Degradation of vulcanised rubber products – Problems and solutions (Degradation by residual chlorine in tap water, metals and ozone due to deterioration in the global environment)

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1. INTRODUCTION

The Achilles heel of rubber and plastics is that, compared with metals, inorganic materials and natural materials such as leather, they are easily degraded and short lived. **Figure 1** compares the rate of degradation of natural organic materials with rubber and plastic materials. Although rubber and plastics are clearly well placed in their initial properties, natural materials have the better properties once a long time has passed. An even starker difference emerges in comparison with metals and inorganic materials. Stored under the correct conditions, metals and other inorganic materials will, like Japanese swords, maintain their properties semi-permanently despite the passage of several hundred years. Rubber and plastics are created by unnaturally enforced polymerisation using high performance catalysts at artificially imposed temperatures and pressures; inevitably, therefore, they are unstable compared with materials nature has wrought over a very long time. As their quality has improved, they have acquired the status of everyday necessities and are now central to much industrial activity. However, they are actually less robust over the long term than is generally supposed: exposed to the natural environment, they slowly lose their intrinsic properties through physical and chemical action until they are no longer serviceable and disintegrate or decompose. Even if it falls short of disintegration, degradation induces all kinds of fault as properties decline. This is because
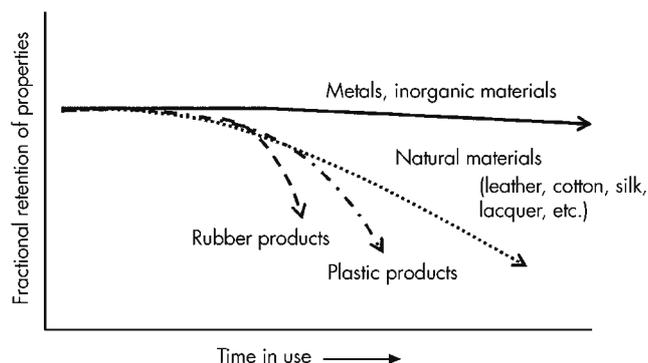

Figure 1. Relation between decline in properties and time in use for different materials

diverse factors progressively degrade the length and state of association of the individual molecular chains wherein the strength of polymer materials resides.

The Environmental Degradation Research Group of the Japan Society of Rubber Industry has made a follow-up survey of the changes with time over a 15 year period when dumbbells of natural rubber and seven different synthetic rubbers made from standard recipes were kept in an unloaded state in instrument shelters [1]. The Group reported that around half the rubbers exhibited a decline in strength of around 50%. It is clear from the report's findings that rubber in particular is prey to marked changes with time.

Furthermore, during use, rubber and plastics are greatly affected by hot water, metal contamination, oils, and more recently also by atmospheric nitrogen oxides (NO_x), sulphur oxides (SO_x) and ozone (O_3) due to deterioration in the environment; although some imperfections inherent in the material are not evident as problems in initial use, the inherent imperfections are prominently exposed once the moulded article as a whole becomes embrittled with advancing degradation. A great deal of effort has been invested in developing or selecting better age-resistors to prevent degradation and enhance the stability and durability of such polymer materials. Nevertheless, it must be accepted that the materials remain "easily degraded and short-lived".

This review looks at the problems associated with the degradation of rubber and ways of combating the problems, dealing in turn with the water degradation (degradation by residual chlorine in mains water), degradation by copper ions dissolved in environmental water, and ozone degradation associated with global environmental deterioration, a topic that has recently been receiving particular attention.

2. WATER DEGRADATION

2.1 Analysis of the Water Degradation of EPDM Packings Due to Residual Chlorine in Mains Water

The residual chlorine concentration in mains water has tended to increase in recent years as the environment has deteriorated. The trend is said to be especially marked around big conurbations in an industrial belt. **Figure 2** shows the residual chlorine concentration of mains water in a number of Japanese cities. The "black speck" phenomenon the rubber industry has been muttering about refers to the so-called softening degradation whereby carbon compounded in the rubber and some of the rubber itself adhere to the fingers

when the surface of EPDM mouldings that have been in constant contact with mains water are vigorously rubbed with the fingers. While no fracture or leakage is involved, tiny fragments of degraded EPDM are shed into the tap water a little at a time from equipment fitted with hose or packings thus exposed. Despite their small size, the black fragments are highly visible as foreign matter when the water is run into a cup for drinking. This degradation by residual chlorine is of two kinds: the softening degradation just referred to, and hardening degradation whereby cracks, etc, develop until eventually the water leaks.

