ANTIOXIDANTS FOR ROADING BITUMEN

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CONTENTS

EXECUTIVE SUMMARY

1. Literature Review

Antioxidants are chemical compounds that, if added to organic materials such as oils, rubber and plastics, delay or reduce the rate of degradation caused by chemical reaction with atmospheric oxygen (autoxidation). The age hardening of bitumen through autoxidation is a major factor limiting the lifetime of chipseal roadways, particularly those with low traffic volumes.

The technical literature up to 1994 dealing with the use of antioxidants to decrease the rate of age hardening in bitumen used for roading chipseals is reviewed. The aim of the review was to establish to what extent the effects of conventional antioxidants on roading bitumens had been investigated, and if their use would extend the lifetimes of New Zealand chipseals.

The general weight of evidence from laboratory studies is that various conventional antioxidants do decrease the rate of age hardening compared to bitumens without antioxidants. The improved performance is significant if translated to actual surfacing lifetimes, but small compared to the improvements often found in other materials such as polymers and lubricating oils. Considerable inconsistencies and contradictions were also found between different studies, which probably reflects the different accelerated aging (oxidation) methods used and the particular bitumens studied.

Much of the work reported does not adequately consider interfering effects such as volatisation or dispersion of the antioxidants during mixing and accelerated aging. The additives' initial effect on bitumen viscosity is also often not properly taken into account. Virtually no research has been done on the chemistry of the antioxidant–bitumen system to attempt to understand why some additives are more effective than others or to explain the general lack of effectiveness compared to antioxidants in other materials subject to autoxidation.

2. Dialkyl Dithiocarbamate Compounds

Lead dialkyl dithiocarbamate compounds showed considerable promise in laboratory studies and lead diamyl dithiocarbamate (LDADC) has been used in field trials in Australia. After five years LDADC has reduced the rate of hardening by 16% (at 2.5% concentration) and 31% (at 5% concentration). At the 5% LDADC level the reduced rate of hardening translates to an estimated increase in seal life of up to 64% (or seven years) for only an approximately 25% increase to the cost of the seal.

7

3.   Hydrated Lime

Hydrated lime ($Ca(OH)_2$) has been shown in laboratory studies to decrease both the rate of oxidation and viscosity increase of roading bitumens. Lime appears to act by absorption of polar species which would otherwise contribute to viscosity increase. Field data on asphaltic mixes tend to confirm the laboratory findings but are not conclusive. A field trial of hydrated lime in chipseal was constructed in Australia in the early 1980s. Although the trials have not been pursued due to inconsistencies in their behaviour, the effect of lime appeared to be limited.

4.   Conclusions

At present the evidence is insufficient to warrant the large scale use of conventional antioxidants or hydrated lime to increase seal lifetimes in low trafficked areas. This review has highlighted the lack of published basic research on the chemistry of antioxidant–bitumen systems. Given the potential benefits of antioxidants in terms of increased seal life, such research would be well justified.

5.   Recommendations

- The progress of the lead diamyl dithiocarbamate (LDADC) trials presently (1994) underway in Australia should be monitored to determine if the current improvement in performance is maintained.

- Construction of full scale field trials at this stage is probably not warranted. However, inclusion of hydrated lime and LDADC samples in the exposure rack trials being monitored under Transit New Zealand Project PR3-0105 should be considered. This will provide valuable information (at a negligible cost) on performance of these materials in New Zealand conditions.

- Research into the chemistry of antioxidants in bitumen at the mechanistic level should be undertaken. This is considered essential to properly understand and develop effective antioxidants for use with roading bitumens. Research in this area is justified on the basis of the large financial savings to be made from even small increases in chipseal lifetimes.

ABSTRACT

The technical literature up to 1994 dealing with the use of antioxidants to decrease the rate of age hardening in bitumen used for roading chipseals was reviewed. Laboratory studies showed that in some cases bitumen treated with antioxidants have reduced hardening rates due to oxidation compared to control bitumens.

Much of the work reported does not adequately consider interfering effects such as volatisation or dispersion of the antioxidants during mixing and accelerated aging. The additives' initial effect on bitumen viscosity is also often not properly taken into account. Virtually no research has been done on the chemistry of the antioxidant–bitumen system to attempt to understand why some additives are more effective than others or to explain the general lack of effectiveness compared to antioxidants in other materials subject to autoxidation.

Lead dialkyl dithiocarbamate (LDADC) compounds showed promise in laboratory studies. One of these compounds was used in field trials in Australia, and after five years the rate of hardening was reduced by 31% at 5% concentration. This reduction was translated to an estimated increase in seal life of 64%, or seven years. In laboratory studies hydrated lime $(Ca(OH)_2)$ has decreased the rate of oxidation and viscosity increase of roading bitumen, but its effect appeared to be limited in the field.

Basic research on the chemistry of bitumen antioxidant systems is lacking even though, given the potential benefits of increased seal life, such research would be justified.

1. INTRODUCTION

Many organic materials degrade through chemical reaction with atmospheric oxygen (autoxidation). This process is the cause of the deterioration of plastics and rubber, the breakdown of lubricants, and the rancidification of edible oils. It is also the principal cause of the age hardening of roading bitumen which is probably the major factor limiting the lifetime of most low trafficked chipseal roads (i.e. most of the roading network).

To delay or reduce the rate of autoxidation of organic materials, a large number of chemical compounds, i.e. antioxidants, have been developed that can be added to the material, and usually require only a few percent by mass to be effective. Although the use of antioxidants in lubricating oils and polymer materials is a well established and routine practice, they are not known to be used in roading bitumen. The cost of antioxidants is generally similar to that of adhesion agents (per kg). Thus, given that the basic chemistry of bitumen autoxidation is generally assumed to be closely related to that of lubricating oils and other hydrocarbons, it would seem that antioxidants developed for use in these other materials should also be of use in delaying the rate of bitumen age hardening.

The technical literature up to 1994 dealing with the use of antioxidants to decrease the rate of age hardening in bitumen used for roading chipseals is reviewed. The review covers the lead antioxidant chipseal trial established in 1986 in Australia by the Australian Road Research Board (now ARRB Management Research), and also the reported effects of hydrated lime in reducing bitumen hardening during asphalt manufacture. The aim of the review was to establish to what extent the effects of conventional antioxidants on roading bitumens had been investigated, and if their use would extend the lifetimes of New Zealand chipseals.

2.   AUTOXIDATION MECHANISM

Only a general outline of the autoxidation process is given below; and a more detailed discussion of the mechanism is given in Appendix 1.

Autoxidation is a chemical process which takes place at ambient temperatures between organic compounds and atmospheric oxygen (Scott 1965, Hawkins 1972). The process takes place by a chain reaction involving chemical species called free radicals.

Initially free radicals are formed through a variety of mechanisms including the action of metal ions (e.g. the vanadium present at trace levels in bitumen), ultraviolet light, and the decomposition of peroxide compounds. Once formed, these free radicals react rapidly with oxygen to form new radicals which react in a variety of ways in a complex chain process. In bitumen this process gives rise to a variety of different reaction products (Petersen 1986, Bell 1989, Herrington et al. 1994), including polar oxygen-containing compounds such as ketones, sulphoxides and carboxylic acids, and results in a hardening of the material.

In many instances autoxidation obeys the behaviour shown in Figure 1a. The first part of the curve is known as the induction period. Free radicals formed are being consumed by natural inhibitor compounds often present in low concentrations, and/or free radical reaction products must build up to a significant level before significant chain reaction occurs. As these inhibitors become exhausted and the levels of free radicals and products (hydroperoxides) increase, the reaction becomes auto-catalytic and the rate of reaction increases markedly. Finally as the availability of reactive sites in the substrate decreases, the overall rate of reaction subsides.

