber such degradation is confined to a thin surface layer³ (typically 0.5 μm thick) mainly because, unlike elemental oxygen, ozone reacts so rapidly with a double bond that none is available for penetration into the rubber bulk. The attack, however, can be sufficient to cause occasional 'frosting' (a white bloom-like appearance) on transparent and coloured surfaces (Fig. 3), and recently links have been drawn between ozone attack and loss in building tack⁴ and decrease in ease of adhesion to polyester cords⁵ upon atmospheric storage of unvulcanized rubber mixes.

Physics

In most diene rubbers the ozone-degraded surface layer is mechanically extremely weak, often resembling a viscous liquid rather than a solid. Rupture of the layer in the vicinity of a stress-raising flaw of the type always present in a vulcanizate surface will expose virgin rubber and crack growth will commence.

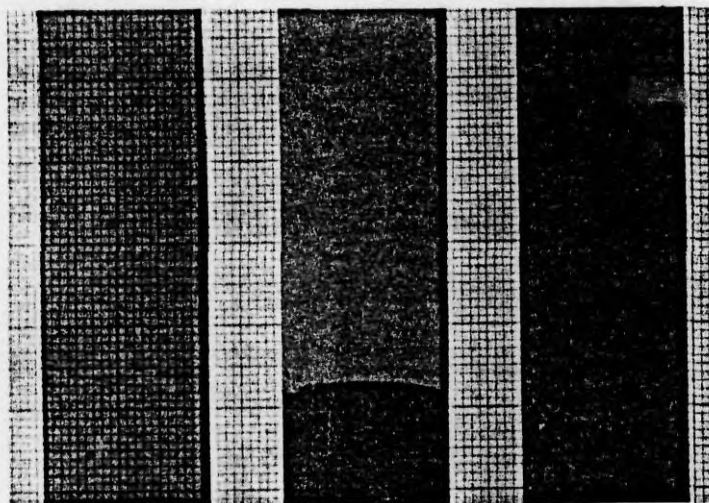


Fig. 3. 'Frosting' in natural rubber. In an unprotected transparent vulcanizate this effect causes loss in clarity because of a bloom-like appearance. Left to right—unexposed; exposed for 3 days at 50 pphm ozone, with bottom part then wiped with acetone; exposed indoors in diffused daylight for 2 years. The test pieces are unstrained.

Definitive work by Braden and Gent,⁶ using a fracture mechanics approach, identified two characteristic parameters for the development of ozone cracks under static strain conditions. In summary, these are as follows.

First, crack growth does not occur until a minimum tearing energy introduced by extending the rubber is exceeded. In the absence of stabilizers this threshold energy is substantially independent of ozone concentration and is broadly similar for all diene rubbers. In practical terms it corresponds to a threshold tensile strain of 3–5%, depending on stiffness.

Secondly, once the threshold condition is exceeded, a single isolated crack grows at an approximately constant rate independent of strain and in direct proportion to the ozone concentration. It is here that differences exist among rubber types. The rate in butyl rubber is an order of magnitude below that in natural rubber and SBR, not because of low unsaturation but because of high internal hysteresis. Raise the

test temperature or add a plasticizer, and the rate increases to the natural rubber level because of greater chain mobility. The resistance shown by polychloroprene is attributed to double bond stabilization by the chlorine atom.

In plane rubber surfaces crack growth is strain dependent.⁷ Just above the threshold value there will be few large enough flaws at the pre-requisite tearing energy and so there will be few cracks. Over this small strain region behaviour will change from an absence of cracks to cracking at its most severe in terms of penetration into the rubber (see Fig. 2). As the strain is further increased other, smaller flaws will be at the threshold tearing energy and the crack density will rise accordingly. At the same time, cracks will grow slowly because of mutual interference and rapid depletion of ozone in the layer of air immediately above the exposed rubber surface.

PROTECTION AGAINST OZONE (see Fig. 4)

The prime objective is to raise the threshold strain of the candidate rubber above the maximum extension encountered in the product and then to ensure this level of resistance is maintained throughout the service life of the product. The alternative, more applicable under dynamic strain conditions where the threshold strain is essentially zero, is to ensure the rate of crack growth is negligible and certainly never becomes severe enough to introduce the risk of more damaging fatigue failure. It should be noted that good protection is still a poor substitute for poor component design. Unnecessary tensile stresses should always be eliminated.

Use an inherently resistant rubber?

For applications subjected to a tensile strain, replacement of a polydiene rubber by a rubber having a saturated backbone seems an immediate solution, especially as some of the candidate materials, notably ethylene-propylene copolymers and terpolymers (EPDM), are marketed for a weathering resistance that does not rely on environmentally sensitive stabilizers. Yet the impact of these resistant rubbers has been selective rather than general, with compounders and end-users quite understandably reluctant to forfeit such properties as resilience, resistance to stress

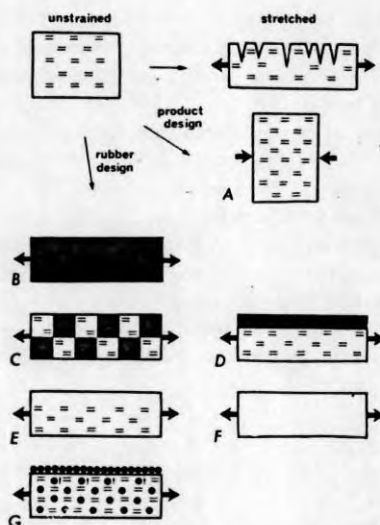


Fig. 4. Protection of unsaturated rubbers against ozone attack. Schematic representation of methods and approaches. A, Elimination of unnecessary tensile strains (e.g. working in compression); B, Replacement by ozone-inert rubber type; C, Blend of rubber types; D, Surface lamination; E, Surface modification; F, Bulk modification; G, Surface-diffusing antiozonant ingredients.

relaxation, tear and abrasion and ease of processing, including green strength, building tack and speed of crosslinking. Increased uptake of special-purpose rubbers such as acrylics and fluorocarbons is also deterred by the very much higher raw materials costs involved.

Some replacement has occurred, notable examples being cable sheathing and building gaskets expected to last more than 20 years. Furthermore, inherent ozone stability is a major reason why EPDM is making such advances in the rapidly expanding market of polymeric membranes for flat roofing.

Mix the strong and the weak?

