

The Oxidative Aging in Ultraviolet Light of Dicumyl Peroxide Vulcanizates of Natural Rubber in Presence of Various Antioxidants

J. R. DUNN

The British Rubber Producers' Research Association, Welwyn Garden City, Herts., England

The oxidative aging of natural rubber vulcanizates at 25°C. under irradiation by ultraviolet light of wavelength 365 m μ has been described in a number of communications from this laboratory. At this wavelength naphthylamines were shown to accelerate degradation of peroxide vulcanizates while substituted *p*-phenylenediamines inhibited it;¹ α -naphthol² and a variety of dithiocarbamates³ were also found to have a protective action. Since some amines and phenolic antioxidants do not absorb light of wavelength 365 m μ but do absorb in the region of 313 m μ , investigations have now been made of the effect of a large number of additives on aging at the shorter wavelength, so that predictions might be made of the most suitable materials to employ in protecting unfilled vulcanizates against crazing in sunlight.

EXPERIMENTAL

Apparatus

Aging was followed by measurement of stress relaxation by means of an instrument similar to that described by Berry, modified so that it could be automatically operated.⁴ The tension in a strip, 3 \times 0.5 \times 0.02 cm., of the vulcanizate held at 100% extension was balanced by the force in a helical steel spring whose extension could be measured by a vernier on the side of the relaxometer. At the point of balance an electrical circuit was completed through a contact on the upper specimen clamp and one on the body of the relaxometer. By means of a relay, completion of this circuit caused the vernier screw to be rotated through 360° by a rotary solenoid (Ledex by National Switch Factory Ltd.) and also caused a mark to be made on the chart of an operations recorder (Evershed & Vignoles Ltd.). Each turn of the head represented a decrease of 0.104 in the vernier reading, and if the initial vernier reading was known, the reading at the times marked on the chart was readily cal-

culated. The results were plotted as graphs of log f/f_0 against time in the usual way.

The light from a compact source lamp (250-w. ME/D type of British Thomson Houston Ltd.) was filtered only by the Pyrex jacket in which the relaxometer was placed; the energy output of the principal ultraviolet mercury lines, according to the manufacturers, and their percentage transmission by the Pyrex jacket are shown in Table I. The relaxometer was irradiated in air in a thermostat maintained at 25°C.

TABLE I

Wavelength, m μ	Energy, watts/steradian	Transmission, %
366.5	1.1	86
334	0.46	80
313.5	0.49	62
303	0.30	42

Materials

In all the experiments described, acetone-extracted highly purified rubber (U.S. Rubber Co.), vulcanized with 3% dicumyl peroxide for 35 min. at 140°C., was employed. Sheets of vulcanizate 0.2 mm. thick were obtained by use of a special mold. These were extracted with hot acetone for 24 hr., dried, and stored *in vacuo* before use.

Additives were introduced into strips of vulcanizate by swelling in the appropriate ethyl acetate solutions overnight and drying *in vacuo*. Concentrations of additives quoted below are those of the swelling solutions of which the rubber imbibed approximately its own weight.

The amines and phenols employed were commercial rubber antioxidants whose source will be noted at the appropriate point in the text. Many of the amines were purified as described previously.¹ The preparation and purification of dibutyl dithiocarbamates and diisopropyldithiophosphates has

also been described elsewhere.^{3,5} The isopropylxanthates were prepared by double decomposition between metal salts and potassium isopropylxanthate prepared by the method of Bulmer and Mann,⁴ and they were purified by recrystallization from acetone. The ultraviolet absorbers were commercial products, Tinuvin P being marketed by Geigy Ltd., U.V.9, U.V.24, and U.V.314, by the Cyanamid Co., and M.D.738 by Armour Hess Chemicals Limited.

RESULTS

Amines

As was observed in 365 m μ light, peroxide vulcanizates containing phenyl- α -naphthylamine (PAN), phenyl- β -naphthylamine (PBN), α,β -dinaphthylamine and β,β -dinaphthylamine all degraded initially more rapidly than the control sample (Fig. 1). However, at the concentration employed (1.4×10^{-3} moles amine/mole rubber) the additives had a marked protective effect in the later stages of degradation. With PAN and α,β -dinaphthylamine this effect manifested itself after about 10% loss of the original network, while with PBN and β,β -dinaphthylamine 20% of the network had degraded before the relaxation rate slowed down. Once again, the initial degradative effect of PBN was found to be most serious at a PBN concentration of 0.7×10^{-3} moles PBN/mole