Roading bitumen does not exhibit an induction or auto-catalytic period (Figure 1b) (Ronvaux-vankeerbergen and Thyrion 1989, Herrington et al. 1994, Petersen et al. 1993, Knotnerus 1972). The hyperbolic shape of the bitumen curve may be related to the formation of oxidation inhibitors (auto-retarding) or more likely is related to the depletion of readily oxidisable species. Recent work suggests that the gradual decrease in oxidation rate is not due to oxygen diffusion effects (Petersen et al. 1993), because bitumens aged at the same temperature under air and high pressure oxygen (300 psi) tend to the same asymptote (Herrington et al. 1994). However, considerable work has to be done before the processes involved are fully understood.
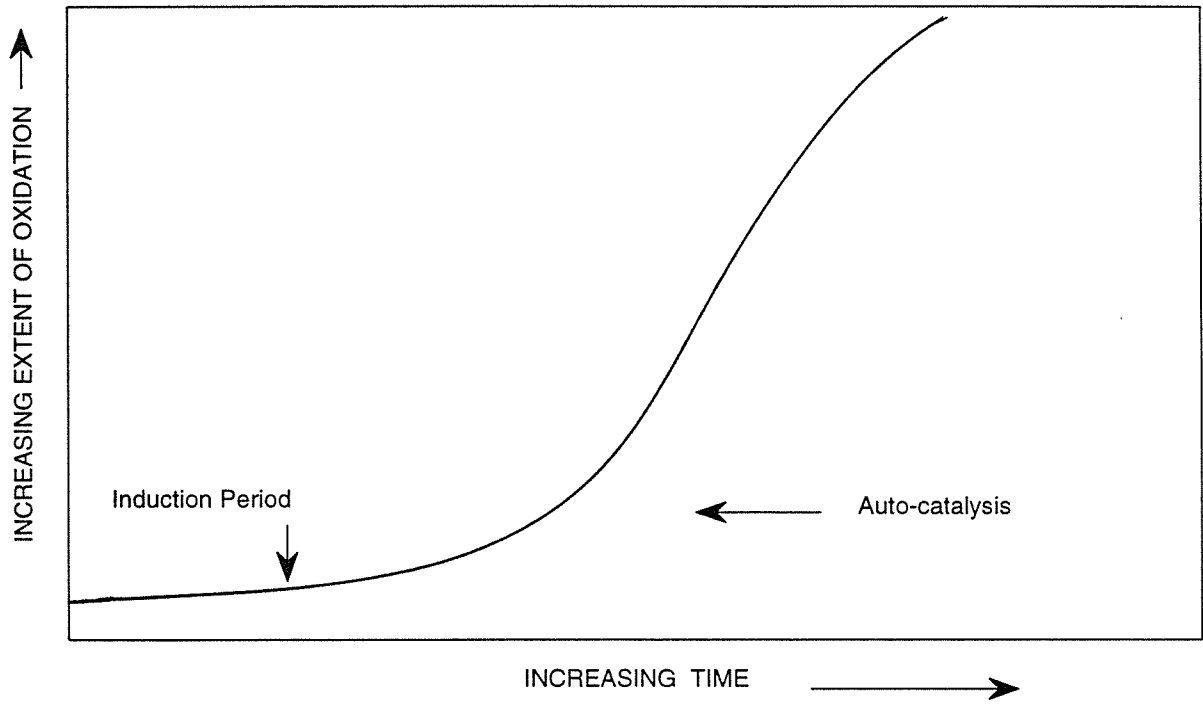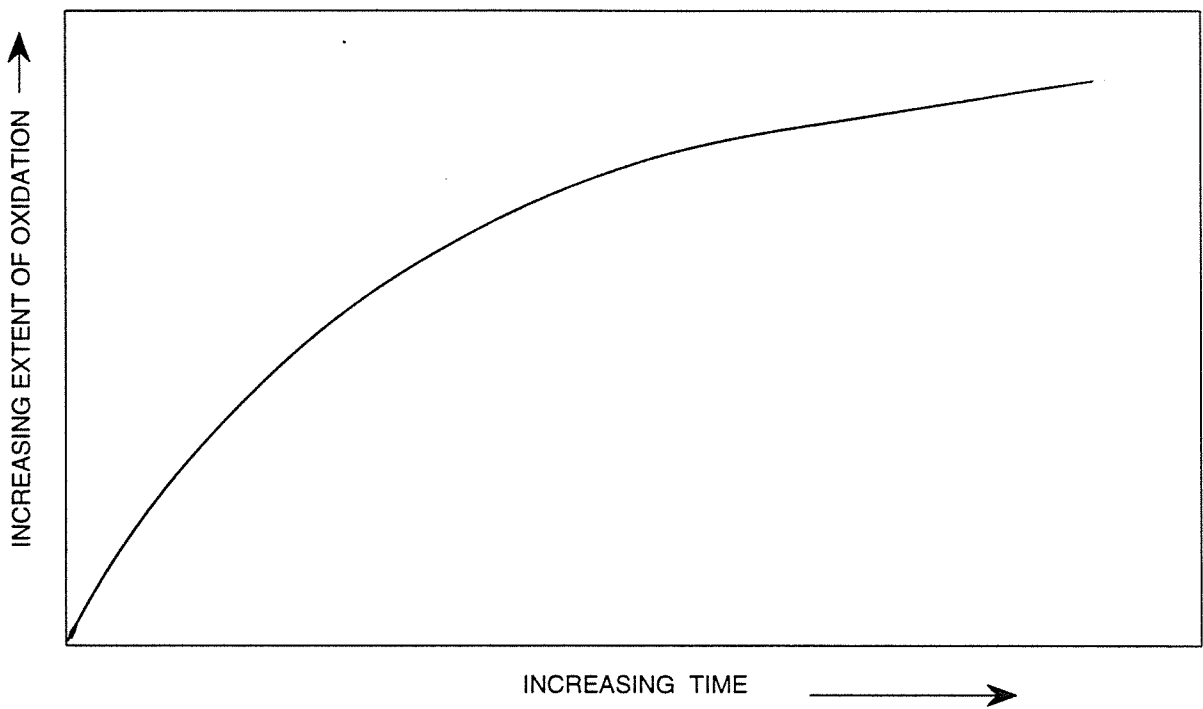
Figure 1a.   Typical autoxidation behaviour.

Figure 1b.   Autoxidation of bitumen.

3. ANTIOXIDANT MECHANISMS

Chemical antioxidants function by two principal mechanisms (Hawkins 1972, Ranby and Rabek 1979, Allen 1986, Brydson 1989):

- preventive antioxidants which in some way inhibit or retard the formation of free radicals in the initiation step; and

- chain-breaking antioxidants which interrupt and stop or retard the chain reaction process.

Preventive antioxidants slow oxidation without changing the overall mechanism, and consist of three main classes (examples are given in Figure 2) based on their mode of action:

- peroxide decomposers
- metal deactivators
- ultraviolet light absorbers

Chain-breaking antioxidants function by introducing competitive processes in the chain reaction. Two main classes of chain-breaking antioxidants (examples are shown in Figure 3) are widely used today:

- amines and
- phenols.

The mechanisms of action of both antioxidation types are discussed in more detail in Appendix 1.

The selection of a particular antioxidant will depend on the product end use and other factors such as toxicity, colour and physical properties. Some antioxidants can also operate by more than one mechanism, and in some cases combinations of different antioxidants have a greater effect than equal concentrations of either individual compound - an effect known as synergism. Another illustration of the complexity of antioxidant chemistry is the fact that above a certain optimum concentration many chain-breaking antioxidants actually act as pro-oxidants, i.e. they accelerate the rate of oxidation.

Depending on the exact mechanism of reaction, chain-breaking or preventive antioxidants are consumed after which oxidation proceeds as if no inhibitor was present. Chain-retarding antioxidants may, in some cases, regenerate and continue to function independently. The relationship between the different modes of action are shown schematically in Figure 4 (Brydson 1988).

Figure 2.   Examples of preventive antioxidants.

Examples or Representative Structure

Peroxide Decomposers

Metal dialkyl dithiocarbamates

$$R-N-\overset{\overset{\displaystyle S}{\|}}{C}-S-M-S-\overset{\overset{\displaystyle S}{\|}}{C}-N-R$$
$$\underset{R}{|} \qquad\qquad\qquad \underset{R}{|}$$
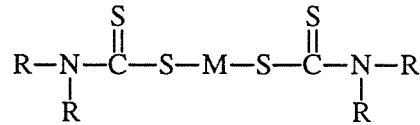
Thiols
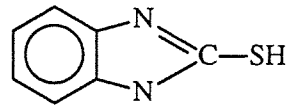
(2-mercaptobenzimidazole)

Metal dialkyl dithiophosphates

$$R-N-\overset{\overset{\displaystyle S}{\|}}{P}-S-M-S-\overset{\overset{\displaystyle S}{\|}}{P}-N-R$$
$$\underset{R}{|} \qquad\qquad\qquad \underset{R}{|}$$
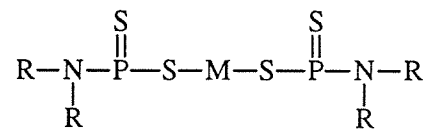
Phosphite esters $(PO)_3P$
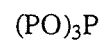
Phenyl sulphides
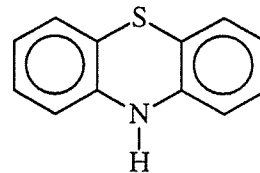
(Phenothiazine)

Metal Deactivators

Chelating agent

$CH=NCH_2CH_2N=HC$
(N,N'-(disalicylidene)ethylenediamine)

Ultraviolet light absorbers

Salicylates

Benzophenones

15
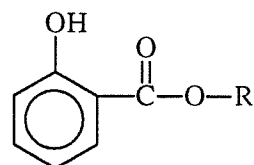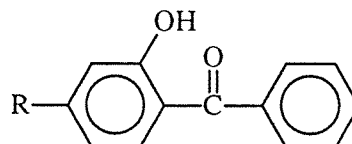
Figure 3.   Examples of chain-breaking antioxidants (free radical traps).

Examples or Representative Structure

<u>Secondary Diarylamines</u>

Ar—NH—Ar

Phenyl napthylamines
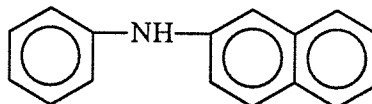
(N-phenyl-2-napthylamine)

Para-phenyl diamines
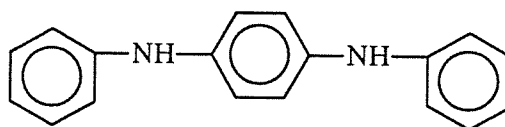
(N,N'-diphenyl-p-phenylenediamine)

<u>Ketone-Amine Condensates</u>

Diahydroquinolines

C_2H_5O

CH_3

CH_3

CH_3
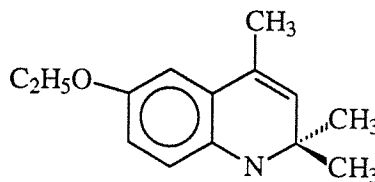
(6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline)

<u>Alkyl Aryl Secondary Amines</u>

Ar—NH—R—NH—Ar

<u>Hindered Phenols</u>

OH

$(CH_3)_3C$ $C(CH_3)_3$

CH_3
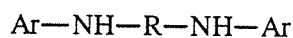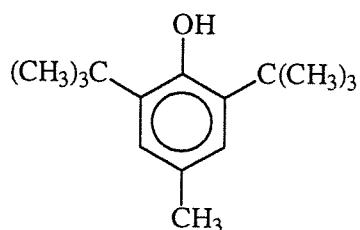
(4-methyl-2,6-di-t-butylphenol)