Blends of polydiene and saturated rubbers find favour in light-coloured applications (e.g. white tyre sidewalls) needing ozone resistance under

dynamic strain conditions and also those applications where surface-acting antiozonant systems are considered objectionable for reasons of appearance or a propensity to stain surfaces in contact. The disadvantage is that physical properties have to be compromised and usually the two (or more) rubbers involved differ markedly in their rates of vulcanization. Such 'cure incompatibility' leads to a phasial disparity in crosslink density and a further sacrifice of vulcanizate properties. Usually at least 25% replacement by the resistant rubber is needed for even a modest (although still useful) enhancement in ozone resistance, and a dramatic improvement can only be expected when sufficient of the resistant rubber is present to form the load-bearing matrix.

A variation of polyblending is lamination whereby a lacquer or outer skin of ozone-resistant rubber is applied over the polydiene vulcanizate. This technique has the advantages that the underlying rubber can act as the stress member without sacrifice in properties and that the exposed rubber can combine weathering resistance with such features as decorative colour and resistance to swelling by oil spillage (e.g. polyurethane paints) and antistatic behaviour (e.g. polychloroprene). The technique, however, is unpopular because it involves an additional fabrication process and the protective coating may be susceptible to scuffing and delamination (especially if the rubbers involved are chemically incompatible, as is usually the case).

Remove the unsaturation?

As a means of improving ozone resistance, hydrogenation of unsaturated rubbers, in the bulk or at the surface, has proved to be unsuccessful in most instances because complete elimination of double bonds cannot be achieved in a viscous, high molecular mass material, least of all on a commercially viable basis. Even a residual 1–2% unsaturation is sufficient for ozone attack as the results⁶ for plasticized butyl rubber testify (and without the presence of an additional methyl pendent group per monomer unit, hydrogenated natural rubber, unlike butyl rubber, will still not enjoy the benefit of internal damping). Recently, hydrogenated grades of nitrile rubber (IV) have been introduced on the market with forecasts that these should find application in products requiring high thermal stability both in air and in aggressive oils.⁸ Ozone resistance has been claimed as an additional benefit but too few results are available

to assess whether the resistance will be raised to that of a fully saturated rubber, given that there may be a residual trace of main chain unsaturation. Less in doubt is the high cost of a post-polymerization process involving dissolution of rubber, hydrogenation aided by expensive catalysts and removal of solvent.

Chlorination is an unsuitable contender because rubber-like properties are ruined.

Use a protective system?

An antiozonant is a compound ingredient that migrates to the rubber surface in a sufficiently high concentration to provide a physical or chemical barrier to ozone. An ideal additive will have the following characteristics:

- (a) Sufficiently soluble in the rubber in order to undergo molecular diffusion to the exposed surface, the flux being such that it is high enough to form or repair a protective surface before ozone attack but low enough to ensure a reservoir of unused antiozonant exists throughout service.
- (b) Effective in a low bulk concentration (i.e. no more than five parts per hundred parts of rubber polymer [phr]).
- (c) Low cost (preferably less than 7 US dollars/kg).
- (d) Without adverse effect on processing of the mix, fabrication, vulcanization and vulcanizate properties. (Note: a prime requirement in general-purpose rubbers is compatibility with organically accelerated sulphur crosslinking systems).
- (e) Effective under static and dynamic strain conditions over a wide range of extensions, the ultimate being crack-free protection up to the breaking elongation or up to the mechanical fatigue limit under dynamic strain conditions (see Fig. 2).
- (f) Persistent activity during storage, product manufacture and service, resistance being shown to loss by oxidation, aqueous or solvent extraction and volatilization.
- (g) Non-discolouring (for non-black rubbers); non-staining (for light-coloured surfaces coming in contact with rubber, fumes or conveyed liquid); no adverse effect on vulcanizate finish.
- (h) Low toxicity during handling and in the finished product, such a requirement being extended to any reaction by-products.

Although most effective, the two types of antiozonant in common use fall short of these ideals, as will become clear below.

Hydrocarbon waxes

If wax is present in vulcanized rubber at a level above its solubility, the excess will be forced to the surface where it will crystallize out to form a bloom which can be a very effective physical barrier against ozone provided it is not disturbed.⁹ Proprietary waxes are usually blends of normal paraffins to which a portion of microcrystalline wax has been added for the purpose of seeding the development of small, closely packed crystals. The detailed composition will vary according to the desired diffusion characteristics but most protective waxes will have a bulk melting point between 60° and 70°C.

The advantages of waxes are:

- (a) Relatively low cost (typically no more than 2 US dollars/kg).
- (b) Non-discolouring.
- (c) No effect on vulcanization chemistry.
- (d) Occasional dual function as a process aid during mixing and fabrication.

In turn, the shortcomings are:

- (a) No protection under dynamic strain conditions—and indeed usually a detrimental effect should other antiozonants be absent.
- (b) High dependence of protection upon exposure temperature because of changes in solubility and diffusion coefficient⁹ (see Fig. 5).
- (c) Loss of efficacy upon storage before service, especially in thin walled products.
- (d) Damage to bloom caused by embrittlement, scuffing and delamination.
- (e) Change in appearance, i.e. loss of shine, flaking and contamination of other surfaces, e.g. smearing.
- (f) In product manufacture, loss in tack and bloom interference with adhesion of substrates and surface treatments such as the chlorination used to reduce dry friction in windscreen wiper blades.

Chemical antiozonants

The introduction of *N,N'* substituted *p*-phenylenediamine antiozonants

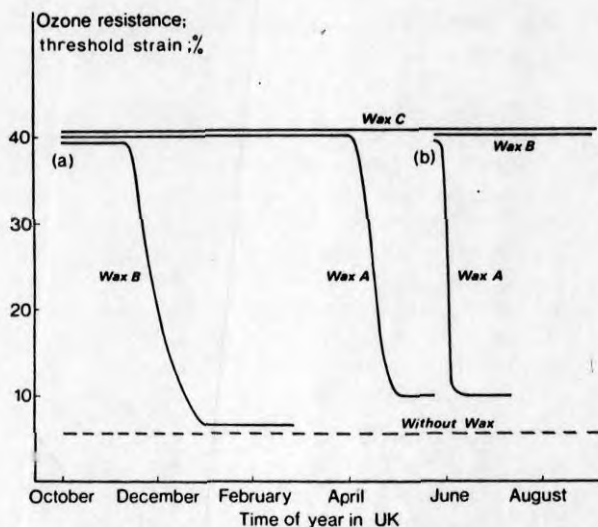
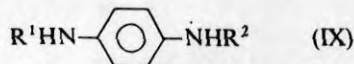


Fig. 5. Temperature-dependence of wax bloom protection. The plot shows the effect of season upon outdoor exposure in the UK. (a) Test begun in autumn. (b) Test begun in summer. Wax A, a paraffin wax of melting point 52°C confers protection in the winter but fails in summer because it becomes soluble in the rubber and cannot bloom. Wax B, a paraffin wax of melting point 67°C, succeeds in summer but fails in winter because its diffusion coefficient becomes too low to repair mechanically or thermally-induced breaks in the bloom. Wax C, a proprietary blend of paraffinic and microcrystalline waxes having a melting point of 65°C, confers year-round protection.