2.2 Softening Degradation Due to Residual Chloride at the Ordinary Low Concentration in Mains Water [2]

2.2.1 Examination of Appearance, Measurement of Hardness

The overall picture presented by a problem item is that it is free from cracks or flaws and has no loss of rubbery elasticity to the touch; on the contrary, it has a soft feel compared with the unused item. Examination of the surface by SEM (scanning electron microscopy) revealed the situation shown in **Figure 3**. Thus, along with severe irregularities in profile, some of the surface appears to be on the verge of detachment or exfoliation, and alongside severe degradation, it is clear significant damage has been done by physical factors of external origin such as water flow. Measurements of surface hardness with a microhardness meter, which generally demonstrate hardening (crosslinking degradation) as a degradation characteristic of EPDM, reveal the opposite in items recovered from service, i.e. substantial softening (depolymerisation), and in areas exposed to water flow in particular, the results point to a softening phenomenon, as shown in **Table 1**.
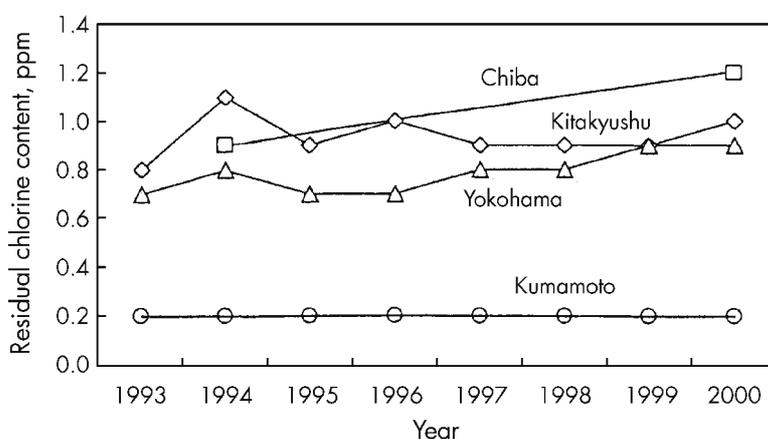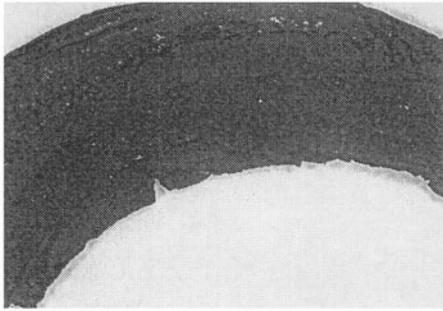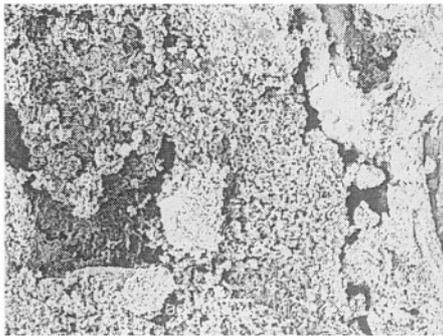

Figure 2. Residual chlorine concentration in mains water

x 12 Stereophotomicrograph

↓ Enlargement

EPDM top 100

x 100 SEM micrograph

Figure 3. Item recovered from service, packing

Table 1. Change in surface hardness of packing		
	Unused item	Recovered item
Surface	69	62
	70	64
↓	71	65
Depth direction	71	66

2.2.2 Measurement of Chlorine Penetration by EPMA

Since items recovered from service were found to have adsorbed moisture during degradation, it was possible that chlorine was penetrating the rubber during service. The chlorine distribution over the cross-section in the recovered material from the surface downward was examined by line analysis with an EPMA (electron probe micro analyzer). As shown in **Figure 4**, there is a high concentration of chlorine in the surface of recovered material: going from the surface towards the interior, the concentration remains high to a depth of ca. 300 μm and then falls abruptly, reaching a constant value at a depth of ca. 400μm. Compared with accelerated degradation, the diffusion-penetration of chlorine clearly extends to some depth in recovered material, suggesting slow degradation over a long time. Thus, as water is adsorbed, chlorine compounds are also adsorbed by the carbon black (CB) with the result that penetration-diffusion of chlorine compounds extends to a far greater depth, and degradation is more vigorous, in items recovered from service than in items exposed to accelerated degradation in residual chlorine of high concentration.

2.2.3 Measurement of Crosslink Density

The chlorine compounds in items recovered from service penetrate and adsorb more deeply than in accelerated degradation. The possibility was therefore inferred that proportionately more polymer chains are damaged; the change in crosslink density due to degradation was therefore determined by the swelling method. It was found that when the unused material was subjected to accelerated degradation in high concentration residual chlorine, typical hardening degradation occurred with increase in crosslink density; in the recovered material, on the other hand, the crosslink density decreased and softening degradation occurred, with decrease in the molecular weight of the polymer. This bears out the above
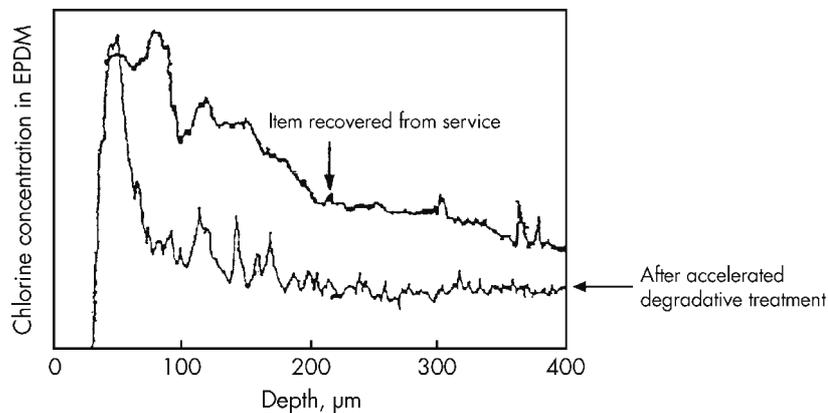

Figure 4. Chlorine distribution profile in the direction of depth by EPMA

findings of hardness measurements on the surface with a microhardness meter, in which the recovered item showed a tendency to much reduced hardness compared with the unused item.

The findings thus point to a very different reaction mechanism in the degradation of recovered material, where degradation occurs over a long time in a relatively mild environment, and accelerated degradation in high concentration residual chlorine. A further analysis of the degradation reaction mechanism was therefore made as follows.