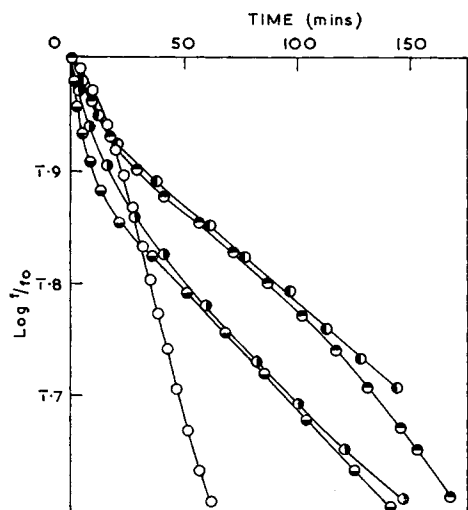


Fig. 1. Comparison of the effect of various naphthylamines at a concentration of 0.7×10^{-3} moles/base mole rubber on the photolytic stress relaxation of a peroxide vulcanizate: (●) phenyl- α -naphthylamine; (○) phenyl- β -naphthylamine; (●) α,β -dinaphthylamine; (○) β,β -dinaphthylamine; (○) no additive.

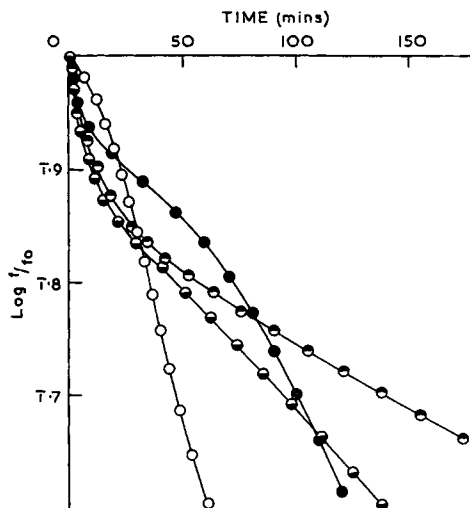


Fig. 2. The effect of varying the concentration of phenyl- β -naphthylamine on the photolytic stress relaxation of a peroxide vulcanizate: (○) no additive; (●) 0.35×10^{-3} moles; (○) 0.7×10^{-3} moles; (○) 1.4×10^{-3} moles amine/base mole rubber.

rubber (Fig. 2). The subsequent inhibitory effect became more marked as the amine concentration was increased. At 0.35×10^{-3} moles PBN/mole rubber, the inhibition persisted only for 50 min., after which the relaxation rate increased again.

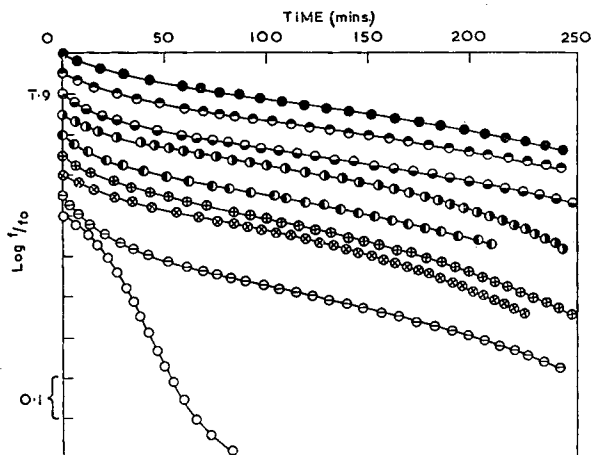


Fig. 3. The influence on the photolytic stress relaxation of a peroxide vulcanizate of various *p*-phenylenediamines introduced by swelling in ethyl acetate solutions (0.7×10^{-3} moles amine/base mole rubber): (●) *N,N'*-diphenyl-*p*-phenylenediamine; (○) *N,N'*-dicyclohexyl-*p*-phenylenediamine; (○) *N,N'*-di-3-(5-methylheptyl)-*p*-phenylenediamine; (○) *N,N'*-di-*sec*-butyl-*p*-phenylenediamine; (○) *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine; (⊗) *N*-phenyl-*N'*-(1-ethyl-3-methylpentyl)-*p*-phenylenediamine; (⊗) *N,N'*-di-2-octyl-*p*-phenylenediamine; (⊖) *N,N'*-dimethyl-*N,N'*-di-(1-methylpropyl)-*p*-phenylenediamine; (○) no additive. (Successive curves have been displaced vertically 0.5 unit.)