(IX) has proved to be the major advance in rubber stabilization within the last 30 years.



where $\text{R}^1 = \text{R}^2 = \text{alkyl (or cycloalkyl)}$

$\text{R}^1 = \text{alkyl (or cycloalkyl)}$; $\text{R}^2 = \text{aryl (usually phenyl)}$

$\text{R}^1 = \text{R}^2 = \text{aryl}$

Activity varies with the nature of the substituent groups¹⁰ as follows.

N,N'-dialkyl substitution. In natural rubber and SBR the threshold strain for crack growth is raised (Fig. 6) and when cracking does occur

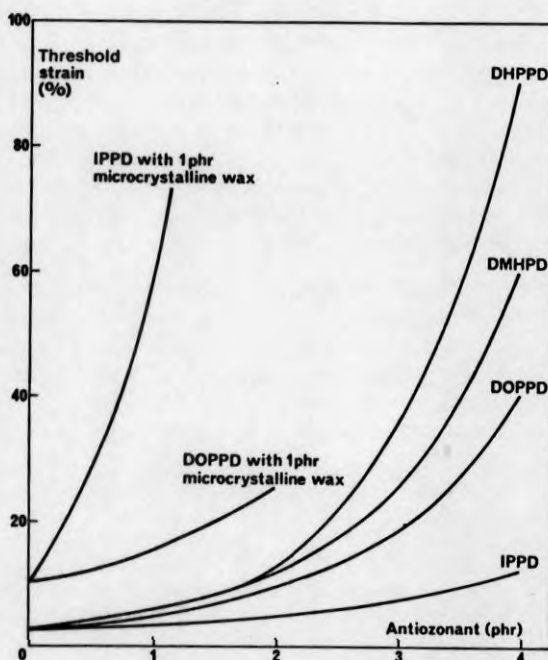


Fig. 6. Enhancement of threshold strain of natural rubber by substituted *p*-phenylenediamine antiozonants. Results were obtained at 25pphm ozone. For abbreviation see text.

the rate of growth is reduced (by a factor of 3–5).¹¹ The sec.-alkyl group is most active, with the best overall balance of properties being given by C₇ and C₈ derivatives. The three commercially available types, normally used at 2–5 phr, are the *N,N'*-di(1,4-dimethylpentyl) derivative (DHPPD) and the two octyl isomers, *N,N'*-di(1-ethyl-3-methylpentyl)-*p*-phenylenediamine (DOPPD) and *N,N'*-di(1-methylheptyl)-*p*-phenylenediamine (DMHPD). Cycloalkyl derivatives are less effective.

N-alkyl-N'-phenyl substitution. The rate of crack growth is again reduced but in general purpose rubbers the threshold strain is not usefully raised unless the derivative is added with a wax or a dialkyl type. The behaviour with wax is synergistic under static strain conditions

and, interestingly, to a much greater extent than possible with a dialkyl derivative⁹ (Fig. 6). Such combinations are in widespread use; for example, in tyres. In essence, the wax provides the basis for static protection and reduces cost, whilst the *p*-phenylenediamine provides dynamic protection and more than compensates for any deleterious effect of the wax bloom.

The three most popular alkyl-phenyl-*p*-phenylenediamines in commercial use have, as alkyl substituent, isopropyl (IPPD), 'hexyl' (i.e. 1,3-dimethylbutyl) and 'octyl' (i.e. 1-methylheptyl).

N,N'-diaryl substitution. Antiozonant activity, as measured under laboratory conditions, is low, and in natural rubber the initial effect on threshold strain and rate of crack growth is usually negligible. The main advantage is high resistance to loss by consumption or volatilization,¹⁰ and in the presence of more active antiozonants the diaryl types can offer some residual protection after prolonged periods or oxidative ageing.

The merits of *p*-phenylenediamines over wax blooms can be summarized as follows:

- (a) Enhancement of ozone resistance under dynamic strain conditions, principally as a result of the reduced rate in crack growth (Table 1).

TABLE 1
Antiozonant Activity of *N,N'*-Substituted *p*-Phenylenediamines under Dynamic Strain Exposure

Antiozonant (phr) ^a	Time to first crack (h) ^b
None	<1
IPPD, 2	24
DHPPD, 2	18
DOPPD, 2	14
DMHPPD, 2	22
IPPD, 2; wax 1	10
IPPD, 2.5; wax 1	14

^a In natural rubber (see text for abbreviations).

^b Using modified De Mattia flex cracking test in which a thin strip is cycled between 0 and ca. 15% strain at 5 Hz in atmosphere of 25 pphm ozone and 30°C. Numerically similar results are found outdoors except that the time to first crack will be in days, not hours.

TABLE 2
Outdoor Protection of Natural Rubber by *N,N'*-Substituted
p-Phenylenediamines

Antiozonant (phr)	Time to first crack (weeks) at 20% extension ^a	
	In shade	Facing sun
None	< 1	< 1
IPPD, 2	< 1	< 1
DHPPD, 4	60	60
DOPPD, 4	> 100	70
DMHPD, 4	60	40
IPPD, 2; wax, 1	> 100	40

^a Results for thin (2mm thick) strips. Longer times to first crack have been found for thicker test pieces able to benefit from the increased reservoir of unused protective agent (see text).

- (b) Activity is much less temperature-dependent and therefore less prone to seasonal variations (Table 2). Diffusion to the surface is chemically induced and so need not depend on supersaturation (unlike waxes).
- (c) Better surface appearance (in black-pigmented vulcanizates).
- (d) Multi-purpose antidegradant activity, with protection being conferred against thermal oxidation, metal ion (e.g. Cu^{++}) catalyzed oxidation and, more characteristically, mechanico-oxidative fatigue. Some anti-radiation and biocidal activity is also displayed.