2.2.4 FT-IR and Solid ^{13}C-NMR Analysis of Degradation Mechanism

The results of FT-IR observations on EPDM degraded by residual chlorine are shown in **Figure 5**. Thus, the material recovered from service gave a spectrum with C=O absorption at 1720 cm^{-1} and a well-defined absorption band at 1640 cm^{-1}, indicative of a C=C bond in the backbone chain, neither of which are seen in the unused material. At the same time, relative to the unused material, the results of ^{13}C-NMR (nuclear magnetic resonance) spectrometry showed an increase in peak intensity corresponding to a main chain methyl group (**Figure 6**) and suggested the possibility that main chain scission had occurred in the recovered material. **Figure 7** shows the mechanism of degradation of EPDM packing recovered from service as deduced from the results of the above FT-IR and ^{13}C-NMR analysis. Stage 1 consists in adsorption of hypochlorous acid little by little from the mains water onto the CB compounded in the EPDM. In stage 2, chlorination would occur in material subjected to accelerated degradation,
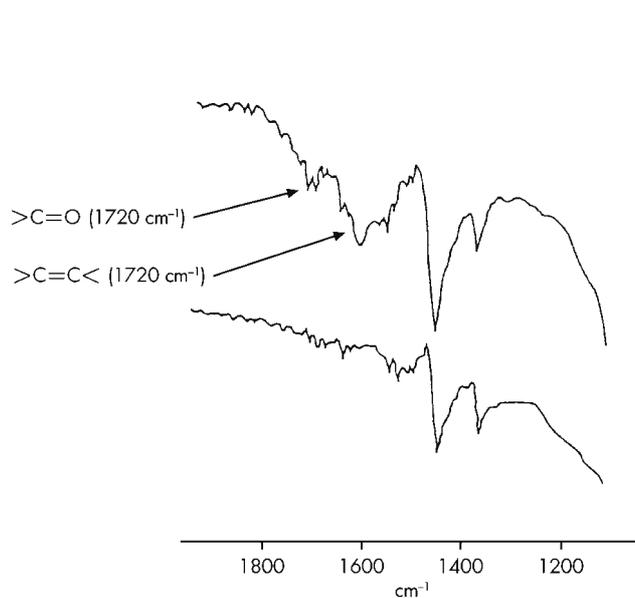
whereas in the recovered material >C=O groups form by oxidation. Proceeding to stage 3, degradation produces CH$_3$ and >C=C by disproportionation of free radical pairs formed by Norrish type I scission of the main chain. Thus, degradation was shown to be accompanied by a decrease in crosslink density and decline in molecular weight due to scission of the main chain, leading to partial breakdown or disintegration of the packing and giving rise to the black speck phenomenon.

2.3 Hardening Degradation of Packings Due to High Concentration Residual Chlorine [3]

When the container contents in a soft drinks factory are being switched from, say, coffee to Japanese tea, the containers are flushed with water containing chlorine at high concentration to eliminate odour. However, the packings used in the water line undergo hardening degradation, cracks then form, and the line leaks. As noted above, a rise in hardness and increase in crosslink density are seen first. A peak indicative of the C-Cl (2p) bond is detected in XPS (X-ray photoelectron spectrometry), while the results of ^{13}C-NMR show that methyl groups in the side chain of the diene component are chlorinated. The degradation mechanism was shown to comprise crosslinking degradation by the reaction scheme shown in **Figure 8**. In short, it was established that (1) the carbon black compounded in EPDM adsorbs chlorine, (2) the chlorine attacks the methyl groups in the side chain of the EPDM diene component, and (3) owing to chlorination of the methyl groups, interaction with other EPDM occurs, the crosslink density rises, the packing hardens, cracks form and water leaks.
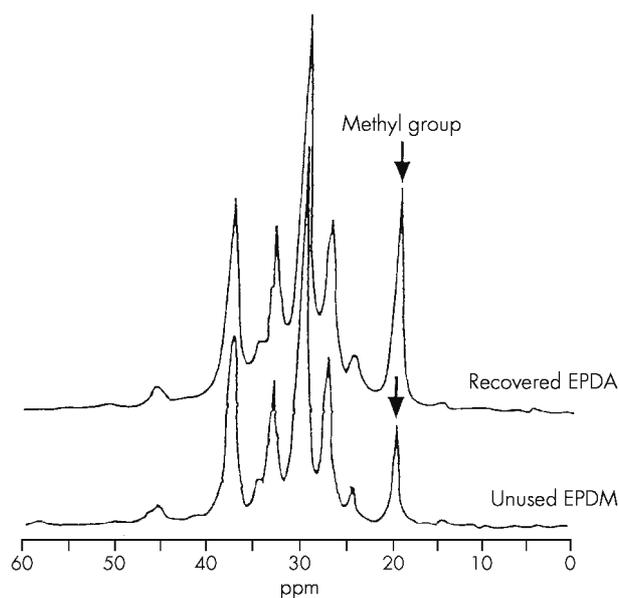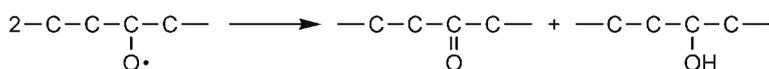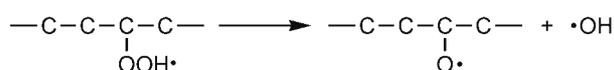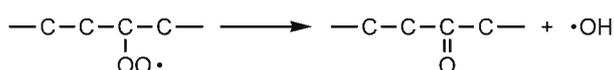

Figure 5. Comparison of FT-IR spectra of EPDM item recovered from service and unused EPDM item
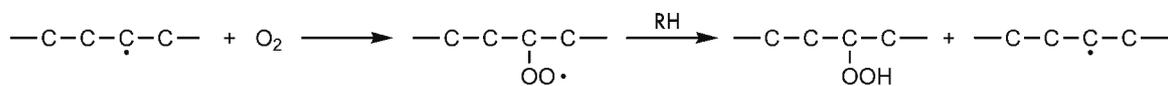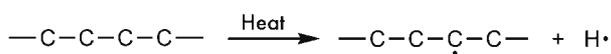