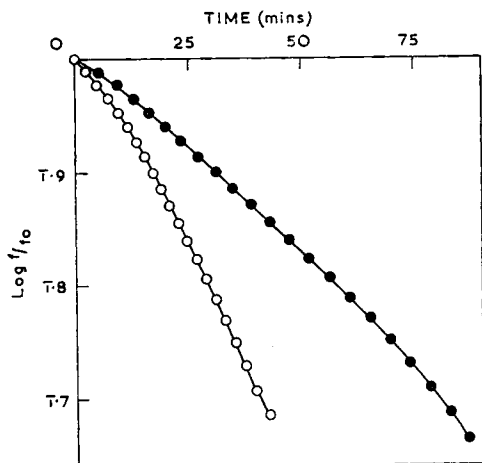


Fig. 4. The effect of diphenylethylenediamine on the photolytic stress relaxation of a peroxide vulcanizate: (●) diphenylethylenediamine (0.7×10^{-3} moles/base mole rubber); (○) no additive.

During the inhibition period the strips were highly colored, but in those samples where the inhibition period was past, the strips had become colorless once again.

On irradiation with wavelengths greater than $300 \mu\mu$, samples containing a variety of *p*-phenylenediamines swollen in from solutions containing 0.7×10^{-3} moles additive/mole rubber all showed a slight increase in degradation rate to begin with, but subsequently degradation was inhibited (Fig. 3). The *p*-phenylenediamines employed were *N,N'*-diphenyl-*p*-phenylenediamine (D.P.P.D., Monsanto Ltd.), *N,N'*-di-*sec*-butyl-*p*-phenylenediamine (Topanol M, I.C.I. Ltd.), *N,N'*-dicyclohexyl-*p*-phenylenediamine (A.B.129, I.C.I. Ltd.), *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine (Antioxidant 4010, J. M. Steel & Co.), *N*-phenyl-*N'*-(1-ethyl-3-methylpentyl)-*p*-phenylenediamine (Universal Oil Products Ltd.), *N,N'*-di-3-(5-methylheptyl)-*p*-phenylenediamine (Tenamene 31, Eastman Kodak Ltd.), *N,N'*-di-2-octyl-*p*-phenylenediamine (Tenamene 30, Eastman Kodak Ltd.), and *N,N'*-dimethyl-*N,N'*-di-(1-methylpropyl)-*p*-phenylenediamine (Eastozone 32, Eastman Kodak Ltd.). The inhibited rate was of the same order with all these additives, and at this stage the strips were highly colored; in all cases degradation speeded up once more after about 200 min., and the color had by then been discharged. The initial acceleration of degradation was serious only in the case of *N,N'*-dimethyl-*N,N'*-di-(1-methylpropyl)-*p*-phenylenediamine, in which all the amine hydrogens were substituted.

In contrast with the *p*-phenylenediamines, diphenylethylenediamine has no initial deleterious effect on aging under $313 \mu\mu$ irradiation, nor does it give rise subsequently to any inhibition period (Fig. 4). Its effect is merely to reduce degradation rate about twofold throughout.

Phenols

In presence of phenolic antioxidants introduced by swelling from 0.2% solutions the relaxation data vary according to the additive employed (Fig. 5). β -Naphthol and 4,4'-butylidenebis(6-*tert*-butyl-3-methylphenol) (Santowhite powder, Monsanto Ltd.) acted only as weak retarders of degradation, and there was only a short inhibition period in presence of α -naphthol and 4,4'-thiobis(6-*tert*-butyl-3-methylphenol) (Santowhite crystals, Monsanto Ltd.). 2,5-Di-*tert*-amylhydroquinone (Santovar A, Monsanto Ltd.) reduced degradation to a very low rate for 150 min., but after that time relaxation speeded up, while protection continued for more than 250 min. in presence of 2,6-di-*tert*-butyl-4-methylphenol (Topanol O, I.C.I. Ltd.) and 2,4-dimethyl-6-*tert*-butylphenol (Topanol A, I.C.I. Ltd.), 2,2'-methylenebis-(4-methyl-6-*tert*-butylphenol) (Antioxidant 425, Cyanamid Corp.), 2,2'-