The shortcomings of *p*-phenylenediamines are as follows:

- (a) A tendency to discolour or to stain, a weakness that confines the use of these antiozonants to essentially black or dark-coloured rubbers.
- (b) Loss in antiozonant activity upon storage and service due to volatilization, leaching and oxidative consumption (Table 3). Resistance to oxidation decreases in the substituent order: diaryl > alkyl-aryl > dialkyl.¹²
- (c) Interference with sulphur vulcanization leading to loss in processing safety, reduction in the efficiency of crosslinking and some

TABLE 3
Effect of Thermal-Oxidative Ageing on Antiozonant Activity of *N,N'*-Substituted *p*-Phenylenediamines

Antiozonant (phr) ^a	Threshold strain (%)		
	Original	After 7 days at 70°C ^b	After 1 year at 20°C
DOPPD, 4	20–25	15	10–15
IPPD, 2; wax, 2	>40	>40	>40

^a In natural rubber.

^b Air oven ageing of unstrained test pieces. The pretreatment has little effect on bulk properties of the vulcanizate but is sufficient to cause the loss of 40% of free DOPPD. Similar results are found on long-term room temperature storage.

depletion in free *p*-phenylenediamine concentration. The worst offenders are again the highly active dialkyl derivatives.

- (d) Occasional interference with rubber to metal bonding especially after storage of unvulcanized 'blanks'.

THE QUEST FOR BETTER CHEMICAL ANTIOZONANTS

A more active *p*-phenylenediamine?

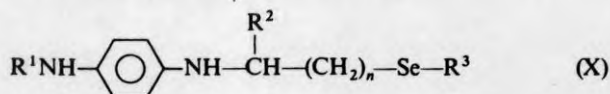
Objective

To modify the substituent groups in such a way that the antiozonant is effective at lower additive levels in the hope that some of the concentration-dependent side effects such as staining and cure interference are reduced. A further aim is an antiozonant better able to withstand high ozone concentrations.

Attempted solution

As the commercially available *p*-phenylenediamines already represent a compromise between antiozonant activity and features such as volatility and toxicity, it seems unlikely that further variation in the size and branching of the alkyl substituents will increase activity on a practicable level.

A route pursued by the MRPRA¹³ has involved the incorporation of a monoselenide linkage in the alkyl chain (X).



Earlier work¹⁴ had shown that dialkyl monoselenides were very efficient ozone scavengers, reacting some 80 times more quickly with the gas than model olefins for rubber could, and up to 20 times more quickly than commercial *p*-phenylenediamines. As rubber antiozonants these monoselenides were ineffective, almost certainly because of their inability to migrate to the exposed surface and then form a protective barrier.

The scavenging activity is retained in the selenium-modified *p*-phenylenediamines. Thus, an alkyl-phenyl derivative containing one monoselenide function decomposes three moles of ozone per mole, 50% more than an unmodified asymmetrical *p*-phenylenediamine. A dialkyl-*p*-phenylenediamine containing two monoselenide functions destroys four moles of ozone per mole. Added to natural rubber, structures such as X extend the time to first crack but the improvement is modest in technological terms and can be matched by adding no more than 1 phr extra of a commercial *p*-phenylenediamine. Moreover, poor protection is conferred by selenium-modified dialkyl-*p*-phenylenediamines, in part because of consumption during vulcanization.

A *p*-phenylenediamine free of side-effects?

Objective

To minimize staining and interference with sulphur vulcanization.

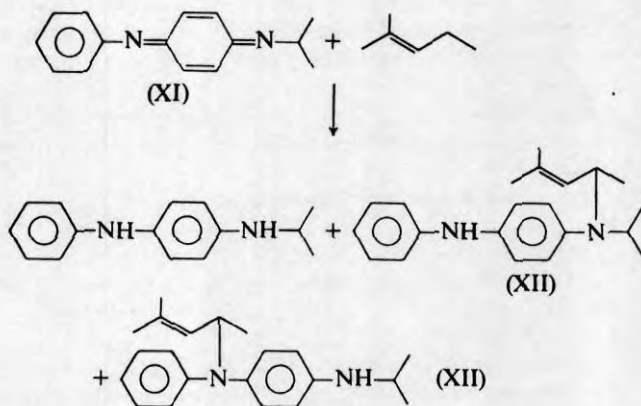
Solutions

For minimal migration staining (for example, in such applications as building gaskets and wiper blades) the rubber industry has been encouraged to use high molecular mass derivatives such as the 'octyl'-phenyl-*p*-phenylenediamine or to use protective systems containing the less mobile diaryl-*p*-phenylenediamines. Some loss in antiozonant activity usually needs to be tolerated unless a wax bloom or part replacement of polymer by a saturated rubber becomes acceptable.

A rubber mix must not vulcanize whilst it is being prepared and

afterwards processed into shape by such equipment as an injection-moulding machine, extruder or calender. The required scorch safety is usually dictated by the detailed vulcanizing system in the case of sulphur crosslinking, and delayed-action sulphenamide accelerators are nowadays in widespread use. Dialkyl (and di-cycloalkyl)-*p*-phenylenediamines can reduce this scorch safety and introduce the risk of premature set-up, especially as comparatively high levels (i.e. 3–5 phr) are needed if other protective agents are excluded.

An effective solution to this problem is to add a prevulcanization inhibitor (PVI), several types of which are now commercially available. Such an inhibitor, however, does not restore the loss in crosslink density that also occurs in the presence of both dialkyl and alkyl-phenyl-*p*-phenylenediamines. An entirely novel approach, again developed by MRPRA,¹⁵ stems from the observation that when the quinone diimine reaction product (XI) of a *N,N'*-disubstituted *p*-phenylenediamine is heated in natural rubber most of it is reduced back to the parent *p*-phenylenediamine. Model olefin studies using the *N*-isopropyl-*N'*-phenyl derivative suggest the following reaction pathway.



Such a reaction is conveniently carried out at, or near, vulcanization temperature in the presence of other compounding ingredients. If a thiazole or sulphenamide-accelerated vulcanizing system is used, the quinone diimines do not reduce scorch safety and, in the case of the *N*-alkyl-*N'*-phenyl derivatives, there is a useful PVI effect. An additional

feature is that quinone diimines do not reduce crosslink density; vulcanizate modulus is retained and even slightly increased.