<u>Hindered Bisphenols</u>

OH   OH

R CH_2 R

R   R
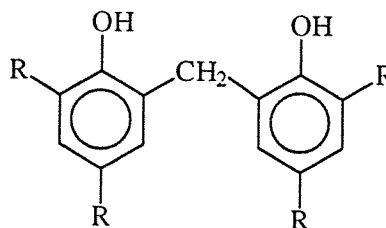
Figure 4.   Behaviour of preventive and chain-breaking antioxidants.
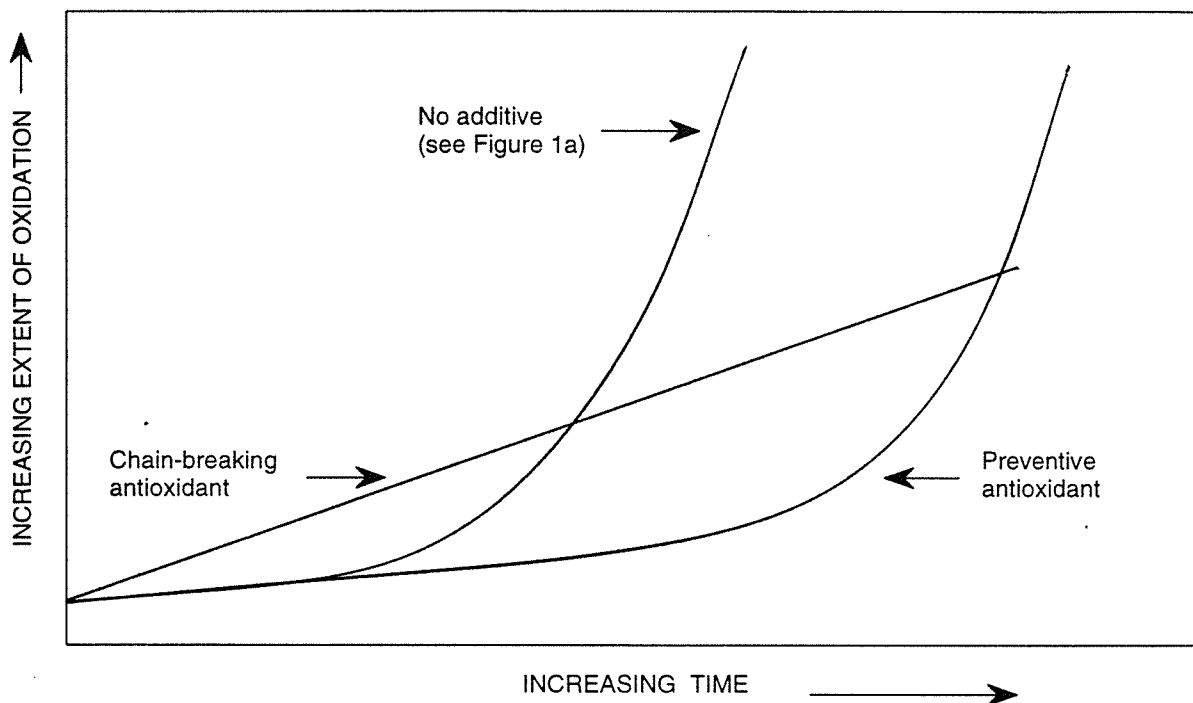
The effectiveness of an antioxidant will depend, in the first instance, on the significance of the process it inhibits on the overall oxidation chemistry. For example, ultraviolet light absorbers will be of little benefit if that is not a major initiation pathway. Similarly, chain-breaking antioxidants will have more effect on systems where the uninhibited kinetic chain length is normally very long (i.e. the number of oxygen molecules reacting per initiation step). Efficient chain-breaking stabilisers will reduce the chain length to a low value approaching unity.

4. CONVENTIONAL ANTIOXIDANTS USED IN ROADING BITUMENS

4.1 Laboratory Investigations

Investigations with the application of antioxidants successfully used in rubber, polymers and lubricating oils have been carried out since the 1950s. These studies principally consist of measuring the effect of a range of antioxidant types on laboratory aging. The selection of the particular antioxidants studied is usually made on the basis of successful application in polymers and lubricating oils.

Comparison of these studies is complicated by the many and varied techniques used to both measure and accelerate aging, and the large number of different bitumens studied.

In most cases oxygen uptake has not been measured directly, and in some cases parameters are measured which may also be affected by other factors.

4.1.1 Beitchman (1959) Study

Beitchman (1959) measured weight loss, softening point and degree of cracking of roofing bitumen films in a weatherometer (an instrument using heat, UV light and water sprays to simulate natural weathering). Aging appears primarily to be induced by UV light, and the temperature of aging is not reported. The antioxidants listed in Table 1 were studied. The author found that, although both peroxide decomposers and chain-breaking antioxidants reduced weight loss to some degree, only peroxide decomposers showed any effect on durability (time for crack formation in the bitumen films) and the observed effects were bitumen dependent.

The most effective compound was the peroxide decomposer, phenothiazine especially if used, with the free radical inhibitor N-phenyl-2-napthylamine (Table 2). However, the effect of the additive varied greatly with the bitumen studied. For example, 2% phenothiazine in bitumen B increased the durability by 500% compared to only an 11% increase for bitumen C at the same concentration.

One drawback of the method used by Beitchman to measure bitumen durability is that the influence of the likely softening effect of the additives on this parameter is not known. The increased durability caused by physical softening cannot be separated from that caused by a chemical antioxidant effect.

Table 1.   Compounds used in the antioxidant studies of Beitchman (1959).

Type	Compound
Peroxide decomposers	Phenothiazine Butyl sulfone Butyl sulfide Phenyl sulfide
Free radical inhibitors	Resorcinol Hydroquinone Diphenylamine t-butyl phenol N,N-diethyl-p-phenylenediamine α-napthylamine N-phenyl-2-napthylamine

Table 2.   Activity of phenothiazine in the antioxidant studies of Beitchman (1959).

Bitumen	Phenothiazine concentration (%)	Softening point (°C)	Durability (average hour to failure)	Average weight change at 549 hours (%)
B	0.0	105	639	−8.45
	0.5	105	692	−5.45
	1.0	103	880	−2.23
	2.0	100	3180	+0.323
C	0.0	-	1210	−3.31
	1.0	-	1361	−3.28
	2.0	-	1340	−0.90
D	0.0	-	1608	−6.32
	1.0	-	1718	−4.02
E	0.0	-	815	−6.43
	1.0	-	859	−4.29
	2.0	-	880	−0.83
F	0.0	-	1450	−4.69
	1.0	-	1540	−3.45

4.1.2 Wurstner et al. (1960) Study

Wurstner et al. (1960) investigated antioxidants with roading bitumens using the thin film oven test and the California shot abrasion test (State of California 1978). The latter consists of measuring the weight lost from asphalt mixes after abrasion with steel shot. Some of the compounds used in this study are not adequately identified, but those that are are listed in Table 3.

Table 3.   Compounds used in the antioxidant study of Wurstner et al. (1960).

Type	Compound
Peroxide decomposers	Phenothiazine Dodecyl mercaptan
Free radical inhibitors	Alkyl phenylenediamine Aryl phenylenediamine t-butyl pyrocatechol Hydroquinone σ-amino phenol Phenyl-β-napthylamine σ-nitrophenol

Results showed the compounds tested to have no significant antioxidant effect. Some compounds, such as phenothiazine, demonstrated a pronounced pro-oxidant effect at 1.5% concentration in direct contradiction to Beitchman's (1959) findings. This may be a function of both differences in the bitumens studied or of the methods used.

These results must be viewed with caution as the additives produced very significant physical softening of the initial binders and the possibility that this effect is influencing correct interpretation of the abrasion test results is not adequately discussed. In addition, the high temperature of the thin film oven test (TFOT) may have resulted in excessive loss of some additives through evaporation.

4.1.3 Martin (1966) Study

Martin (1966) studied eight different bitumens (25°C penetration of 20 to 40) with 12 antioxidants at 1-2% concentration. The bitumens were from three sources; two were refined from Venezuelan and Kuwaiti crudes, the third was naturally occurring Trinidad Lake bitumen. Bitumen films (40 μ thick) were oxidised at 300 psi of oxygen and 65°C for 72 hours. Other samples were exposed outdoors. The antioxidants studied are given in Table 4.

In addition to compounds operating by the mechanisms discussed in Appendix 1, various alkalis were also studied. It was proposed that these may operate by neutralising acids formed as oxidation products (see Section 7.3 for further discussion on hydrated lime). After oxidation of the bitumens, viscosity measurements at $30\,^\circ C$ and $10^{-4}s^{-1}$ were made and ratios of viscosity before and after aging were calculated. The precision of these measurements is not stated.

Table 4.   Compounds used in the antioxidant study of Martin (1966).

Type	Compound
Free radical inhibitors	Phenyl-β-napthylamine 4-methyl-2-6-di-t-butylphenol Mixed arylamine NN-DI-sec-butylphenylenediamine
Peroxide decomposers	Phenothiazine Tetramethylthiuram disulphide Mercaptobenzothiazole
Ultraviolet absorbers	2,2'-dihydroxy-4-methoxybenzophenone
Alkalis	Sodium hydroxide Sodium carbonate Magnesium metal

All of the additives produced some reduction of hardening rate though none were more effective in controlling oxidation in the dark, while both peroxide decomposers and free radical inhibitors were equally effective in the outdoor exposure trial. Some of the additives had a pro-oxidant effect. The ultraviolet absorbers performed poorly in the outdoor exposure trial. This was attributed to the high coefficient of absorption of bitumen and because the wavelengths that activate bitumen oxidation extend well beyond the ultraviolet into the visible region. In later studies (Martin 1968, 1971) 33 antioxidants were investigated (see Table 5). Unfortunately many of these were not particularly well defined chemically.

Oxidation was carried out as described for Martin's (1966) study discussed above. Results obtained for an air-blown Kuwaiti bitumen ($25\,^\circ C$ penetration of 28, softening point $72\,^\circ C$) are presented in Table 5. The data have been recalculated to show the percentage change in viscosity ratio (i.e. hardening index).

All the free radical inhibitors and half of the peroxide decomposers showed antioxidant activity, the former being more effective in photo-oxidant conditions. None of the additives were so effective as to confer an induction period on the reaction. The metal deactivating agents had little effect and this was ascribed to naturally occurring vanadium and possibly nickel being present as co-ordinated complexes and not available for reaction.

Of particular interest is that ferric chloride, zinc chloride and aluminium chloride at 2% concentration, which can be used to promote hardening during air blowing operations, were not pro-oxidant under the ambient and near ambient temperatures used in this study. This suggests that the role of trace metal contaminants in promoting bitumen autoxidation may be negligible and certainly warrants further investigation.

Martin also investigated potential synergism of antioxidant combinations and found no pronounced effects though the phenothiazine, N-phenyl-2-napthylamine combination, found effective by Beitchman (1959), was not studied. The most effective compound, zinc diethyl dithiocarbamate, was also found to be effective in Arabian (25°C penetration of 87, softening point 49.5°C) and Kuwaiti (25°C penetration of 90, softening point 48°C) roading grade bitumens. The ethyl compound was found to be more effective than methyl, butyl or benzyl derivatives.