Figure 6. Comparison of solid ^{13}C-NMR spectra of EPDM recovered from service and unused EPDM

(1) Adsorption of residual chlorine into carbon black

(2) Oxidation by residual chlorine

$$2HClO \longrightarrow 2HCl + O_2$$

$$-C-C-C-C- \xrightarrow{\text{Heat}} -C-C-\underset{\bullet}{C}-C- + H\cdot$$

$$-C-C-\underset{\bullet}{C}-C- + O_2 \longrightarrow -C-C-\underset{\underset{OO\cdot}{|}}{C}-C- \xrightarrow{RH} -C-C-\underset{\underset{OOH}{|}}{C}-C- + -C-C-\underset{\bullet}{C}-C-$$

$$-C-C-\underset{\underset{OO\cdot}{|}}{C}-C- \longrightarrow -C-C-\underset{\underset{O}{\|}}{C}-C- + \cdot OH$$

$$-C-C-\underset{\underset{OOH\cdot}{|}}{C}-C- \longrightarrow -C-C-\underset{\underset{O\cdot}{|}}{C}-C- + \cdot OH$$

$$2-C-C-\underset{\underset{O\cdot}{|}}{C}-C- \longrightarrow -C-C-\underset{\underset{O}{\|}}{C}-C- + -C-C-\underset{\underset{OH}{|}}{C}-C-$$

(3) Decrease in molecular weight due to β-scission of polymer chain

$$-C-C-\underset{\underset{\bullet}{\overset{H}{|}}}{C}-C- \longrightarrow -C=C + \cdot C-C-$$

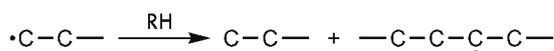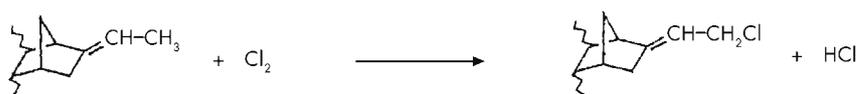$$\cdot C-C- \xrightarrow{RH} C-C- + -C-C-\underset{\bullet}{C}-C-$$

Figure 7. Mechanism of molecular fragmentation by residual chlorine in EPDM packings recovered from service in mains water
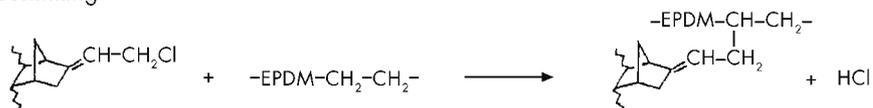
(1) Adsorption of residual chlorine into carbon black

(2) Chlorination of methyl group in side chain of diene component

(3) Hardening and depolymerisation of EPDM
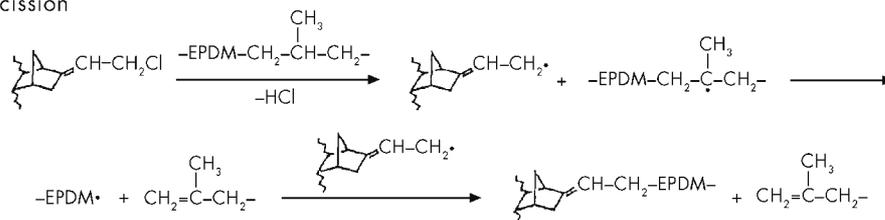
- **Crosslinking**

- **β-scission**

*Figure 8. Mechanism of EPDM degradation due to high concentration residual chlorine*

1) Crosslink density: Setting this on the high side suppresses increase in the rates of change of mass and volume, and is effective in preventing penetration of chlorine from the water into the rubber. A highish crosslink density in the range that preserves functionality as a rubber product is effective.

2) Carbon black: Adequate reinforcement can be imparted by choosing an FT carbon of low water absorption but lower reinforcing capacity, or using it in combination with highly reinforcing HAF black.

3) Silica: Acidic grades confer some chlorine resistance but alkaline grade silica inhibits chlorination and oxidation of the polymer and filler by neutralising the hypochlorous acid.

4) Age resistor: Choose an age resistor that does not leach into the water flow, e.g. one with a large molecular weight.

Although any one of (1)-(4) will impart resistance to chlorinated water, combinations of the measures should make it possible to design a compound for packings of good chlorinated water resistance in which a synergistic effect or extended service life can be expected.

3. DEGRADATION BY METALS, ESPECIALLY COPPER [5]

Susceptibility to metals denotes degradation of the polymer through the catalytic effect (redox reaction) of metal ions in promoting auto-oxidation of the polymer. Reaction is especially sensitive to copper: degradation is sufficiently promoted to warrant description as "copper attack", having a major impact on the polymer. It can even occur with the non-polar polymer polyethylene (PE) and the champion among resistant synthetic rubbers-fluorinated rubber.
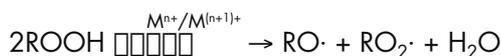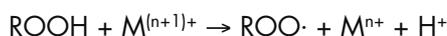
The order of effect of different metal elements on rubbers and plastics is as follows:

Co > Mn > Cu > Fe > V >> Ni > Ti = Ca = Ag = Zn > Al > Mg
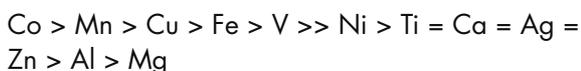
The metals of greatest effect, such as cobalt (Co) and manganese (Mn), usually have little opportunity to make contact with rubber and plastics in an everyday setting. However, the metals copper (Cu) and iron (Fe) are used in large amounts, and copper especially causes noticeable damage. There is often direct contact with these metals after forming: the sheathing of copper wire with polyvinyl chloride (PVC) or polyethylene (PE) is a good example. As we shall see later, recent demands for energy conservation have created many more opportunities for contact with copper because of its high thermal conductivity.