Antiozonant activity is in accord with the level of *p*-phenylenediamine generated *in situ* (typically 60–70% of the quinone diimine concentration). On the evidence of model studies the remaining quinone diimine becomes attached to the rubber chain as mono-*N*-alkenylated *p*-phenylenediamines (XII) and, indeed, some rubber antioxidant activity persists after solvent extraction of the vulcanizate.

Longer life antiozonants?

Objective

To produce a protective system able to confer long time resistance (over several years) and thus requiring an antiozonant resistant to depletion by physical loss or chemical consumption.

Solutions

The exposed rubber surface in need of protection against ozone cracking is also the site at which *p*-phenylenediamine antiozonants are most susceptible to loss by such agencies as heat (volatilization), water and solvents (leaching) and oxygen (direct oxidation and consumption as antioxidant).

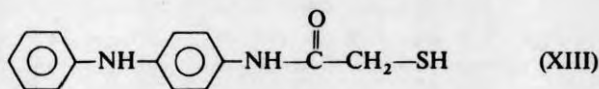
The rubber industry has pursued the problem on four fronts.

The first, already referred to, involves the partial replacement by the less active diaryl-*p*-phenylenediamines and/or the use of higher molecular mass antiozonants, the most notable example of which in recent years has been the steadily growing replacement of IPPD by the less volatile, less water-extractable and more rubber-soluble, *N*'-hexyl-*N*'-phenyl-*p*-phenylenediamine. Both the latter antiozonants are only sparingly soluble in water, but water is usually available in plentiful supply outdoors and the solubility of alkyl-phenyl and dialkyl-*p*-phenylenediamines can increase markedly under slightly acidified conditions.¹⁶

The second approach, applicable only where bulk permits, is to have a reservoir of antiozonant available within the thickness of the product or, as has been suggested for tyre treads, within the underlying carcass area. The reservoir effect, which is simply an increase in available free antiozonant per unit surface exposed area, is considered a major reason why leaching by rainfall is less critical in a tyre than in a thin-walled windscreen wiper blade.

The third approach, in this instance intended to reduce wasteful oxidative consumption of a *p*-phenylenediamine, is to add a conventional chain-breaking antioxidant alongside the antiozonant in the hope this may compete for oxygen and peroxy radicals. Some success has been claimed¹⁷ but the mechanism of binary systems is not understood and few long-term results are available.

The three routes outlined above are in practical use, depending only on commercially available materials. The final approach, that of binding *p*-phenylenediamine structures on to the rubber chain, remains speculative. Work undertaken at MRPRA¹⁸ has shown that the thermal 'ene' reaction between an olefin and a C-nitrosoaniline results in the formation of a *N*-alkenyl-*N'*-alkyl (or phenyl)-*p*-phenylenediamine, which, in the case of natural rubber, means a *p*-phenylenediamine pendent group attached to a long chain polyisoprenyl substituent. In solvent-extracted, thin vulcanized sheets such a modification displays strong antioxidant activity comparable with that of a mobile, conventionally substituted *p*-phenylenediamine and, at higher dosages, some resistance to mechanico-oxidative fatigue is evident. No antiozonant activity, however, is shown once any unbound reaction products are extracted, a finding supporting the generally prevalent view that an ability to diffuse to the exposed surface is an important, if not essential, criterion for antiozonant protection. More encouraging results for bound antiozonant activity have since been reported by Katbab and Scott¹⁹ for structures derived from thiol-amine adducts (XIII).



Non-staining antiozonants?

Objective

To produce a general-purpose, non-discolouring and non-staining chemical antiozonant having an activity under static, and especially dynamic, strain conditions comparable to that of disubstituted *p*-phenylenediamines.

Attempted solutions

The lack of a non-staining antiozonant suitable for light-coloured articles of natural rubber or SBR operating under dynamic strain

conditions or in circumstances where a wax bloom is considered objectionable remains one of the major outstanding problems of rubber stabilization, and it is because of the absence of such an additive that replacement of polydiene rubbers, in part or totally, by saturated main chain elastomers has occurred.

The patents literature shows there has been no shortage of attempts in what has essentially been an empirical 'bottle searching' exercise. Measures of success have been claimed for a wide variety of chemical types, representative samples of which are as follows: 2, 4, 6-substituted phenols, 2, 6-dialkoxyphenols, thio-bis-phenols, *o*-aminophenols, *o*-aminothiophenols, enol ethers of monohydric alcohols or diols, methyl 3-cyclohexene carboxylates, thiosemicarbazides, hydrazine derivatives, zinc bis (benzimidazolyl mercaptide), aryl borates, wood tar distillates, *p*-phenylenediamine-alkylene oxide reaction products, piperidine derivatives, *p*-alkoxy-*N*-alkylanilines, *N*-substituted ureas, *N*-substituted thioureas, dithiocarbamates (organic and metallic), linseed oil, benzofurane derivatives, cyclic acetals and ketals, unsaturated ethers.

Most of the above are indeed non-staining and, sadly, nearly all are ineffective antiozonants for natural rubber. The two exceptions are substituted thioureas and metal dithiocarbamates. Tributylthiourea has been marketed as an antiozonant, but its activity falls well short of that of a dialkyl-*p*-phenylenediamine and sacrifices must be accepted in scorch safety (the material is an accelerator) and even in appearance since the exposed surface can become tacky enough to attract dust.⁹ Zinc dialkyl-dithiocarbamates, whose activity is confined to reducing the rate of crack growth,¹¹ are amongst the most potent sulphur vulcanization accelerators and, at the levels needed, scorch resistance is prohibitively low.

More successful non-staining antiozonant protection has been achieved in polychloroprene rubber,²⁰ which even responds to additives as diverse as linseed oil and various conventional antioxidants. The last three materials in the above list are the basis of commercially available antiozonants for this rubber and their activity can extend to blends containing other polydiene rubbers.

MECHANISTIC STUDIES OF ANTIOZONANT ACTIVITY

Our understanding of antiozonant mechanisms has lagged behind technological development, with progress, until comparatively recently,

being seriously handicapped by the absence or limited availability of surface-sensitive analytical equipment. Centre of most attention has been the ability of a *p*-phenylenediamine, added in low bulk concentrations, to raise the threshold strain for crack initiation at the exposed surface. It is useful to review, in a little detail, the progress made in this area to illustrate how complex the chemistry of surface stabilization can be.

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. Much less certain is 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.