Notes to Table 5 (on opposite page):

[a]   Compound type F   =   free radical inhibitor
                      P   =   peroxide decomposer
                      M   =   metal deactivator
                      C   =   alkylation catalyst
[b]   Powder
[c]   Liquid
[d]   Hardening index = <u>viscosity at 30°C $10^{-4}s^{-1}$ after oxidation</u>
                                        initial viscosity
[e]   65°C 300 psi oxygen
[f]   Outdoor exposure

Table 5. Compounds used in the antioxidant study of Martin (1968).

Compound	Type[a]	Change in hardening index[d] (%)	
		Thermal oxidation[e]	Photo-oxidation[f]
Nil	F	-	-
1-phenyl-β-naphthylamine	F	−33	−50
1-phenyl-α-naphthylamine	F	−28	−52
2,3-dimethyl-6-tert-butyl phenol	P	+1	−54
Dibenzthiazyl disulphide	M	−23	−43
N,N disalicylidene-1,2-diaminopropane	F	−13	−53
Acetone diphenylamine condensate	F[b]	−36	−53
Acetone diphenylamine condensate	F[c]	−5	−32
Tert-butyl cresol	F	−31	−47
N,N-di-2-naphthyl-p-phenylenediamine	F	−32	−47
N-phenyl-N-isopropyl-p-phenylenediamine	F	−36	−35
Tetraethyl thiuram disulphide	P	−6	−33
Bis-salicylidene-1,2-diaminoethane	M	−33	−51
Octylated diphenylamine	F	−14	−57
N,N-di-2-napthyl-p-phenylenediamine with 2 mercaptobenzimidazole	M	−6	−30
2 mercaptobenzimidazole	P	−23	−46
Phenol amine aldehyde condensate	F	−5	−58
Lead monoxide	P	−31	−56
Substituted xylenol	F	−13	−40
Ferric chloride	C	−33	−64
Complex phenol	F[b]	−34	−35
Xylenol aldehyde condensate	F	+27	−52
Aluminium chloride	C	−41	−48
Xylenol aldehyde condensate	F	−34	−55
Styrenated phenol	F	−14	−54
Zinc chloride	C	−28	−27
Complex phenol	F[c]	−15	−57
Phenothiazine	P	−18	−30
Mixed arylamines	F	−40	−52
Tribasic lead sulphate	P	−45	−65
Aldehyde ammonia ethyl chloride condensate	P	−41	−54
N,N-di-sec-butyl-p-phenylenediamine	F	−17	−26
Tetramethyl thiuram disulphide	P	−54	−52
Zinc diethyl dithiocarbamate	P	−65	−48
Phenanthroline	M	−30	−38

4.1.4 Januszke (1971) Study

Januszke (1971) also studied zinc and lead dialkyl dithiocarbamates as well as 22 other antioxidants (Table 6) and carbon black. Initial oxidation studies were carried out at 135°C for 24 hours using 20 micron films. The rate of viscosity (35°C, 0.05 s^{-1}) before aging to that after aging was used to evaluate antioxidant performance. The changes in hardening index using Januszke's results have been re-calculated and are also presented in Table 6. They show percentage decrease in hardening. Changes of less than 10% in this table are probably only experimental variation.

Most compounds show a significant decrease in hardening index though some show a pro-oxidant effect. A number of compounds have essentially no effect either way. ZDC and the corresponding lead compound (LDC) were found to be most effective, reducing the hardening rate by ~62%. Longer term exposure (13 days) of bitumen at 100°C with these two additives confirmed the initial findings. The stability of ZDC and LDC to bitumen handling temperatures was studied by heating the pure compounds at 150°C for three days. Weight loss was negligible and no differences in the infrared spectra were observed.

The effects of carbon black at ~4% concentration were less than that for ZDC, but hardening was reduced compared to the uninhibited bitumen. Various carbon blacks were tested and those with the greatest surface area were found to be most effective. Mixtures of carbon black and ZDC and LDC showed a synergistic effect, i.e. a 1:1 mixture of carbon black with either ZDC or LDC reduces the rate of hardening of asphalt more than the same concentration of either ZDC or LDC alone.

A number of other studies of the effect of carbon black in bitumens have been carried out (for example by Button and Little 1987, Lohrey 1992). However, the emphasis has been on the ability of the material to improve surfacing lifetimes through modification of physical properties (as with polymers) related to deformation of asphalt mixes and low temperatures rather than inhibition of oxidation. Given the known ability of carbon black to alter bitumen temperature sensitivity, the exact mechanism operating that gives rise to the findings of Januszke is not clear.

Table 6.   Compounds used in the antioxidant study of Januszke (1971).

Compound[a] (2% by weight)	Trade name	Change in hardening index[b] (%)
Zinc diisopropyl dithiophosphate		−13
N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine	Santoflex 13	+15
N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine	Santoflex 77	+5
Bis(6-tert-butyl-4-hydroxy-2-methylphenyl) sulfide	Santowhite crystals	+8
N-phenyl-N'-isopropyl-p-phenylenediamine	Nonox ZA	+20
N-phenyl-N;-stearyl-p-phenylenediamine		−13
Zinc dibenzyl dithiocarbamate	Arazate	−16
Ferric dimethyl dithiocarbamate	Fermate D	+14
Zinc ethylene-bis(dithiocarbamate)	Zineb	+22
2-naphthalenethiol	Vulcamel TBN	+27
Tetraethylthiuram disulfide	Vulcafor TET	−5
Zinc dialkyl dithiophosphate	Lubrizol 1395	−10
Poly(ethylenethiuram monosulfide)		−28
Bis(cyclopentamethylene)thiuram disulfide		−2
Bis(6-tert-butyl-4-ethyl-2-hydroxyphenyl methane)	Antioxidant 425	−42
N,N'-bis(cyclohexyl)dithio-oxamide		−25
Reaction product of 6-tert-butyl-3-methylphenol and sulfur dichloride	Santowhite MK	+10
Thio-bis(di-sec-amylphenol)	Santowhite L	−9
Lead diethyl dithiocarbamate		−61
3-phenyl-1,2-dithiolane-3-thione		+17
Zinc diethyl dithiocarbamate	Vulcafor ZDC	−63
Zinc dimethyl dithiocarbamate	Ziram	−47
6-tert-butyl-2,4-dimethylphenol	Topanol A	−1
Tetramethylthiuram disulfide	Vulcafor TMT	−24

Notes to Table 6:

[a]   The bitumen used was Kuwaiti, 25°C penetration of 82, softening point 46°C.

[b]   Hardening index = $\frac{\text{viscosity at 35°C 0.05 s}^{-1}\text{ after oxidation}}{\text{initial viscosity}}$

Changes less than 10% are probably not significant.

4.1.5 Traxler and Shelby (1973) Study

Traxler and Shelby (1973) measured the ratio of viscosity at 25°C (0.05 s^{-1}) before and after aging of 10 micron bitumen films, aged on glass plates at 35°C under 320-420 nm light (peak intensity 366 nm, 1000 mw/cm^2) for 18 hours. The peroxide decomposer, zinc diethyl dithiocarbamate (ZDC) (see Figure 2), and a proprietary antioxidant, UOP-256 (blend of p-phenyldiamines (free radical inhibitors)), were evaluated using the above conditions.

ZDC reduced the observed increase in hardening of three different bitumens by an average of 43% (range 13-58%) (Table 7).

Thirty-nine bitumens were mixed with UOP-256 to give 1% concentration. Volatility of the additive was negligible at the temperatures used in blending (107°C). UOP-256 reduced the increase in hardening by an average 60% (range 23-91%).

Table 7. Effect of zinc diethyl dithiocarbamate (ZDC) on bitumen hardening in the antioxidant study of Traxler and Shelby (1973).

Bitumen number	Grade and year	ZDC (%)	Original viscosity P x 10^6 (%)	Viscosity after aging (η) P x 10^6	Hardening index (η/ρ_o)	% change in hardening index
1	AC-10 (1969)	0	0.88	136	155.0	-
		2	0.86	76	89.0	–42.5
		3	1.08	74	68.0	–57.5
2	AC-20 (1969)	0	2.7	140	52.0	-
		2	3.0	84	28.0	–42.5
		3	3.4	80	24.5	–57.5
6	AC-10 (1969)	0	0.66	57	85.0	-
		1	0.80	42	53.0	–37.0
		2	0.74	31	42.0	–50.0
6	AC-20 (1969)	0	1.82	88	48.5	-
		1	2.00	52	26.0	–47.0
		2	2.18	66	30.3	–37.0
11	AC-10 (1969)	0	0.88	16	18.5	-
		2	1.50	17	11.3	–39.0
11	AC-20 (1969)	0	2.56	17	6.7	-
		2	2.00	11.6	5.8	–13.0

4.1.6 Haxo and White (1974) Study

Haxo and White (1979) have studied the antioxidant activity of a number of lead dialkyl dithiocarbamates (Table 8). The rolling thin film oven test (RTFO) at 163°C and oven aging of 2 μ bitumen films at 60°C and 100°C were used to evaluate the additives. The volatility of the additives under these conditions was found to be insignificant. The dialkyl dithiocarbamates were used at levels of 1-2% in a number of different bitumens, and oxidation was measured by viscosity changes at 60°C and 25°C (0.02 s^{-1}). Haxo and White's data for RTFO oxidation are presented in Table 9, in which the data have been recalculated to show the percentage change in hardening index. In nearly all cases a reduction in the rate of hardening is observed, although the changes are somewhat smaller than others have observed for the dialkyl dithiocarbamates (Tables 5, 6 and 7). The authors suggest that the effectiveness of the antioxidants increase with the alkyl chain length, and that this factor possibly relates to increasing additive solubility in bitumen. Their data (Table 9), however, do not really support this contention.

Table 8.   Lead dialkyl dithiocarbamate compounds used in the antioxidant study of Haxo and White (1979).