Likewise with rubber, when an NR rubber ring is hooked on a brass-plated catch, the material in contact with the plating becomes tacky and unserviceable in less than a week. The effect is due to molecular fragmentation, allowing the rubber to be sheared by the slightest force. When the rubber ring is hooked on an iron nail, on the other hand, nothing untoward happens. The brass used for plating is an alloy of copper and zinc (Zn), and although the copper concentration is lower than for pure copper, the NR contains double bonds in the polymer chain and is therefore susceptible to attack. We need to be aware of copper attack when designing materials. The damage by metals increases in severity the higher the temperature and humidity, high temperature additionally promoting thermo-oxidative degradation. The principle is as follows: the metal ions catalytically decompose hydroperoxide to free radicals by redox reaction, thus promoting chain reaction.

$$ROOH + M^{n+} \rightarrow RO\cdot + M^{(n+1)} + OH^-$$

$$ROOH + M^{(n+1)+} \rightarrow ROO\cdot + M^{n+} + H^+$$

$$2ROOH \xrightarrow{M^{n+}/M^{(n+1)+}} RO\cdot + RO_2\cdot + H_2O$$

In the initial stages the metal ions react directly with the polymer to generate free radicals. There has recently been an increase in the number of buildings fitted with installations that have an energy recycling function, aimed at conservation of the global environment; in long term use, metal ions elute from the copper heat exchangers, pipes, etc, and the metal ion concentration of the mains water rises. In particular, ionisation is encouraged by residual chlorine in the water and the higher temperature. This imposes harsh conditions on rubber O-rings and has an intimate bearing on the increase in water leakages. Furthermore, the metal combines synergistically with the previously considered degradation by residual chlorine in the water to cause even more severe degradation of the rubber. This is because copper ions penetrate the interior of the mouldings via voids and crazing in the partially chlorine-degraded and disintegrating rubber surface. It should be possible to increase endurance substantially by adding copper inhibitors to control metal attack (copper attack) and by raising the cure density above normal, as advocated to combat residual chlorine.

4. SHORT WAVELENGTH ULTRAVIOLET RADIATION AND OZONOLYSIS [6]

4.1 Mechanism of Ozone Degradation

Diene rubber products with double bonds in the polymer chain, such as NR, SBR and NBR, are highly vulnerable to attack by ozone. The recent deterioration in global environment is producing a gradual rise in the ozone concentration of the atmosphere (normally 0-4 pphm). Ozonolysis is a classic form of degradation and it has long been supposed that the sundry problems of

ozonolysis had been solved. However, deterioration in the global environment has given rise to a serious resurgence of the problem for rubber materials. First we need to consider how ozone and the short wavelengths of ultraviolet radiation are linked.

4.2 Mechanism of Formation of Ozone

The O_3 that occurs in nature is evolved as air ascends. The UV wavelength close to the earth's surface is at its shortest about 290 nm and O_3 does not form. This is because formation of O_3 requires the high energy carried by wavelengths of less than 240 nm; only then does O_2 dissociate to monatomic oxygen, which binds immediately with O_2 present in the vicinity to form O_3. This can be proven by switching on a low pressure mercury lamp emitting wavelengths below 240 nm, whereupon the odour of ozone immediately pervades the surrounding air. Sunlight carries a substantial dose of low wavelength radiation once the height above ground level exceeds 90 km: its action in dissociating O_2 to O is intense, and as there is little O_2 available, oxygen exists only as O. At 70 km above the ground, however, just the right amount of O_2 is present for O to produce O_3, and so a thick ozone layer is formed at 50-10 km, protecting the earth from harmful ultraviolet radiation. The ozone we normally encounter has been transported close to the earth's surface from the ozone layer in minute traces by meteorological factors. Since ozone is very highly oxidising, it had been presumed that this ozone, which oxidises dust and other pollutants, is immediately consumed in polluted areas of intense urban activity; thus, while the ozone level was high along the coast and in the mountains where the air is clean, almost no ozone could be found in cities. More recently, because a gas mixture of oxygen plus the NO_x and hydrocarbons discharged from motor vehicles is converted to ozone by short wavelengths (300 nm or less) even in the weak ultraviolet reaching the ground, the converse is happening and ozone is being evolved at high concentration in conurbations where NO_x is abundant. As remarked above, therefore, ozone damage is on the increase again.
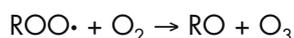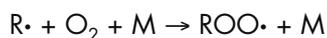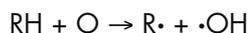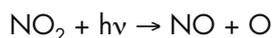
$$NO_2 + h\nu \rightarrow NO + O$$

$$RH + O \rightarrow R\cdot + \cdot OH$$

$$R\cdot + O_2 + M \rightarrow ROO\cdot + M$$

$$ROO\cdot + O_2 \rightarrow RO + O_3$$

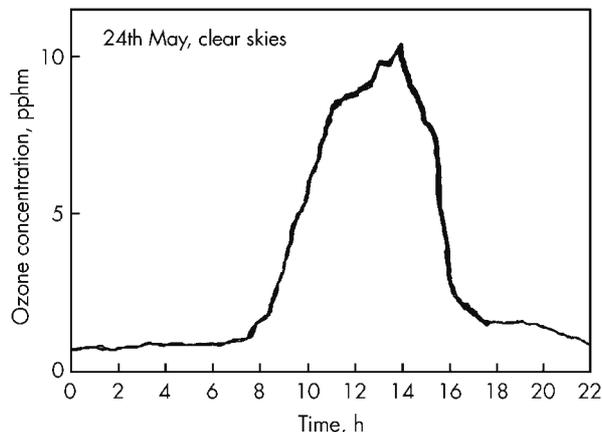**Figure 9**. Mechanism of ozone generation in urban environment

Figure 10. Around the clock variation in ozone concentration

Figure 9 shows the ozone generation mechanism for exhaust gas from urban vehicles. The variation in ozone concentration close to an urban intersection is illustrated in **Figure 10**.