Theory 1

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.²¹

Evidence

(a) Reaction products between *p*-phenylenediamines and previously ozonized olefins. (b) Detection of bound nitrogen in the rubber after solvent extraction.²¹

Merits

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.

Shortcomings

(a) Does not adequately account for enhancement in threshold strain because statistically some chain scission would be expected. (b) The polymer-bound nitrogen level is within the experimental error of the analytical method (Kjeldahl) used,²² and, as it has been measured in a bulk sample, the increase could be due to non-ozone routes. (c) Ozone resistance can fall if a previously exposed surface is wiped with solvent.⁷

Theory 2

The antiozonant reacts with the zwitterion or ozonized rubber to form a stress-free, low molecular mass film capable of repair upon rupture.²³

Evidence

As theory 1.

Merits

(a) As theory 1. (b) Cracking cannot occur because the antiozonant-modified degraded surface undergoes stress relaxation.

Shortcomings

As theory 1(b).

Theory 3

The antiozonant scavenges ozone before it can attack the rubber.²⁴

Evidence

(a) Solution studies show that *p*-phenylenediamines react with ozone more quickly than do olefins. (b) Development of cracks after long-term exposure when the free antiozonant reservoir has been exhausted.

Merits

(a) Explains extended delay for crack initiation. (b) Reduction in rate of crack growth.

Shortcomings

(a) More effective ozone scavengers than *p*-phenylenediamines are not antiozonants.¹⁴ (b) 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 the incidence of ozone.²⁵

Theory 4

The antiozonant reacts with ozone to form a stress-free protective film which prevents the ozone reaching the rubber surface.^{7,26}

Evidence

(a) Visible evidence of a film less extensible than the underlying rubber (Fig. 7). (b) 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. (c) Similar film develops on the ozone-inert rubber EPDM.

Merits

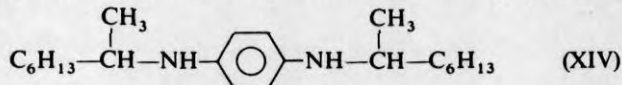
Accounts for enhancement of threshold strain over an extended period (which may be indefinite in absence of weathering and other non-ozone causes of surface disturbance).

Shortcomings

Does not explain some dependence of antiozonant activity on rubber type.

The degraded-antiozonant protective film mechanism has gathered strength over the last 15 years as a result of elegant work undertaken by Lake⁷ at MRPRA and Lattimer *et al.*²⁷⁻²⁹ at the Goodrich Research and Development Center in the USA. Approaching the problem as a physicist, Lake showed that the thickness of the ozone-induced layer increased in proportion to the square root of exposure time (which accords with diffusion theory). He also calculated that the antiozonant, in his case DOPPD, could diffuse sufficiently quickly through to the surface to react with ozone to form a coherent, monomolecular thick layer in less time than an ozone crack could grow to the same depth. Such a layer could then bridge any potential cracks and its effectiveness would depend on there being a sufficiently high antiozonant dosage in the bulk of rubber to counteract the ambient ozone concentration. Theory estimates of this relationship between ozone concentration and minimum antiozonant level for protection showed reasonably good agreement with experimental evidence.

Using scanning electron microscopy and a range of sophisticated spectroscopy equipment, Lattimer *et al.*²⁸ have confirmed the existence of a surface layer derived entirely from diffused antiozonant; in this instance, DMHPD (XIV). The composition of the underlying rubber



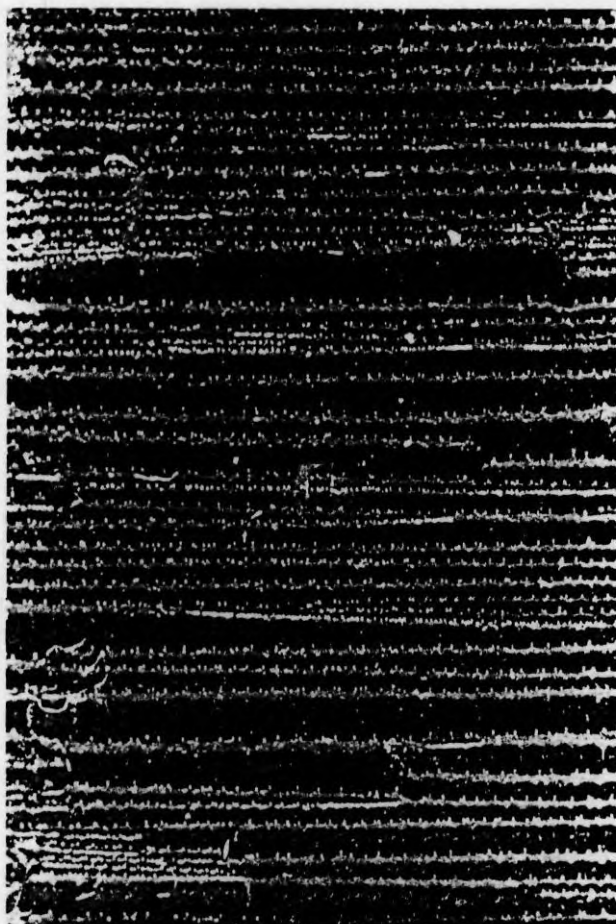
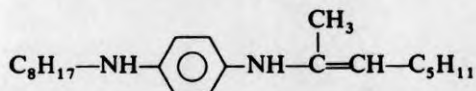
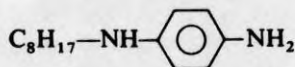
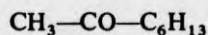
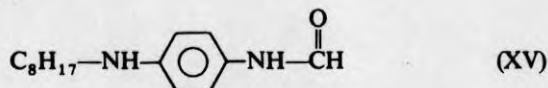


Fig. 7. Surface layer formed by *N,N'*-dialkyl substituted *p*-phenylenediamine. This photograph shows the film formed on an ozone-exposed EPDM vulcanizate containing DOPPD (see text). The vulcanizate has been stretched to rupture the less extensible film, the underlying rubber surface being the light-coloured strips across the test piece. The film can be removed by wiping with acetone. Similar behaviour occurs in natural rubber.

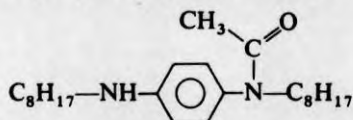
was unaltered by exposure to ozone (although exposure in the unstrained state would be expected to minimize the extent of degradation).