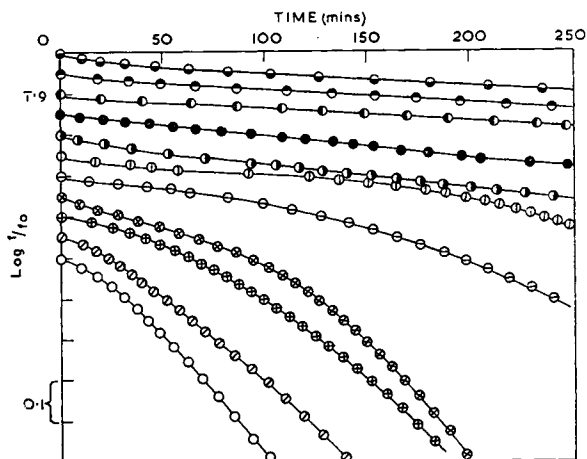


Fig. 5. Comparison of the effect of various phenolic antioxidants introduced by swelling from 0.2% ethyl acetate solution on the photolytic stress relaxation of a peroxide vulcanizate: (●) 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol); (⊙) 2,2'-methylenebis(4-ethyl-6-*tert*-butylphenol); (⊕) 2,4-dimethyl-6-*tert*-butylphenol; (⊖) 2,2'-thiobis(6-methylphenol); (⊗) 2,6-di-*tert*-butyl-4-methylphenol; (⊘) 2,5-di-*tert*-amyl hydroquinone; (⊙) 4,4'-thiobis(6-*tert*-butyl-3-methylphenol); (⊕) α -naphthol; (⊕) 4,4'-butylidenebis(6-*tert*-butyl-3-methylphenol); (⊙) β -naphthol; (○) no additive. (Successive curves have been displaced vertically by 0.05 unit.)

methylenebis(4-ethyl-6-*tert*-butylphenol) (Antioxidant 2246, Cyanamid Corp.), and 2,2'-thiobis-(6-methylphenol) (Santowhite C.M., Monsanto Ltd.); approximately the same steady relaxation rate was attained in presence of all these materials. In presence of Antioxidant 425, Antioxidant 2246, Santowhite C.M., and Topanol O, all relatively colorless and nonstaining antioxidants, the initial rate of degradation was greater than the steady rate subsequently attained.

Dithiocarbamates, Dithiophosphates, and Xanthates

A number of dibutyldithiocarbamates were tested as antioxidants in light of wavelength exceeding $300\text{ m}\mu$ by introduction into peroxide vulcanizates by swelling from 0.2% solutions of the metal salts or 0.3% solutions of the alkylammonium salts. Many of them reduced the rate of relaxation to a low steady value, independent of the nature of the cation, from the commencement of irradiation (Fig. 6). In no case was the protection very long-lived; the nickel salt, which was the most stable, protected for only 150 min. The lifetimes decreased in the following order: Ni > Pb > Zn > Cd > dibutylammonium > Ba > dimethylcyclohexylammonium. Copper and cobalt dibutyldithiocarbamates reduced the initial relaxation rate, but to a lesser extent than the foregoing, while the iron salt had a somewhat deleterious effect.

Nickel, zinc, and lead diisopropyl-dithiophosphates also afforded a marked initial protection against light aging but it was short-lived (Fig. 7).

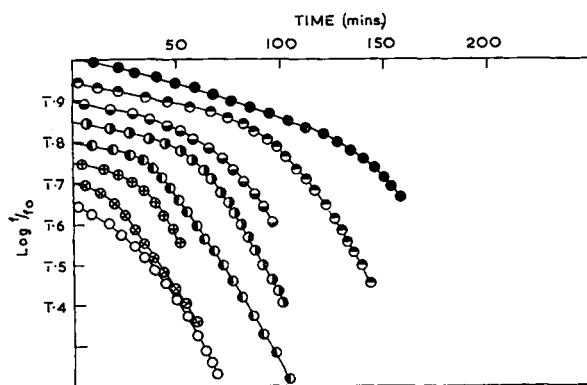


Fig. 6. Comparison of the effect of various dibutyldithiocarbamates introduced by swelling from 0.2% ethyl acetate solution on the photochemical stress relaxation of a peroxide vulcanizate: (●) Ni; (◐) Pb; (◑) Zn; (◒) Cd; (◓) dibutylammonium; (⊕) Ba; (⊗) dimethylcyclohexylammonium; (○) no additive. (Successive curves have been displaced vertically by 0.05 unit.)

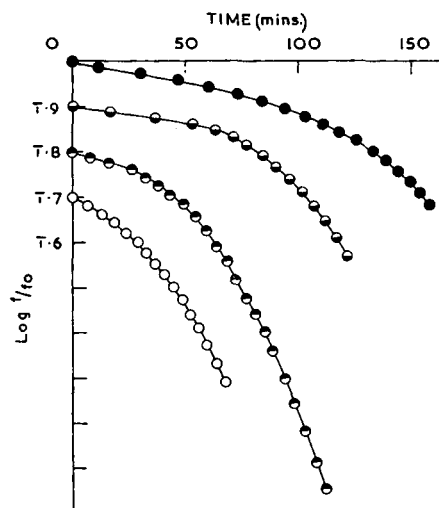


Fig. 7. Comparison of the effect of various diisopropyl-dithiophosphates introduced by swelling from 0.2% ethyl acetate solutions on the photochemical stress relaxation of a peroxide vulcanizate: (●) Ni; (◐) Zn; (◑) Pb; (○) no additive.