Chemical composition	Designation	C-atoms in alkyl chain	Lead content (%)	Melting point (°C)
Lead dimethyl dithiocarbamate	LDMDC	C_1	46.5	270-275
Lead diethyl dithiocarbamate	LDEDC	C_2	41.1	170-180
Lead dibutyl dithiocarbamate	LDBDC	C_4	33.6	45-55
Lead diamyl dithiocarbamate (50:50 blend with oil)	LDADC-50	C_5	15.4	Liquid
Lead diamyl dithiocarbamate (oil free)	LDADC	C_5	30.8	Liquid
Lead cyclopentamethylene dithiocarbamate	LCPMDC	C_5	30.8	-5
Lead octyl dithiocarbamate	LDODC	C_8	24.7	35-45
Lead Armeen HT-isopropyl-dithiocarbamate[a]	LHTPDC	C_5-C_{18}	21.0	45-60
Lead di"coco"dithiocarbamate[b]	LCCDC	C_{12}	17.9	30-38
Lead di"hydrogenated tallow"-dithiocarbamate[c]	LDHTDC	C_{18}	15.0	42-48
Lead di"arachidic-behenic"-dithiocarbamate[d]	LDABDC	C_{20}-C_{22}	12.9	38-46

[a]   Composition not specified.
[b]   From coconut oil.
[c]   From hydrogenated tallow.
[d]   From a peanut oil fraction consisting mainly of arachidic and behenic acids.

A limited number of outdoor exposure trials were also conducted involving asphalt briquettes and chipseals containing lead dialkyl dithiocarbamates. In all cases the additives appeared to reduce the rate of age hardening, although the effect is slight and the exposure times were relatively short for a field trial (up to 15 months). Chipseals (approximately 1.2 ℓ/m^{-2} application rate, Californian bitumen) containing up to 1.3% w/w of lead di"coco"dithiocarbamate (see Table 8) were constructed. After six months an average reduction in age hardening index of 14% was observed compared to control samples.

Table 9.   Effect of lead dialkyl dithiocarbamates on bitumen aging in the antioxidant study of Haxo and White (1979).

Lead dialkyl dithiocarbamate[a]	Percentage change in hardening index[b, c]			
	Californian (San Joaquin)	Venezuelan (Boscan)	Arkansas (Smackover)	Canadian (Redwater Alberta)
LDMDC, C_1	-	-21	-	-
LDEDC, C_2	-6	-17	+5	-40
LDADC, C_5	-4	-5	-	-
LDCCDC, C_{12}	-1	-10	-	-
LDHTDC, C_{18}	-10	-19	-	-
LDABDC, C_{20-22}	-8	-9	-	-
LCPMDC, C_5	-11	-	-	-
LHTPDC, C_{18}/C_3	-16	-	-	-

[a]   Concentration not specified, probably 1-2% w/w.

[b]   Hardening index = $\dfrac{60\,°C\ viscosity\ after\ RTFO}{initial\ 60\,°C\ viscosity}$

[c]   Bitumens are all 25°C penetration of 60 to 70.

4.1.7   Gokhale et al. (1985) Study

Gokhale et al. (1985) have studied the performance of a number of antioxidants in bitumen including two lead dialkyl dithiocarbamates. Asphalt mixes were prepared at 140°C with 80/100 (25°C) penetration grade bitumen and were aged in an oven at 60°C with a slow stream of air sucked through the matrix. The aged bitumen was recovered from the aggregates using the Abson procedure (ASTM D1856-75: ASTM 1994a), and 60°C viscosities and 25°C penetrations were measured. The probable presence of residual extraction solvent was not allowed for. Levels of residual solvent are likely to be higher in the more aged samples, but the effects would be similar for both control and test samples. The effect of the antioxidants on 60°C viscosity is presented in Table 10. The authors' data have been used to calculate hardening indices.

As in previous studies, the dialkyl dithiocarbamates proved most effective in reducing oxidation. The results were somewhat better than those found by Haxo and White (1979) but comparable to the 61% improvement in hardening index reported by Januszke (1971) for lead diethyl dithiocarbamates. By correlating the penetration changes in bitumen from field trials to those from the accelerated aging procedure, an increase in service life from four to seven years was predicted if lead diethyl dithiocarbamate was used.

Jogendra et al. (1981) have also confirmed the antioxidant effects of the dialkyl dithiocarbamates in laboratory experiments.

Table 10. Compounds used in the antioxidant study of Gokhale et al. (1985).

Compound (2% by weight)	Change in hardening index[a] (%)	
	25°C pen	60°C viscosity
Bitumen[b]	-	-
Phenothiazine	-9	-5
N-phenylnapthyl-β-amine	-14	-13
Mercaptobenzothiazole	+13	+6
Lead cyclopentamethylene dithiocarbamate	-36	-26
Lead diethyl dithiocarbamate	-45	-45

[a] Hardening index = $\dfrac{\text{property after aging } 60\,^\circ\text{C for 672 hours}}{\text{property before aging}}$

[b] 25°C penetration of 90, softening point 44.5°C.

4.2 Field Trials of Lead and Zinc Dialkyl Dithiocarbamates

Following Martin's (1968, 1971) work and that of Haxo and White (1979) discussed above, several field trials were sponsored by the International Lead Zinc Research Organisation (ILZRO).

4.2.1 Canadian Trial
A 1 km trial strip of asphaltic concrete with 2% lead dialkyl dithiocarbamate was constructed in Ontario, Canada in 1982 under the auspices of the Ontario Ministry of Transportation and Communication (Smith and Carr 1983, Radkte and Carr 1984). Unfortunately little information on the fate of these trials was available at the time of writing (though this is being sought).

4.2.2 Australian Trials

A trial involving zinc diethyl dithiocarbamate (ZDC) was carried out by ARRB (now ARRB Management Research) in 1969 using ZDC levels of 0-4% (Tilley and Martin 1970, Dickinson 1976) and air-blown 85/100 25°C penetration grade bitumens. Up to 35% of the added ZDC reacted immediately with the bitumen at mixing temperatures (160°C).

However, an increase of 50% was still observed in the durability oven test value (AS 2341.13: Standards Association of Australia 1986a) for a 2% ZDC blend and 91% for a 3% blend. The viscosity of bitumen recovered from the seals showed that the ZDC apparently reduced hardening for up to two years in some cases. After six years, however, there was no significant difference between the ZDC and control sections in any of the trials.

The implication is that either the experimental error involved in the recovery and viscosity measurement is greater than believed or the ZDC or reaction products are acting as pro-oxidants to increase the oxidation rate after the first one or two years. A drawback of the trials was the fact that as ZDC is a powder with limited bitumen solubility. Effective chipseal of the ZDC powder in bitumen was a severe problem, and in most of the trials it was not achieved.

Another set of chipseal trials have been constructed in Australia using lead diamyl dithiocarbamate (LDADC) (Oliver and Holtrop 1986, Oliver 1987). This compound is a liquid and readily soluble in the bitumens used. Three Middle East class 170 (approximately 80/100 (25°C) penetration grade) bitumens of different durability values were used with LDADC concentrations of up to 5% by mass. In durability oven tests LDADC is rapidly consumed but it increases durability values by up to 40%, at 4% concentration.

Bitumens not used in the trial showed even larger increases of up to 88%. After two years, examination of the recovered bitumens by infrared spectroscopy (Huxtable and Oliver 1989, Oliver 1986, 1991) showed that essentially all the antioxidant had been consumed except in the sections containing over 4% LDADC. Binder hardening had been reduced compared to the control sites (Oliver 1989). Similar observations were made after 4-5 years.

Sections containing 2.5% LDADC had hardened about 84% as much as the control sections, and the 5% LDADC sites were 69% as hard as the control. An increase in lifetime (time to reach a viscosity of 5.67 log Pa.s 45°C 0.005 s^{-1}) from 11 to 13 (20%) years was tentatively predicted for the 2.5% sites and from 11 to 18 years (60%) for the 4% sites.

5. COMMERCIALLY AVAILABLE ANTIOXIDANTS FOR BITUMEN

Several patents have been obtained for various antioxidant compounds and formulations for use in bitumen. None of these are known, however, to have led to successful commercial application. Eberhard et al. (1970) have patented a mixture of 1.5% palmitic acid and 1.5% 3,3'dioctyldiphenylamine which is claimed to increase the stability of 30 μ bitumen films by 145%. Samoto (1975) reports that mixtures of bitumen and 2,2'-thiobis(4-methyl-6-t-butyl phenol) and triphenyl phosphite or tris(nonylphenyl) phosphate prevented bitumen deterioration after three days' storage at 150°C. Details of this and Eberhard's work were not available at the time of writing. Sakagami and Kobayashi (1965) aged seven bitumens under ultraviolet light. Phenothiazine and hydroquinone at 3% by weight were found to reduce asphaltene formation and the formation of carbonyl species. Unfortunately a translation of the full paper was not available at the time of writing.

A few products have been promoted commercially as bitumen antioxidants, but at the present time (1994) only those manufactured by Lubrizol Corporation are on the market[1].

Higgins (1987) has presented data on the performance of a number of these products. Bitumens were aged using the RTFO procedure but for seven days at 102°C. Bitumen hardening was measured in terms of viscosity at 60°C, 25°C penetration and 25°C ductility. Bitumens containing 1-6% of additive were added and reduced the final attained viscosity (60°C) and penetration (25°C) compared to control samples (Table 11). Unfortunately the initial unaged values were not reported so that hardening rates cannot be compared. This comparison is important as, from other data presented, the additives may have caused an initial softening of the samples.

Table 11. Results of the antioxidant study of Higgins (1987) using a commercially available bitumen antioxidant.

Bitumen grade[a]	% antioxidant	Viscosity (60°C) after aging[b] (poise)	Penetration at 25°C (dmm)
AR4000	0	20335	10
	1	17300	14
	2	14045	16
	4	10170	17
AC20	0	99500	8
	2	85840	9
	3	13406	17
	4	11905	17
	6	11466	19

[a] ASTM D3381-92 (ASTM 1994c)

[b] Seven days in rolling thin film oven at 102°C. Initial viscosities were not supplied. To convert Poise to Pa.s, divide by 10.

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[1] 29400 Lakeland Boulevard, Wickliffe, Ohio 44092, USA.

Data were also presented by Higgins (1987) to show that Marshall stabilities (ASTM D1559-89: ASTM 1994b) of asphalts containing the antioxidants showed only small percentage increases after aging compared to control samples. However, experimental details of the aging procedure were not provided. Accelerated aging of compacted asphalt blocks is difficult without altering the mix properties because of mechanical effects not related to oxidation (Bell et al. 1989, 1992).