4.3 The Action of Ozone on Diene Rubbers and the Crack Initiation Mechanism

Figure 11 shows the action of ozone on double bonds. Ozone attacks the double bond to produce an ozonide, which is unstable and cleaved at the O-O linkage, with formation of a zwitterion. Aldehyde or ketone is also formed. The intermediate products are stabilised by four routes [8]. As to the mechanism of ozone cracking initiation, on the other hand, opinions diverge. Generally speaking, a vulcanised rubber surface contains numerous minute flaws and irregularities in profile which are enlarged by elongation of the rubber. Ozone also has a great effect when residual stresses from forming and processing persist within the rubber. When the rubber is under elongation, the amount of ozone penetrating and rate of permeation-diffusion are large compared with the unstretched rubber; the ozone can then attack the double bonds in the defects directly, facilitating crack initiation. If the breaks in the molecular chain then recombine, crosslinking occurs and the polymer stabilises. Hence, if rubber is left in a high concentration ozone atmosphere in an unstretched state with the molecular chains unoriented, the surface hardens as a result of crosslinking; the material then feels solid to the touch, but since ozonolysis is a surface reaction and hardening is limited to the extreme outer surface, countless cracks develop the instant the slightest of stresses is applied.

Thus, the outer surface and interior will present completely different rubbery states. Inspection of appearance to identify microcrack initiation is a technique much used for routine appraisal of ozonolysis, but ozonolysis is in fact very difficult to appraise by observation since it coexists with fatigue (in which microcracks develop as in ozonolysis) and ordinary oxidative degradation.
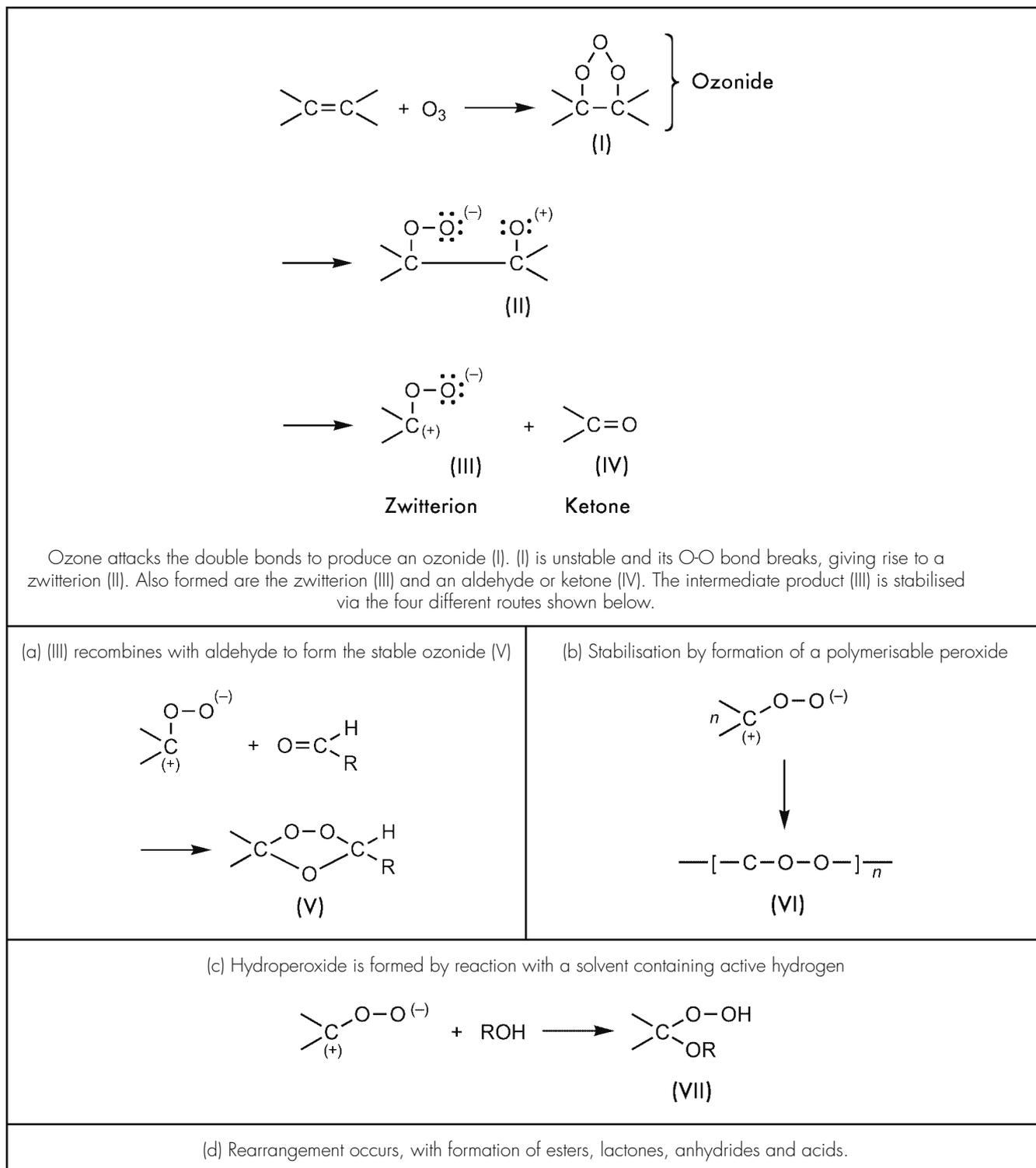
Ozone attacks the double bonds to produce an ozonide (I). (I) is unstable and its O-O bond breaks, giving rise to a zwitterion (II). Also formed are the zwitterion (III) and an aldehyde or ketone (IV). The intermediate product (III) is stabilised via the four different routes shown below.