The effect of metal isopropylxanthates swollen in from 0.2% solution in ethyl acetate varied considerably according to the nature of the cation (Fig. 8). The zinc, antimony, chromium, and nickel salts initially had a powerful inhibiting effect, but the induction periods for the Zn and Sb salts were only 50 and 100 min., respectively. The Ni and Cr salts remained active for at least 300 min., and data obtained on another sample of rubber (Fig. 11) showed the induction period in presence of nickel isopropylxanthate to be 700 min. The relaxation rate was not so markedly

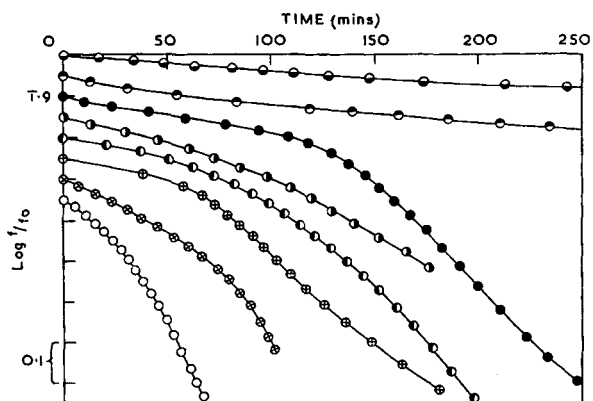


Fig. 8. Comparison of the effect of various isopropylxanthates introduced by swelling from 0.2% ethyl acetate solution on the photochemical stress relaxation of a peroxide vulcanizate: (◐) Ni; (◑) Cr; (◒) Sb; (◓) Mn; (◔) Co; (⊕) Zn; (⊗) Pb; (○) no additive. (Successive curves have been displaced vertically by 0.1 unit.)

reduced by the palladium and bismuth isopropylxanthates, although the effect of the former was long-lived, and the lead salt merely gave rise to a slight retardation in relaxation rate.

Ultraviolet Absorbers

The commercial absorbers of ultraviolet light Tinuvin P, a benzotriazole derivative of undisclosed composition (Geigy Ltd.), U.V. 9 (2-hydroxy-4-methoxybenzophenone), U.V. 24 (2,2'-dihydroxy-4-methoxybenzophenone), and U.V. 314 (2,2'-dihydroxy-4-*n*-octoxybenzophenone) (Cyanamid Corp.) all reduced the rate of photolytic degradation of peroxide vulcanizates slightly in the absence of added antioxidant. In combination with 0.2% antioxidant 2246, 0.2% of any of these ultraviolet absorbers dramatically reduced the rate of photochemical degradation and improved the lifetime of the antioxidant (Fig. 9), Tinuvin P being the most effective. M.D. 738, whose formula is unknown, also reduced the rate of aging but did not improve the lifetime of the antioxidant. The protective effect of phenolic antioxidants 2246 or 425 in combination with Tinuvin P was far greater than that of the antioxidants alone (Fig. 10). In presence of Antioxidant 425 and Tinuvin P the initial rate of degradation was faster than in presence of antioxidant 2246

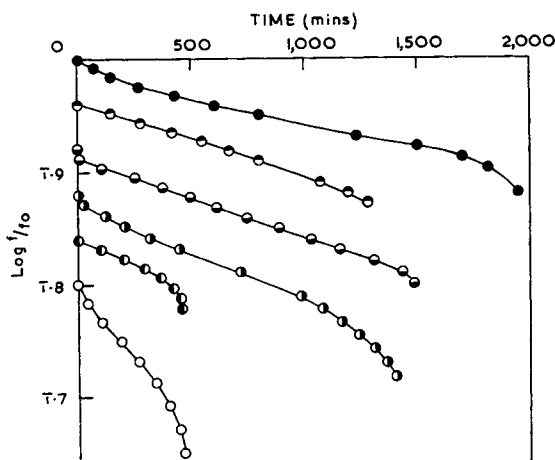


Fig. 9. Comparison of the improvement in photochemical aging of a peroxide vulcanizate brought about by combining 2,2'-methylenebis(4-ethyl-6-*tert*-butylphenol) with various ultraviolet absorbers, all additives being introduced by swelling from a 0.2% ethyl acetate solution: (●) Tinuvin P; (●) 2-hydroxy-4-methoxybenzophenone; (●) 2,2'-dihydroxy-4-*n*-octoxybenzophenone; (●) 2,2'-dihydroxy-4-methoxybenzophenone; (●) M.D. 738; (○) no additive. (Successive curves have been displaced vertically by 0.05 unit.)