Limited data were also supplied by Higgins (1987) on a field trial which was laid using 2% of a Lubrizol product in 1985 in Ohio, USA. Cores were taken after nine months and those from the antioxidant-treated site were found to have superior properties. For example, the Marshall stability (60°C) for the control site had almost doubled (91%) while that of the treated site had increased by only 16%. Unfortunately details of the trial, for example the repeatability of data from the core samples which is likely to be variable, were not provided.

6. HYDRATED LIME

Hydrated lime (calcium hydroxide, $Ca(OH)_2$) has been used for many years as an anti-stripping agent in asphaltic mixes. In 1971, hydrated lime was reported also to reduce age hardening of bitumen in asphalt mixes (Chachas et al. 1971). Samples were taken from existing pavements constructed with and without lime, the bitumen was recovered, and viscosity (60°C and 135°C) and penetration (25°C) measurements were made.

The results showed on average smaller percentage increases in viscosity for lime-treated sites as opposed to non-limed sites. Given that many other variables were involved and were not accounted for, these results must only be considered indicative. Data were provided for three sites with and without 1% lime (by weight of mix). Using the data provided for viscosities after one and three years to calculate percentage increases, then the lime appeared to be, if anything, increasing the rate of hardening (Table 12). Field trials and laboratory mixes were prepared and sampled up to 500 days exposure. Though the addition of lime appeared, in most cases, to be reducing the rate of hardening, there was a large scatter in results and, as initial viscosities were not presented, relative hardening rates cannot be compared exactly.

Table 12. Field trial results of hydrated lime as antioxidant (Chachas et al. 1971).

Site	% Air voids	% change in hardening rate[a] with 1% lime added[b]	
		2 years	3 years
1-15-2(15)61	9.2	−7	+3
F-014-1(5)	4.5	+14	+15
1-70-2(4)61	6.4	+55	+38

[a]   Hardening index = $\dfrac{\text{viscosity at } 60°C \text{ after 2 or 3 years aging}}{\text{viscosity at } 60°C \text{ after 1 years aging}}$

[b]   By weight of mix.

Chachas et al. also prepared mixes with and without 1% lime in the laboratory using 11 different bitumens. After 24 hours the bitumen in these mixes was extracted and recovered. Samples with lime showed on average a 13% smaller increase in viscosity than the control samples (Table 13). A drawback of the experimental approach is that the lime was removed from the bitumen during the extraction process. (Extraction is of course unavoidable if the bitumen from road samples is to be examined.)

Table 13. Laboratory study of lime as antioxidant (Chachas et al. 1971).

Bitumen number	Original viscosity (poise)[a]	Viscosity without lime after extraction	Increase in viscosity (%)	Viscosity with lime after extraction	Increase in viscosity (%)	% change in % increase in viscosity
0111	768	1243	61.8	874	13.8	−48.0
0211	903	1163	28.8	1114	23.4	−5.4
0323	1178	1544	31.1	1518	28.9	−2.2
0421	980	1570	60.2	1480	51.0	−9.2
0522	1460	2070	41.8	1796	23.0	−18.8
0611	705	1186	68.2	1014	43.8	−24.4
0732	987	1604	62.5	1266	28.3	−34.2
0812	862	1334	54.8	1258	45.9	−8.9
0921	2526	3333	31.9	2912	15.3	−16.6
1023	1326	1882	41.9	1741	31.3	−10.6
1131	1309	1904	45.5	1735	32.5	−13.0

[a]   Without lime added, 60°C.
        Divide Poise by 10 to convert to Pa.s.

The question could be raised, however, as to whether the reduction in hardening is caused by an antioxidant effect or whether polar (viscosity building) species are simply absorbed onto lime particles and removed during extraction. That lime does function in this way was demonstrated in a later study by Plancher et al. (1976).

In Plancher's work, bitumen dissolved in solvent was mixed with lime to form a slurry. The bitumen was then recovered from the solvent and aged under a range of conditions. Lime-treated bitumens were found to have both lower viscosities (before aging) than untreated samples, and to have greater resistance to oxidative hardening measured by viscosity increase (25°C 0.05 s^{-1}) and chemical analysis (measurement of carbonyl species).

Plancher's results suggested that lime operates in two ways. First, it removes (by chemisorption) polar pro-oxidant species present in the unaged bitumen. This absorption effect reduces the rate of formation of oxidation products when the bitumen is aged. Second, it is also likely to absorb a fraction of the oxidation products that are formed, removing these viscosity building components from the bulk of the bitumen. On addition of lime to neat bitumen, however, the viscosity is likely to rise because of the effect of the lime as a filler, even though absorption of polar molecules is proceeding.

The effectiveness of lime to reduce the rate of hardening of bitumen in laboratory tests has been confirmed by other workers. In a short summary paper Welch and Wiley (1976) described the aging of asphaltic concrete briquettes for two years outdoors with 0-1.0% (by weight of mix) hydrated lime added. The added lime reduced the rate of binder hardening and the effect increased in proportion to the lime concentration. The effect varied, however, with the bitumen source. Edler et al. (1985) aged 60/70 and 80/100 (25°C) penetration grade bitumens using a variety of methods, between 65°C and 163°C. Oxidation was measured (with the lime still present) by viscosity at 45°C (0.05 s^{-1}) and increase in the carbonyl absorbance (1700 cm^{-1}) of the infrared spectrum.

Changes in the molecular size profiles (by gel permeation chromatography in tetrahydrofuran, presumably with the lime filtered out) were also monitored. Data for bitumens containing 6% and 12% lime aged by an extended RTFO test (1.25 mm film, 163°C, 75 min) are given in Table 14. The initial viscosity increased on addition of the lime but the rate of hardening was significantly reduced. The increase in carbonyl absorbance and percentage of large molecular size species were also reduced in the lime-treated samples. The latter also showed reduction in unaged bitumens containing lime, suggesting that high molecular weight species or polar molecules capable of associating into larger agglomerations are being absorbed into the lime particles.

Table 14.   Effects of hydrated lime on bitumen hardening (Edler et al. 1985).

Bitumen grade	% lime	Viscosity (Pa.s)		Hardening index[b]	Change in hardening index (%)
		Original	ERTFOT[a] residue		
60/70	0	4.37 x 10³	4.40 x 10⁵	1.060	-
	6	6.40 x 10³	1.80 x 10⁵	0.281	-73
	12	1.18 x 10⁴	2.01 x 10⁵	0.170	-84
	0	1.91 x 10³	1.48 x 10⁵	0.772	-
	6	3.40 x 10³	5.74 x 10⁴	0.169	-78
	12	5.73 x 10³	6.49 x 10⁴	0.113	-85

[a]   Extended rolling thin film oven test 75 min at 163°C, 1.25 mm film.
[b]   Hardening index = viscosity (45°C 0.05 s^{-1}) after aging
              viscosity (45°C 0.05 s^{-1}) before aging

Dickinson (1980) also reported a reduction in the rate of hardening of five Middle East (80/100 (25°C) penetration grade) bitumens with addition of cement kiln dust (containing hydrated lime). These findings were confirmed by a later study (Dickinson 1981). A heavy Arabian (Australian class 170, approximately 80/100 (25°C) penetration grade) bitumen was aged for 10 days using the Australian durability oven procedure (AS 2341.13: Standards Association of Australia 1986a) at 100°C. Resistance to aging was measured by viscosity (sliding plate, AS 2341.5: Standards Association of Australia 1986b) at 45°C (0.005 s^{-1}).

Bitumen containing commercial hydrated lime (~80% $Ca(OH)_2$) at 6.4% had a viscosity of 5.36 log Pa.s compared to 5.65 for the control (reduction of 5%). Approximately 12% lime resulted in a viscosity of about 5.23 log Pa.s after aging (reduction of 7.4%).

The experimental procedure involved removal of the lime before the viscosity measurement. Thus the results show that the lime has retarded oxidation or effectively absorbed viscosity-building oxidation products. They do not show, however, the viscosity increase caused by the lime acting as a filler, although in practice this could be allowed for by initially selecting a slightly softer bitumen grade. The concentration of $Ca(OH)_2$ present was found to be critical as ground limestone, basalt and cement kiln dust were ineffective.

Edler et al. (1985) found an increase of approximately 0.5 log Pa.s in addition of 12% lime to 80/100 bitumen, though the size of the increase would depend markedly on bitumen type and lime particle size distribution.

A field trial chipseal was constructed by ARRB in 1980 in Australia with a 170 class bitumen and 1.5%, 2.9% and 6.1% lime by mass. Further trials were laid in 1981/82 with up to 15% hydrated lime (Tredrea and Dickinson 1983), and in 1985 (Tredrea 1988) using class 170 and the softer class 50 (approximately 180/200 (25°C) penetration grade). The lime was in-line blended without serious difficulties using a hopper arrangement. Stirrers in the spray tankers prevented sedimentation and spraying was carried out as normal.

Table 15. Effect of hydrated lime on bitumen durability value (Dickinson 1981, Patrick 1987).

Bitumen	Source	% lime added[a]	Durability value[b]	Increase in durability value (%)
Class 170 (approx 80/100 (25°C)pen.grade)	Safaniya + propane precipitated Light Arabian	0 12	10 15	50
Class 170	Not stated	0 10	18 23	28
Class 50 (approx 180/200 (25°C)pen.grade)	Not stated	0 10	14.5 18	24
80/100 (25°C) pen.grade	Safaniya (air-blown)	0 12	5.3 6.5	23

a   Commercial hydrated lime by mass of bitumen.
b   AS 2341.13, AS 2341.5 (Standards Association of Australia 1986a, b).

The effect of lime addition on the age hardening of the bitumens used in the trials was also measured. A summary of these data in terms of the effect on the durability value (the number of days to reach a viscosity of 5.67 log Pa.s) is given in Table 15. Data from measurements made in New Zealand on Safaniya 80/100 (25°C) penetration grade bitumen are also included (Patrick 1987). In each case an increase in durability is observed, though this is small in the case of the New Zealand-tested bitumen (within the one day repeatability of the test). Problems were encountered with inconsistent results during monitoring of the Australian trials and they have unfortunately been discontinued (P.F. Tredrea, pers. comm. 1994)

A dedicated field trial to test the antioxidant effect of hydrated lime has not been constructed in New Zealand. Some work has, however, been carried out on two friction course surfacings (in close physical proximity to one another), constructed within one year of each other, in Christchurch (Patrick 1987). One had been constructed with approximately 5.1% lime (by mass of bitumen), the other without. The binder from each was extracted and recovered (with the lime removed) and the viscosities were measured (Table 16).