Analysis of the antiozonant exposed to ozone in the absence of rubber confirmed the long anticipated complexity of *p*-phenylenediamine ozonation products. Twenty-seven distinct reaction products were detected, half having a molecular mass below that of the free antiozonant. Spectra were consistent with structures depicted below beneath suggested reaction pathways.

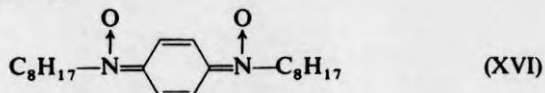
Side chain oxidation



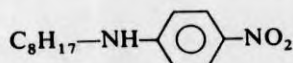
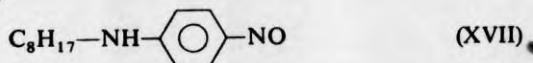
Aldehyde insertion (using CH₂O from side chain oxidation)

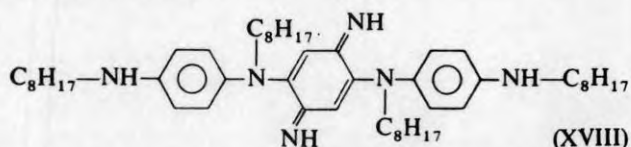


Nitroxide radical pathway



Amine oxide pathway



Bandrowskii base formation

Such materials were also detected in a layer taken from an exposed rubber surface, but there was much less evidence of the higher molecular mass Bandrowskii base products (XVIII—which, in any case, can be formed via non-ozone routes). The layer also contained unreacted *p*-phenylenediamine, indicating diffusion of antiozonant (a liquid) through the ozonized layer (a solid or very viscous liquid). The Goodrich workers concluded that the layer consisted essentially of comparatively low molecular mass reaction products such as amides (XV), nitrones (XVI) and nitrosoaryls (XVII). Hydrogen bonding between the highly polar groups present in these products might, in part, explain the coherence of the layer, but the existence of high molecular mass, polymeric structures, undetected by the analytical methods employed, cannot be excluded. Lattimer *et al.*²⁸ regard the presence of unreacted antiozonant in the layer as evidence of a combined scavenger-protective film mechanism in order to lend credibility to a previous hypothesis²² that the surface layer of ozonized *p*-phenylenediamine is itself unable to prevent ozone penetration. This hypothesis is intended to explain development of ozone cracking once the reservoir of unreacted antiozonant has been exhausted. It should not be forgotten, however, that ozone can gain access to the underlying rubber through mechanically or thermally induced fissures in the relatively brittle surface layer, just as ozone can in the case of more inert wax blooms cycled to sub-zero temperatures. Occurrence of isolated cracks after prolonged outdoor (weathered) exposure seems more easily explained on the basis of physical rupture of the layer rather than diffusion of ozone throughout a permeable surface.

Our understanding of the behaviour of asymmetrical alkyl-aryl-*p*-phenylenediamines is much less complete. Degraded-antiozonant layer formation is less evident at the additive levels normally used for protection—which is in accord with the much weaker enhancement of threshold strain. The ozonation reaction products are again a complex mixture, but Bandrowskii bases are absent and nitron formation

appears to be a dominant feature.²⁹ A reported preference for attack at the alkyl substituent may provide a clue to the weaker static strain protection.

TESTS AND TECHNIQUES

Ozone resistance testing

Laboratory ozone test cabinets operating at higher-than-atmospheric concentrations are now commonplace, offering speed, and, in natural weathering terms, improved reproducibility. Test conditions vary, but by far the most popular combination at present is an ozone concentration of 50 pphm, a chamber temperature of 40 °C, a rubber test piece stretched to 20% elongation, an exposure period of 3–4 days and a requirement that there should be no cracks visible under $\times 2$ to $\times 7$ magnification.

Standard tests of this type are finding their way into an increasing array of product specifications and, in doing so, are placing their own demands on selection of rubber type and protective system.⁹ They have proved to be less successful for development or type approval work than for compound quality control, given the influence upon the efficacy of antiozonants exerted by such environmental factors as seasonal temperature variation (wax solubility/diffusion—see Fig. 5), rainfall (*p*-phenylenediamine leaching) and oxygen (wasteful *p*-phenylenediamine consumption accelerated by heat). Also, the already mentioned dependence of *p*-phenylenediamine antiozonant activity upon ozone concentration means that an accelerated test requires the use of an antiozonant level that the product may not need³⁰ (see Fig. 8). Because of its bulk, that product may have the benefit of an antiozonant reservoir denied to a thin (usually 2 mm thick) test piece. The higher antiozonant level merely increases costs and the risk of adverse side-effects—and service conditions may reveal the antiozonant type to be the wrong one because of non-ozone influences.

What is the ozone concentration?

Alongside their British Standards equivalents, the current internationally agreed test procedures for ozone resistance, ISO 1431/1 for static strain testing and ISO 1431/2 for dynamic strain testing, do not specify a

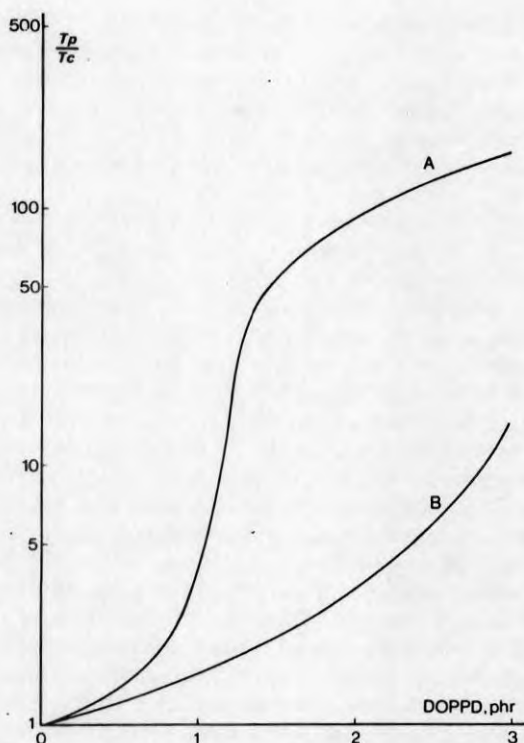
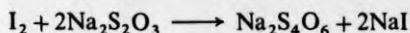


Fig. 8. Effect of ozone concentration on activity of *N,N'*-dialkyl substituted *p*-phenylenediamine. In this Figure the ratio (T_p/T_c) of the time to first crack of a DOPPD-protected natural rubber vulcanizate to the time of the first crack of unprotected vulcanizate is plotted against the level of antiozonant present for 'A', atmospheric exposure in the UK, and 'B', an accelerated laboratory test conducted at 25 ppm ozone. In each case the test extension is 20%.

method for the determination of ozone concentration in test cabinets. Failure to do so comes after completion of ISO/TC 45 interlaboratory tests showing unsatisfactory agreement for the previously standardized titration method and persistent differences between the results of this and instrumental techniques.³¹

The traditional procedure, depicted in the reactions below, has

involved absorption of the ozonized air into a buffered potassium iodide solution, reaction of the liberated iodine with a known excess of sodium thiosulphate and titration of the unreacted thiosulphate with a standard iodine solution. In the 'back titration' procedure, the thiosulphate is included in the iodide solution to minimize iodine loss through volatilization during passage of the ozonized air and agitation.