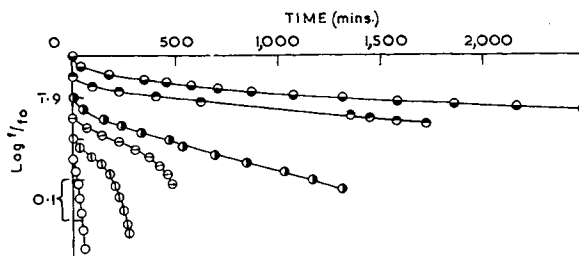


Fig. 10. Comparison of the effect of Tinuvin P on the photochemical aging of a peroxide vulcanizate in presence of phenolic antioxidants, additives having been introduced by swelling from 0.2% ethyl acetate solutions: (●) 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) + Tinuvin P; (●) 2,2'-methylenebis(4-ethyl-6-*tert*-butylphenol) + Tinuvin P; (●) 2,5-di-*tert*-amyl hydroquinone + Tinuvin P; (●) 2,2'-methylenebis(4-ethyl-6-*tert*-butylphenol); (●) 2,5-di-*tert*-amyl hydroquinone; (○) no additive. (Successive curves have been displaced vertically by 0.05 unit.)

and Tinuvin P, but the steady rate of relaxation subsequently attained was somewhat slower. This effect could also be seen when these antioxidants were compared in absence of Tinuvin P (Fig. 5), but it was not then so striking. In presence of Santovar A, which by itself was not very stable, the lifetime of the antioxidant was much prolonged by addition of ultraviolet absorber.

Tinuvin P did not appreciably improve the protection afforded by nickel dibutyldithiocarbamate (Fig. 11) or by nickel isopropylxanthate, although it did improve the rate of relaxation after the antioxidant had been exhausted. Nor did it improve the weak inhibitory effects of zinc diisopropylidithiophosphate or zinc isopropylxanthate, but it increased the useful lifetime of zinc dibutyldithiocarbamate fivefold.

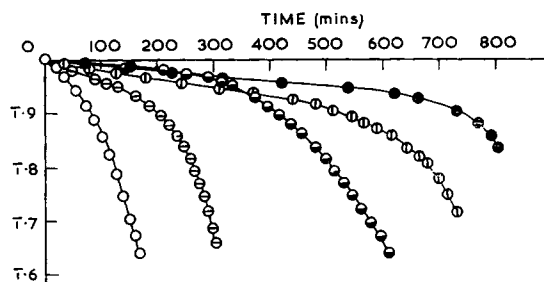


Fig. 11. The effect of Tinuvin P on the photochemical aging of a peroxide vulcanizate containing zinc and nickel dibutyldithiocarbamates, additives having been introduced by swelling in 0.2% ethyl acetate solutions: (●) nickel dibutyldithiocarbamate + Tinuvin P; (●) nickel dibutyldithiocarbamate; (●) zinc dibutyldithiocarbamate + Tinuvin P; (●) zinc dibutyldithiocarbamate; (○) no additives.

DISCUSSION

Naphthylamines photosensitize the degradation of peroxide vulcanizates in light of wavelength 300 $m\mu$ and greater just as they do in 365 $m\mu$ light,¹ but the relative increase in degradation rate is smaller because the vulcanizates itself absorbs strongly at 300 $m\mu$ and relaxes rapidly in the absence of additive. The existence of an optimum concentration (0.7×10^{-3} moles/base mole rubber) of PBN, which causes the most serious degradation, is evident once again. The amount of photosensitization does not, as might be expected, increase continuously with increasing PBN concentration, because a protective effect becomes obvious as relaxation proceeds, and this is more pronounced at higher concentrations. This effect was originally considered to be due to absorption of all radiation by PBN near to the surface of the vulcanizate, so that the rubber in this region was completely degraded while the underlying material remained undegraded and continued to support stress. In such an event, relaxation should cease once the outer layers have completely degraded, but in fact it slowed down to a steady rate and eventually accelerated again (Fig. 2). During the slow stage the samples were highly colored, and this color disappeared as the rate speeded up, indicating that the eventual slowing down of relaxation must be due to a colored oxidation product of the naphthylamines, which subsequently is itself destroyed. PAN and α,β -dinaphthylamine, which are very susceptible to oxidation on storage, are less damaging in ultraviolet light than PBN and β,β -dinaphthylamine, and the latter, which does not readily discolor, gives the least efficient protection against light. The colored product might act either as a true antioxidant or as an ultraviolet absorber, the former being likely, since the ability of the oxidation products of PBN to act as antioxidants has previously been shown.⁶