The results showed the lime to have no effect, but should be regarded as tentative as no information on initial binder viscosities or uniformity of lime dispersion was available.

Table 16.   Effect of hydrated lime on bitumen hardening in the field (Patrick 1987).

Site	Viscosity (log Pa.s)[a] Age (years)					Hardening index[b]
	2	3	4	5	6	
No lime	-	4.76	4.81	5.28	5.28	1.1
5.1% lime	4.52	4.86	4.98	5.23	-	1.1

[a] At 45°C 0.1 s^{-1}.
[b] Hardening index = $\dfrac{\text{viscosity after 5 years}}{\text{viscosity after 3 years}}$

7. EFFECTS ON SEALING PRACTICE

Most asphalt concrete mixes in New Zealand are used in urban areas, and causes of failure attributed to heavy traffic volumes are probably more significant than age hardening. Discussion is thus restricted to chipseal surfacings for which, being used on low traffic volume roads, age hardening is a significant cause of failure.

7.1 Handling

Neither conventional antioxidants nor hydrated lime should present any special handling or operational difficulties. Hydrated lime is frequently used at present as an anti-stripping agent in friction course mixes. Spraying of bitumen modified with up to 12% lime has been carried out without difficulty in Australia. Lime is, however, an abrasive solid and increased wear on pumping and spraying equipment would be expected. Handling and use of conventional antioxidants would probably be similar to the use of amine adhesion agents, although the exact handling requirements, safety precautions, etc. would depend somewhat of course on the particular compound used.

7.2 Costs to Chipsealing

Hydrated lime costs approximately $1/kg[2] at the 10% level, and this would add about 2-3% to the cost of a chipseal[3]. An increase in expected life of at least five months would be necessary before any savings are apparent[4]. Laboratory results indicate that increases of three years are feasible though this has yet to be demonstrated in practice.

Costs of conventional antioxidants range greatly. The most studied antioxidants, lead and zinc dialkyl dithiocarbamate, cost in the order of $10/kg. At the 4% level (as used in the Australian trial) they would add 20% to the cost of the chipseal. The Australian trial suggests that lifetime increases of 60% are realistic, as they more than cover the initial capital costs. In effect this means the expected life for a state highway chipseal would increase from about 9 to 14½ years.

These analyses are very approximate but indicate that the use of antioxidants is quite realistic economically.

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[2] Costs in NZ$ as at 1995.

[3] Assuming bitumen costs $0.50/kg, is applied at a rate of 1.5 ℓ/m^2, and the total chipseal cost is $2.00/m^2$.

[4] This figure is based on the average non-state highway seal life of 16 years (Ball and Herrington 1995).

7.3 Effects on Use of Amine Adhesion Agents

The possible reactions of conventional antioxidants with amine adhesion agents are too varied to be considered without specific compounds in mind. Both additives are likely to be present in very low concentrations (a few percent), reducing the likelihood of any interaction. This aspect of antioxidant use would require further investigation.

Hydrated lime is basic in nature and so unlikely to absorb (basic) amine adhesion agents as it does bitumen carboxylic acids and other carbonyl compounds. By absorbing existing bitumen acids, however, it may reduce the amount of adhesion agent thought to be lost through reaction with these acids to form less active amides.

7.4 Effects on Emulsion Manufacture

The suitability of a conventional antioxidant for use in emulsion manufacture will depend on the chemistry of the particular compound in question. Control of solution pH is a critical parameter in emulsion manufacture. Hydrated lime would likely cause difficulties in emulsion manufacture due to its basicity, making its use as an antioxidant impractical. The particulate nature of lime will also adversely affect particle size distribution and gives rise to coarsening and eventually breaking.

7.5 Effects on Environment

Loss of antioxidant compounds or hydrated lime into the environment is most likely while they are being added to the mix and during spraying operations. Unless very volatile compounds are used, significant loss of antioxidants from the completed seal through water leaching or evaporation is unlikely. However, the likelihood of leaching metals or other additives from the seal will depend to a large extent on the water solubility of the particular compounds (and their oxidation products) in question.

Environmental and worker monitoring was undertaken during the Australian lead diamyl dithiocarbamate trials (Oliver 1989a). Samples taken from soils adjacent to the sealing site before and 13 months after sealing showed no increase in lead concentrations. Similarly blood samples taken from workers showed exposure to lead during the sealing operations was unlikely to pose a health hazard. Similar findings were reported during the construction of the Canadian trial.

8. CONCLUSIONS

8.1 Effectiveness of Conventional Antioxidants

A large number of different compounds have been investigated since the 1960s. Most of the studies have been empirical in nature and no explanation of the sometimes contradictory or inconsistent results were given. In general, however, beneficial effects (often quite large) have been observed both in resistance to thermal oxidation and photochemical oxidation. Antioxidants of both peroxide decomposer and free radical inhibitor types have proved successful, but not consistently, in all bitumens.

Only a very few field trials have been constructed, using lead and zinc dialkyl dithiocarbamate antioxidants. The Australian zinc diethyl dithiocarbamate trial was unsuccessful probably because of difficulties in dispersion of the antioxidant (a powder). Very promising results, indicating substantial (20-60%) increases in life, have been observed in a later chipsealing trial incorporating lead diamyl dithiocarbamate. Another trial of lead dialkyl dithiocarbamate antioxidants has been constructed in Canada, though whether it has been successful or not is not known.

The Australian trials are of particular relevance to New Zealand as they are chipseals (the major surfacing type in New Zealand) constructed using bitumens of Middle East origin (the bitumen used in New Zealand). No trials have been conducted in New Zealand.

Commercially available bitumen antioxidants have been marketed from time to time though they do not seem to have resulted in any significant use, and virtually no data on their performance have been published. The composition of these agents is proprietary, so whether they represent compounds specifically designed for bitumen or are merely "repackaged" antioxidants from the polymer or lubricants field is not known.

Noticeably absent from the literature are in-depth studies on the basic chemistry of bitumen antioxidant systems. Most researchers have used viscosity increase to measure the extent of oxidation. Although this is of immediate practical interest, it provides little information on the chemical processes occurring. Often the compounding effects of the antioxidant on the initial bitumen viscosity or the effect of volatile loss during high temperature aging have not been adequately considered. Very few researchers have attempted to monitor reaction products formed or antioxidant loss during the oxidation process.

The solubility or lack of it for the antioxidant in the bitumen being studied is another factor usually not considered. An added complication is that most studies have used oxidation conditions quite unrelated to long term in-service aging. Recent research indicates that the temperature used to accelerate oxidation can alter the relative rates of oxidation of different bitumens. Thus two bitumens with similar rates at 60°C may have very different rates at 160°C. This appears to be related to the degree of structuring in a bitumen and also to the relative temperature dependence of the different oxidation reactions taking place (Herrington et al. 1994, Petersen et al. 1993, Lau et al. 1993).

The oxidation products or ratios of products formed at high temperatures may be different to those occurring at lower temperatures which may in turn alter the mechanism and effectiveness of particular antioxidant compounds.

Although the investigations conducted to date suggests that antioxidants could provide significant benefits in roading bitumens, more research on the underlying processes involved in bitumen oxidation is needed.

For example, although circumstantial evidence supports the role of transition metal ions at oxidation catalysts in bitumen, little hard unambiguous evidence backs this up. Correlations are sometimes found between vanadium content and increase in oxidation rate for different bitumens, but cause and effect have not been adequately demonstrated. Given that on the molecular level the functional groups found in bitumen are similar to those in other hydrocarbon systems (e.g. lubricating oils), it seems unlikely that fundamentally different oxidation mechanisms are operating. Quantitative differences are, however, likely and these seem most likely to be related to the ability of bitumens to form inter-molecular associations even in polar solvents. Research to elucidate these effects is considered necessary to select or design antioxidants to sufficiently retard bitumen age hardening.

8.2 Effectiveness of Hydrated Lime

Evidence that hydrated lime ($Ca(OH)_2$) retarded age hardening first arose in the 1970s. Lime functions in this retardation by absorbing polar species already present in the bitumen and formed on oxidation. Both the rate of oxidation and rate of increase of viscosity are reduced. Field trials of asphaltic concrete in the United States have confirmed to a limited extent the laboratory findings. The hydrated lime chipseal trials laid in Australia in the early 1980s gave inconsistent data and monitoring has not been continued. The effect of lime appeared to be limited, however (P.F. Tredrea, pers. comm. 1994).

Although no dedicated trial has been carried out in New Zealand, observation of limed and unlimed friction course surfacings in Christchurch in 1987 (Patrick 1987) revealed no difference in binder hardening rates.

The effectiveness of lime has been quite clearly demonstrated (at least in laboratory studies), and its mechanism is reasonably well understood. The likely performance of lime in the field will probably depend to a large extent on the ability to effectively disperse it throughout the bitumen matrix.

9. RECOMMENDATIONS

- The progress of the lead diamyl dithiocarbamate (LDADC) trials presently (1994) underway in Australia should be monitored to determine if the current improvement in performance is maintained.

- Construction of full scale field trials at this stage is probably not warranted. However, inclusion of hydrated lime and LDADC samples in the exposure rack trials being monitored under Transit New Zealand Project PR3-0105 should be considered. This will provide valuable information (at a negligible cost) on performance of these materials in New Zealand conditions.

- Research into the chemistry of antioxidants in bitumen at the mechanistic level should be undertaken. This is considered essential to properly understand and develop effective antioxidants for use with roading bitumens. Research in this area is justified on the basis of the large financial savings to be made from even small increases in chipseal lifetimes.