(a) (III) recombines with aldehyde to form the stable ozonide (V)

(b) Stabilisation by formation of a polymerisable peroxide

(c) Hydroperoxide is formed by reaction with a solvent containing active hydrogen

(d) Rearrangement occurs, with formation of esters, lactones, anhydrides and acids.

Figure 11. Mechanism of reaction of ozone with double bonds

4.4 Appraisal of Ozonolysis by Examination of Appearance

From time to time, rubber products that have developed microcracks are brought to the author's laboratory at the Chemicals Evaluation and Research Institute for appraisal of this kind. **Figure 12** shows a typical scanning electron micrograph of the surface in ozone-degraded NBR. Countless microcracks have formed in the surface. Characteristically, examination of the cross-section reveals the presence of countless cracks, just as at the surface. The worrying aspect of ozone cracks is that each grows a little at a time by a process of stress concentration from the exterior, sooner or later acting as the starting point for bulk fracture.
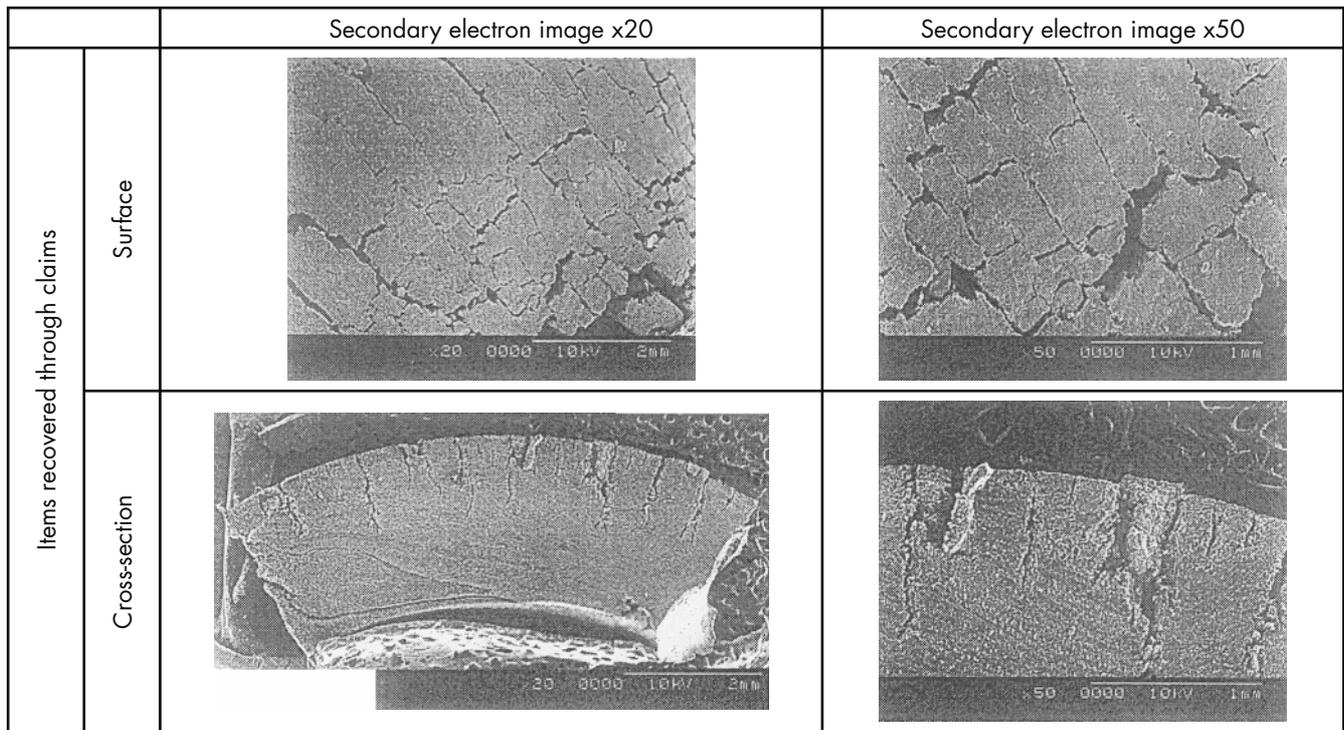
		Secondary electron image x20	Secondary electron image x50
Items recovered through claims	Surface		
	Cross-section		

Figure 12. Typical scanning electron micrograph of the surface of ozone degraded NBR

4.5 FT-IR Microscopy (Fourier Transform Infrared Spectral Analysis)

The difference between fatigue degradation and ozonolysis is that ozonolysis is characterised by the appearance of prominent absorption by hydroxyl groups (OH) at 3400 cm^{-1} in assessment by surface reflection. The appearance of this absorption is a characteristic result of ozonolysis in diene rubber and affords an extremely effective way of assessing degradation. Although it occurs after only a short time in the presence of ozone, the reaction responsible is a typical surface reaction, i.e. it does not extend into the interior of the rubber layer. It can therefore be efficiently detected by surface reflection mode FT-IR microscopy.