As had been predicted from an examination of their spectra,¹ the *p*-phenylenediamines also initially accelerated stress relaxation, but highly colored reaction products were rapidly produced, and the relaxation was inhibited until the color was discharged. All *p*-phenylenediamines had much the same effect upon light aging, but since they all gave rise to severe staining during their inhibitory period, they are of no practical use in light-colored vulcanizates. Le Bras⁷ recently suggested that the protective effect of amines against light aging might be due to network reformation by crosslinking. The protective effect

noted in this work and also that to which Le Bras refers¹ cannot be due to crosslinking, since the aging has been followed by measurement of continuous stress relaxation which follows network breakdown only. The possibility of crosslinking cannot be overlooked, however, and would be manifested in increased permanent set in samples after aging. A comparison of the permanent set of a control without additive and a sample which had contained *N*-phenyl-*N'*-cyclohexyl-*p*-phenylenediamine, both of which were 60% degraded, showed that the increase in unstretched length was 40% in each case; with other amines also, the amount of permanent set was found to depend only on the extent of degradation. Crosslinking cannot, therefore, be considered as an important factor in the protective effect of amines against light.

It had been suggested that diphenylethylenediamine might be a useful antioxidant at 313 $m\mu$ since it absorbs only slightly at this and at higher wavelengths.¹ However, although this additive does not accelerate degradation at 313 $m\mu$ it is of no value since it affords only slight protection throughout degradation.

The behavior of phenols as light antioxidants depends markedly on the position and nature of the substituent groups on the phenol. It appears essential that the *ortho* positions should be blocked so as to reduce the possibility of reactions at the hydroxyl group which would destroy the phenol uselessly. β -Naphthol with all *ortho* positions free is ineffective, while α -naphthol and Santowhite powder, both of which have one free *ortho* position, are only weak antioxidants in this system. Santovar A, which also has one free *ortho* position at each hydroxyl group, protects well against light aging, but its action is short-lived; in this case the substituent is bulky *tert*-amyl. In the remaining phenols, all the *ortho* positions were blocked, and all protected very well. Furthermore, none of them seriously discolored the rubber, although in no case did the rubber remain completely colorless; it appeared essential that some of the colored product should have appeared for the rate of aging to reach its minimum, since the rate of relaxation initially decreased and attained a low steady value.

The addition of ultraviolet absorber Tinuvin P still further reduced the rate of relaxation in presence of a hindered phenol (Fig. 10), and the results obtained by combining Tinuvin P and Santovar A show that the presence of ultraviolet absorber also prolongs the life of the antioxidant.

It is much more obvious from the results obtained in presence of Tinuvin P that the maximum inhibition is not exhibited until some stain has appeared in the rubber. The technological importance of the combination of ultraviolet absorbers with hindered phenolic antioxidants has already been discussed,⁸ and it is now clear that those absorbers which are derived from benzophenone compare fairly well with Tinuvin P (Fig. 9).

It has already been pointed out that a variety of dialkylthiocarbamates act as antioxidants in rubber irradiated with 365 m μ light,³ although some of them are short-lived. This was also true in light of shorter wavelengths (Fig. 6), but the lifetime of dithiocarbamate introduced from 0.2% solution was only about 50 min. The inhibited rate was independent of the cation, but the lifetime varied, the nickel dibutylthiocarbamate being the longest lived. Metal diisopropylthiophosphates also protected against 313 m μ light for a short while, but none of these materials were sufficiently long-lived to be useful in practice.

Nickel isopropylxanthate, which has been advocated as a very efficient protective agent in light,⁹ does indeed compare very favorably with hindered phenols without added ultraviolet absorber (Fig. 8); it is not, however, improved by the addition of Tinuvin P. This protective action is not specific to the nickel salt, as has previously been implied, for equally good results were obtained with chromium isopropylxanthate, while the antimony, manganese, cobalt, and zinc salts reduced relaxation to the same inhibited rate, although they were somewhat short-lived. Palladium and bismuth salts retarded relaxation as if they were acting as ultraviolet absorbers. It was conceived that the stability of the nickel and chromium salts might be due to the formation of complexes, but this seems unlikely in view of the fact that neither cobalt nor manganese isopropylxanthates have long-lived protective action. Karmitz⁹ suggested that the protective role of nickel isopropylxanthate is partially that of an ultraviolet absorber, and, while this cannot be its only mode of protection, since it is known that many dithiocarbamates including that of nickel protect against thermal as well as photolytic aging, the fact that the nickel salt is particularly long-lived may be due to its absorbing harmlessly radiation which would otherwise cause the rubber to oxidize and necessitate the intervention of the nickel salt as a true antioxidant. Some evidence that the nickel salts do, in fact, act as ultraviolet absorbers

has been obtained by comparing the effect of Tinuvin P on samples containing zinc and nickel dibutylthiocarbamates (Fig. 11). Addition of Tinuvin P to a sample containing the zinc salt markedly reduced the inhibited rate and extended the period of inhibition, whereas in presence of the nickel salt addition of Tinuvin P effected no substantial improvement in relaxation rate or inhibition period. As stated above, Tinuvin P is also without effect in the presence of nickel isopropylxanthate, which suggests that these nickel salts are already acting as ultraviolet absorbers, as well as antioxidants.