It is now known that the result of the above text-book reactions is affected not only by the stage of thiosulphate addition but also by the buffer type for KI, the quantity of KI, the manner in which the ozonized air is circulated and the method of determining the end-point. The stoichiometry of the reactions is also questioned since the traditionally preferred phosphate buffer appears to give results up to 30% higher than expected, whereas a boric acid buffered titration produces results similar to those of instrumental techniques.³¹ It has been suggested that the discrepancy arises from secondary reactions whereby hydrogen peroxide formed during the passage of ozone through the phosphate buffer liberates additional iodine. This explanation is disputed by another authority³² on the grounds that (a) any hydrogen peroxide could only arise from ozone with no increase in the overall level of available oxidant and (b) the measured ozone concentration reaches a plateau once a critical strength of phosphate buffer is exceeded.

Faced with such uncertainty, the ISO/TC 45 Degradation Tests Working Group responsible for ozone testing is currently considering, for reference purposes, adoption of the instrumental UV absorption method based on the Beer-Lambert law. Costs aside, this method does offer the advantage of continuous monitoring, as does also the instrumental electrochemical method increasingly favoured by rubber laboratories in the UK and the remainder of Europe.

A quite separate issue, again under discussion within ISO/TC 45, is the discovery in the USA³³ that, at a given ozone concentration, the rate of ozone cracking varies with atmospheric pressure. A change in barometric pressure, usually between laboratories sited at different attitudes, alters the all-important rate of collision between ozone and the exposed surface. This is considered a further cause of interlaboratory variation. To resolve the problem, ASTM is now specifying test cabins

ozone concentrations in terms of partial pressure. At 760 torr and 25°C, 1 pphm is equivalent to 1.1 mPa.

Analytical techniques

As so well demonstrated by the antiozonant work undertaken by Goodrich,²⁷⁻²⁹ ozone degradation and stabilization studies will be considerably facilitated by the emergence of surface chemistry techniques. Good use can be made of scanning electron microscopy (SEM) coupled with attenuated total reflectance spectroscopy, as well as field description, electron impact and atomic composition variants of mass spectroscopy. Other contenders include X-ray photo-electron and secondary ion mass spectroscopy. However convenient, solution (bulk) studies of ozonolysis and of prospective antiozonant behaviour have been shown to be misleading because no allowance is made for the contribution of diffusion effects.

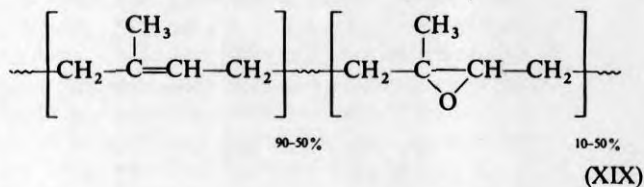
OUTSTANDING PROBLEMS AND NEEDS

In summary, these include the following.

Stabilization

- (i) A general-purpose, non-staining antiozonant for natural rubber and SBR (criteria will include improved resistance under dynamic strain conditions and an ability to pass accelerated ozone tests of the type mentioned earlier).
- (ii) A chemical antiozonant suitable for the oil-resistant nitrile rubber notwithstanding the development of hydrogenated derivatives. (This rubber is much less responsive to *p*-phenylenediamines than other polydienes are, and it is also used in applications where frequent contact with solvents may lead to antidegradant extraction. The reported absence of a protective, degraded-antiozonant layer upon exposure indicates that either such a layer is soluble in the rubber, which is highly polar, or unreacted *p*-phenylenediamine cannot migrate to the surface because of its very low diffusion coefficient in nitrile rubber.⁷)

- (iii) A chemical antiozonant suitable for epoxidized natural rubber (XIX). (This recently introduced chemically modified form,³⁴ intended for applications requiring higher damping, lower gas permeability and some measure of oil resistance, is also more difficult to protect with *p*-phenylenediamine antiozonants. Like nitrile rubber, it is polar and has a higher T_g than natural rubber.)



- (iv) A chemical antiozonant suitable for peroxide (i.e. free radical crosslinked) vulcanizates. (*p*-Phenylenediamines severely reduce crosslinking efficiency and are consumed during the reaction. Protection is usually confined to wax blooms and hence static strain exposure.)
- (v) Antiozonants or protective systems designed to withstand hostile service environments in which heat and fluid contact may cause antiozonant depletion (see earlier). Further investigation of antiozonant/antioxidant blends to minimize oxidative decay of the more active *p*-phenylenediamines.

Testing

- (i) Further investigation of the factors governing ozone concentration as determined by the traditional titration method (see earlier). Evaluation of alternative instrumental methods.
- (ii) Better correlation between accelerated laboratory test results and service performance.
- (iii) More information on the effects of oxidative ageing and leaching pretreatments on ozone resistance.
- (iv) More information on the effects of dynamic strain and intermittent static/dynamic strain exposure. (Most existing test data for protection systems and existing specification requirements relate to static strain exposure.)

Mechanistic studies

- (i) Continued investigation of the surface chemistry of *p*-phenylenediamine antiozonants using modern analytical techniques. Topics needing attention include:
 - (a) Variation in response among different rubbers.
 - (b) Strain dependence of antiozonant activity.
 - (c) Mechanism of *N*-alkyl-*N'*-phenyl-*p*-phenylenediamine activity.
 - (d) Behaviour under dynamic strain conditions.
- (ii) Synergism between waxes and *p*-phenylenediamines, including the difference between alkyl-phenyl and dialkyl types (see above).
- (iii) Protection of polychloroprene rubber by non-staining antiozonants.

ACKNOWLEDGEMENT

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