Since a large amount of carbon black is invariably added as reinforcer to diene rubbers, the IR beam is absorbed in surface reflection analysis by conventional FT-IR, making it virtually impossible to obtain a good information signal. In reflection mode microscopy, however, the beam from the light source is stopped down by a beam condenser to a diameter of several tens of nm and therefore supplies intense light energy per unit area; this means that a reflection spectrum carrying a whole range of information is easily obtained.

Figure 13 compares the spectra of an unused diene rubber (NBR) and material that has undergone ozone cracking by surface reflection mode FT-IR microscopy. For assessment of ozonolysis, it is preferable to combine the two methods, i.e. FT-IR and SEM observation of the
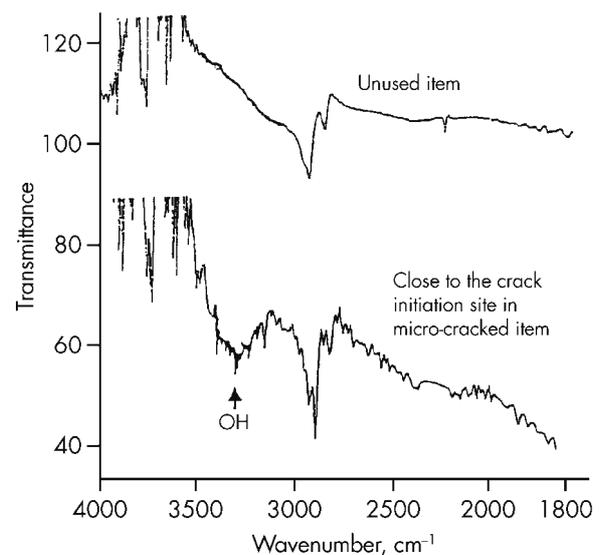
Figure 13. Comparison of spectra of unused item and ozone cracked material by surface reflection mode FT-IR microscopy

state of cracking on the surface and cross-section as shown above.

In fatigue degradation, peroxy radicals are generated in the polymer before cracks form by fatigue fracture; stress then promotes fragmentation of the polymer oxy-radicals formed by auto-oxidation, facilitating formation of terminal groups. Consequently, the concentration of the terminal groups shown in **Table 2** increases. In

Table 2. Terminal groups formed by fatigue degradation

$-CH=CH_2$	$(910\ cm^{-1})$
$-CH_3$	$(1397\ cm^{-1})$
$-COOH$	$(1710\ cm^{-1})$
$-COH$	$(1735\ cm^{-1})$

Figure 14. Time to ozone crack initiation in relation to change in HNBR (iodine number)

physical terms, fatigue in cured rubber entails scission of vulcanization bonds and a decrease in crosslink density; it is therefore desirable to look for depression of the glass transition point by DSC (differential scanning calorimetry). In ozonolysis, on the other hand, we have seen that degradation is a surface reaction, and measurement of glass transition point therefore requires a sample of at least 5 mg; as it is impossible to detect a change, no depression in glass transition point is observed.

4.6 Measures to Combat Degradation

Anti-ozone measures have already been implemented in products such as belts. HNBR is used for this purpose, since its polymer is resistant to ozone. Satisfactory resistance is thereby obtained to ozone at the concentration levels that have prevailed over the past decade or so. However, because of environmental deterioration, the ozone concentration in the environment has now increased to the stage where present means of combating ozone are simply overwhelmed.

Specifically, this means "highly hydrogenated HNBR" of stronger ozone resistance must be chosen as the polymer. **Figure 14** shows the relation between the fractional hydrogenation (iodine number) of HNBR and the time to ozone cracking. Ozone resistance increases the more highly hydrogenated the HNBR. This approach naturally entails the design of compounds resistant to ozone. Under static conditions, for instance, compounds are easily designed by combining paraffin waxes of different molecular weight with microcrystalline wax which, while slow to bloom, provides a protective film permitting highly stable and enduring control of ozonolysis.

The above approach is not so effective for "dynamic rubber". Under dynamic conditions, "compound design combining amine-based age resistors" is effective for preventing ozonolysis. For instance, with the more ozone-sensitive NR and NBR, the *p*-phenylenediamine age resistors IPPD and 6PPD may be combined. This combination is effective for NBR. NBR itself is a polar rubber, bloom is minimal, and hence while not as effective as with NR and SBR, the action lasts for a long time. Ozonolysis is often seen in items making contact with air, for example at "sites much exposed to the outside air" in the case of automotive components, or pneumatic control components such as diaphragms and packings.
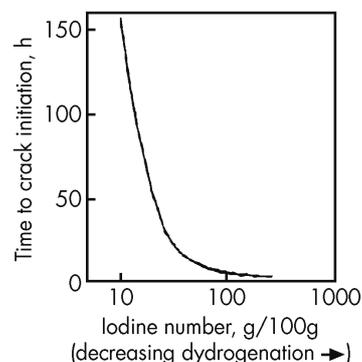
The aforementioned solution of compound design is hence to be recommended and should afford a longer service life.

5. CONCLUSIONS

Recent summers have been exceptionally warm, setting new records. This change in global environment is in turn producing all kinds of "change" in our immediate surroundings. In the local rice fields in Tochigi Prefecture where the writer lives, the hull comprising the outermost shell of the grain has been growing appreciably longer and thicker than hitherto to protect the kernel from the exceptional heat [9]. Like rice, the organic materials rubber and plastics will have to adapt if they are to be protected from changes in the global environment. Likewise with mankind, the incidence of cataract in the elderly is increasing in response to shorter wavelength radiation. This has meant that we ourselves are now having to use sunglasses.

Many different highly functional polymers are now marketed. However, to hold down the cost of responding to environmental challenge, we should not forget the orthodox approach of modifying existing, inexpensive polymers.

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