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Synopsis

The oxidative degradation of peroxide vulcanized natural rubber at wavelengths of 300 m μ and above has been studied by the technique of stress relaxation. Substituted naphthylamines and *p*-phenylenediamines, particularly the former, initially photosensitize the degradation of the vulcanizate but subsequently give rise to colored products which act as antioxidants. The protective action of these amines is not due to network formation. Completely hindered phenols have been shown to be powerful antioxidants of long life, but nonhindered phenols are not good antioxidants against light. The combination of an ultraviolet absorber with a hindered phenol gives excellent protection which is only fully developed when a little of the phenol has been oxidized to a colored compound. Many dithiocarbamates, dithiophosphates, and xanthates protect against light, but their effect is short-lived except in the case of nickel and chromium isopropylxanthates. The peculiar stability of these materials is attributed to their acting as both ultraviolet absorbers and antioxidants. Since the addition of

ultraviolet absorber to the nickel and chromium xanthates does not further increase their effectiveness, the combination of a hindered phenol and an ultraviolet absorber is the most potent protective agent against light for incorporation into translucent rubber vulcanizates.

Résumé

La dégradation oxydante du caoutchouc naturel vulcanisé par du peroxyde, à des longueurs d'onde de 300 m μ et au delà a été étudiée par la méthode de relaxation à la tension. Des naphthylamines et des *p*-phénylènediamines substituées, surtout les premières, photosensibilisent initialement la dégradation du vulcanisat mais dans la suite donnent naissance à des produits colorés qui agissent comme anti-oxydants. L'action protectrice de ces amines n'est pas due à la formation d'un réseau. On a montré que des phénols complètement substitués étaient des anti-oxydants puissants de longue durée mais que des phénols non substitués ne sont pas de bons anti-oxydants contre la lumière. La combinaison d'une substance absorbant l'ultraviolet avec un phénol substitué fournit une excellente protection qui n'est complètement active que lorsqu'un peu de phénol a été oxydé en composé coloré. De nombreux dithiocarbamates, dithiophosphates et xanthates protègent contre la lumière mais leur effect est de courte durée sauf dans le cas des isopropylxanthates de nickel et de chrome. La stabilité particulière de ces substances est attribuée à leur action conjuguée d'absorbant de lumière ultraviolette et d'anti-oxydant. Puisque l'addition d'absorbant de lumière ultraviolette aux xanthates de nickel et de chrome n'accroît pas leur efficacité, la combinaison d'un phénol substitué et d'un absorbant de lumière ultraviolette constitue l'agent protecteur le plus puissant contre la lumière

pour l'incorporation dans les caoutchoucs translucides vulcanisés.

Zusammenfassung

Der oxydative Abbau von Peroxyd-vulkanisiertem Naturkautschuk bei Wellenlängen von 300 m μ und darüber wurde nach dem Spannungsrelaxationsverfahren untersucht. Substituierte Naphthylamine und *p*-Phenylendiamine, und zwar besonders das erstere, photosensibilisieren anfänglich den Abbau der Vulkanisate, geben aber dann Anlass zur Bildung gefärbter Produkte, die als Antioxydantien wirken. Die Schutzwirkung dieser Amine geht nicht auf eine Vernetzungswirkung zurück. Phenole mit völliger sterischer Hinderung erwiesen sich als wirksame Antioxydantien mit langer Lebensdauer, Phenole ohne sterische Hinderung sind jedoch keine guten Antioxydantien gegen Licht. Die Kombination eines UV-Absorbers mit einem Phenol mit sterischer Hinderung liefert eine ausgezeichnete Schutzwirkung, die sich erst voll entwickelt sobald ein Bruchteil des Phenols zu einer gefärbten Verbindung oxydiert wurde. Viele Dithiocarbamate, Dithiophosphate und Xanthate schützen gegen Licht, ihre Wirkung ist jedoch von kurzer Dauer, mit Ausnahme des Falles von Nickel- und Chromisopropylxanthat. Die besondere Stabilität dieser Stoffe wird darauf zurückgeführt, dass sie sowohl als UV-Absorber als auch als Antioxydantien wirken. Da ein Zusatz eines UV-Absorbers zu Nickel- und Chromxanthat deren Wirksamkeit nicht weiter erhöht, bildet die Kombination eines Phenols mit sterischer Hinderung und eines UV-Absorbers das bestwirksame Schutzmittel gegen Licht zum Einbau in durchscheinende Kautschukvulkanisate.

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