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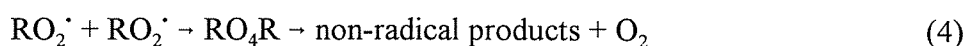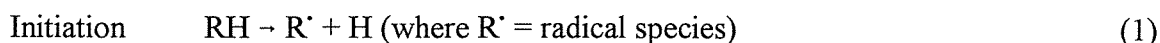# APPENDIX 1. CHEMISTRY OF AUTOXIDATION AND ANTIOXIDANTS

APPENDIX 1.   CHEMISTRY OF AUTOXIDATION AND ANTIOXIDANTS

A1.1   AUTOXIDATION

The autoxidation of many hydrocarbons can be described by the following mechanism (scheme 1) (Scott 1965, Ranby and Rabek 1979, Bateman 1954):

Scheme 1

Initiation	$RH \rightarrow R^{\cdot} + H$ (where $R^{\cdot}$ = radical species)	(1)
Propagation	$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$	(2)
	$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$	(3)
Termination	$R^{\cdot} + R^{\cdot} \rightarrow RR$	(5)
	$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow RO_4R \rightarrow$ non-radical products $+ O_2$	(4)
	$R^{\cdot} + RO_2^{\cdot} \rightarrow RO_2R$	(6)

Reaction (2) is very fast, so that at partial pressures of oxygen equivalent to or greater than air, $R^{\cdot} \ll RO_2^{\cdot}$, the only termination reaction of significance is (4).

Under steady state conditions $RO_2^{\cdot}$ is assumed to be constant and the rate of radical formation (1) must be exactly balanced by the rate at which free radicals are removed in the termination reaction (4).

The two propagation reactions can be ignored since $RO_2^{\cdot}$ formed in one is consumed in the other. The rate of initiation R_i is thus equal to the rate of termination:

$$R_i = R_t = 2 \, k_t \, [RO_2^{\cdot}]^2 \qquad (7)$$

thus
$$[RO_2^{\cdot}] = \left(\frac{R_i}{2 \, h_t} \right)^{1/2} \qquad (8)$$

As reaction (2) is very fast, the rate of oxygen uptake, R_{ox} (the rate of oxidation), will be controlled by the rate at which $RO_2^{\cdot}$ abstracts hydrogen from the hydrocarbon RH:

$$\frac{-d \, [O_2]}{dt} = R_{ox} = kp \, [RO_2^{\cdot}] \, [RH] \qquad (9)$$

Substituting equation (8) into (9) gives:

$$R_{ox} = kp \left(\frac{R_i}{2\ h_t} \right)^{1/2} [RH] \tag{10}$$

Hence the rate of oxidation depends only on the concentration of hydrocarbon. The ratio $kp/k_t^{1/2}$ is known as the oxidisability, and it can be determined by using a radical initiator such as azoisobutyronitrile (AIBN). This compound decomposes at a known rate to two radical products so that $R_i = 2k_i$ [AIBN]. This rate is assumed to be large compared to other initiation mechanisms which may be operating and which are ignored.

If oxygen is in short supply (as may be the case at the bottom of a bitumen film in chipseal surfaces) then equation (2) becomes rate limiting so that:

$$\frac{-d\ [O_2]}{dt} = R_{ox} = k\ p\ [RO\ ]\ [O_2] \tag{11}$$

and the principal termination reaction is between alkyl radicals (5).

The concentration of alkyl radicals can be calculated from the assumption that at steady state conditions:

$$R_i = R_t = k'_t\ [R^{\cdot}]^2$$

thus

$$[R\ ] = \left(\frac{R_i}{h'_t} \right)^{1/2}$$

and

$$R_{ox} = kp' \left(\frac{R_i}{k'_t} \right)^{1/2} [O_2]$$

The rate is thus first order with respect to $[O_2]$.

In conditions of oxygen concentrations between the extremes, a more complex equation involving all three termination equations is valid.

A typical autoxidation curve is shown in Figure 1a (in Section 2 of this report). During the induction period, free radical numbers are low and are building up. Initiation can be caused by light, metal ions or the decomposition of adventitious peroxidic impurities. Decomposition of hydroperoxides (formed in reaction (3)) can lead to chain branching (not shown in scheme 1) and an exponential increase in radical numbers. This gives rise to the auto-catalytic portion of the curve. Finally as levels of alkylperoxy radicals ($RO_2^{\cdot}$) increase, termination reactions become significant and steady state reaction occurs. Reaction subsides as available reactive sites are depleted.

The autoxidation curve for Safaniya (180/200 penetration grade) bitumen is somewhat different (see Figure 1b, in Section 2 of this report)). No induction period or auto-catalysis is observed, suggesting the presence of radical initiators. The most likely candidates are transition metal ions known to be present at levels up to ~100 ppm. The gradual decline in reaction rate is probably related to the depletion of reactive species and not auto-retardation, i.e. to the inhibition of the reaction by the reaction products themselves (Herrington et al. 1994). However, many of the fundamental aspects of the chemistry of bitumen oxidation are not properly understood.

A1.2 ANTIOXIDANTS

The two principal types of antioxidant (Hawkins 1972, Brydson 1989, Allen 1986, Ingold 1961) are:

(1)   preventive antioxidants which in some way inhibit or retard the formation of free radicals in the initiation step;

(2)   chain-breaking antioxidants which interrupt and stop or retard the chain reaction.

A1.2.1 Preventive Antioxidants

Three main classes of antioxidants (AH) are recognised (examples are given in Figure 2, in Section 3 of this report):

(a)   peroxide decomposers;

(b)   metal deactivators; and

(c)   ultraviolet light absorbers and related compounds.

(a)   *Peroxide decomposers* react with the hydroperoxides formed in reaction (3) of Appendix 1, scheme 1 to give non-radical products:

ROOH + AH → non-radical products
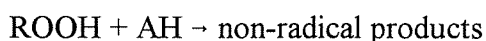
(b)   *Metal deactivators* are usually chelating agents which form complexes with the metal ions. It should be noted that chelating agents which deactivate some metals may have a pro-oxidant effect with others.

(c)   *Ultraviolet light absorbers* are designed to protect against the formation of radicals caused by the absorption of light. The greatest damage is caused by wavelengths less than 400 nm, but as the atmosphere absorbs most wavelengths less than 300 nm, the 300-400 nm region is of most concern. Light in this region has sufficient energy to cause dissociation of many C-C bands and some C-H bands (e.g. benzylic). Antioxidants designed to protect against such damage act in two principal ways, as
•   light absorbers and
•   quenching agents.

Light absorbers act by absorbing light and converting the energy into heat (e.g. carbon black[e]) or give rise to stable, non-radical products (e.g. σ-hydroxybenzophenones).

Quenching agents act by reacting with a photo-excited hydrocarbon (R*) before radical formation:

$$R \xrightarrow{h\nu} = R*$$

$$R* + Q \rightarrow R + Q*$$

$$Q* \rightarrow Q + \text{energy emitted (e.g. fluorescence)}$$
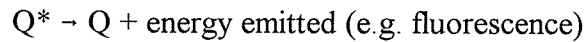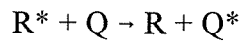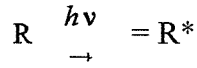
The importance of photo-oxidation in the overall age hardening of bitumen in chipseals is unclear. Because of its highly light absorbing nature, light penetration beyond the first few microns is negligible. The photo-oxidised layer is likely, however, to be disturbed by weathering and traffic so that fresh bitumen may be continually exposed. Micro-cracks formed at the surface may also provide easier access for oxygen to the bulk of the film than would otherwise be the case (Bell 1989, Oliver and Gibson 1972, Dickinson et al. 1958, Knotnerus 1972, Martin and Tilley 1969, Traxler and Shelby 1973).

A1.2.1 Chain-Breaking Antioxidants

When antioxidants (AH) functioning by this mechanism are present, a number of possible alternative reactions are possible (scheme 2 below) in the autoxidation pathway described in scheme 1.

Scheme 2

Initiation	$RH \rightarrow R^\bullet + H$	(as in uninhibited oxidation)	(1)
	$AH + O_2 \rightarrow A^\bullet + HO_2^\bullet$	(O_2 attack on antioxidant)	(2)
Propagation	$R^\bullet + O_2 \rightarrow RO_2^\bullet$		(3)
	$RO_2^\bullet + RH \rightarrow ROOH$		(4)
	$RO_2^\bullet + AH \rightarrow ROOH + A^\bullet$	(chain transfer)	(5)
	$A^\bullet + RH \rightarrow AO_2H + RO_2^\bullet$	(chain transfer)	(6)
	$AH + R^\bullet \rightarrow A^\bullet + RH$	(chain transfer)	(7)

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[e]   Carbon black also functions as an antioxidant by other mechanisms (Ranby and Rabek, 1979: 364-365).

Termination $R^{\bullet} + R^{\bullet} \rightarrow RR$ (8)

$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow$ non radical products   (9)

$R^{\bullet} + RO_2^{\bullet} \rightarrow RO_2R$ (10)

$RO_2^{\bullet} + A^{\bullet} \rightarrow RO_2A$ (chain-breaking)   (11)

$A^{\bullet} + A^{\bullet} \rightarrow AA$ (chain-breaking)   (12)

Reactions (1), (3), (4), (8), (9) and (10) are as in uninhibited oxidation. The key feature of this type of antioxidant is the stability of the radical (A) that is formed. This is far more likely to react with another radical $R^{\bullet}$, $RO_2^{\bullet}$ or $A^{\bullet}$ than with the substrate $RH^{\bullet}$.

The antioxidant participates in the reaction in a number of ways (Hawkins 1972):

•   Initiation by direct attack of oxygen on the antioxidant to produce chain-initiating free radicals (reaction (2)). This step is actually pro-oxidant.

•   Chain transfer with the antioxidant in which the radical derived from the antioxidant reacts in some way to reform a propagation, free radical (reactions (5), (6) and (7)). This will retard the rate of oxidation if reaction (6) is rate limiting, i.e. alkyl peroxy $(RO_2^{\bullet})$, or alkyl radicals $(R^{\bullet})$ are removed from the system by the antioxidant and "replaced" with $A^{\bullet}$ radicals which regenerate the $RO_2^{\bullet}$ or $R^{\bullet}$ radicals at a slower rate.

•   Termination by hydrogen donation to $RO_2^{\bullet}$ (as in reaction (5)), followed by reaction of the antioxidant radical with a second $RO_2^{\bullet}$ (reaction (11)). Two kinetic chains are thus terminated per molecule of antioxidant consumed. This process is more likely than reaction (6) unless excess antioxidant is present.

As with uninhibited oxidation, chain transfer (7) and chain-breaking termination reactions (1) and (2) involving alkyl radicals $(R^{\bullet})$ are less likely than those involving $RO_2^{\bullet}$ radicals, except at very low oxygen concentrations.