

The Aging of Thiuram Disulfide Vulcanizates and Their Mechanism of Vulcanization

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INTRODUCTION

Tetraalkylthiuram disulfides, particularly the methyl and ethyl isomers, are well known as vulcanizing agents for natural rubber, producing, in the absence of sulfur, vulcanizates very resistant to high temperature oxidative degradation. It has recently been shown^{1,2} that this aging resistance is due, in large part at least, to the presence in the vulcanizate of zinc dialkyldithiocarbamates formed during the curing;³ after acetone extraction the vulcanizate ages rapidly but can be protected by reintroduction of dithiocarbamate.

A systematic study has now been made of the effect of extent of vulcanization on the oxidative aging by heat or ultraviolet light of thiuram-vulcanized rubber and of the aging behavior of rubbers crosslinked by different tetraalkylthiuram disulfides in equimolecular quantities.

Use was made of the technique of stress relaxation⁴ in which the decay during aging of the tension in a strip held at constant extension is followed. Crosslinking reactions which occur during aging produce new crosslinks in equilibrium in the extended strip and therefore have little or no effect on the tension. Consequently, these "continuous" measurements determine only the amount of degradation occurring.⁵ Crosslinking reactions were followed by using the somewhat different "intermittent" technique, in which the aging is carried out with the strip of rubber unstrained for the greater part of the time, but extended periodically to a constant length for a period sufficient to enable the force required to be measured. This type of measurement takes into account both the remaining undegraded network and any crosslinks formed during aging.⁵

EXPERIMENTAL

Materials

Tetramethylthiuram disulfide (TMT) and tetraethylthiuram disulfide (TET) were commercial

products produced by Monsanto Ltd. The tetrabutyl analogue (TBT) was prepared from a 47% aqueous solution of sodium dibutyldithiocarbamate (Tepidone, du Pont de Nemours & Co.) by oxidation with chloramine-T by a method similar to that used by Bulmer and Mann⁶ in the preparation of alkyl xanthogen disulfides from xanthates.

Vulcanization

The following recipes were used: pale crepe, 100 parts; zinc oxide, 5 parts; TMT, 4.0 parts: pale crepe, 100 parts; zinc oxide, 5 parts; TET, 4.9 parts: pale crepe, 100 parts; zinc oxide, 5 parts; TBT, 6.5; the amounts of vulcanizing agent being adjusted so that equivalent quantities were used. Stearic acid was omitted from the recipes after having been found to have no effect on the aging. Sheets, 10 cm. × 10 cm. × 0.02 cm., were produced in a suitable mold under a pressure of about 1 ton/in.² at 140°C. for vulcanization times as given in Table I. One half of each sheet was extracted continuously with hot acetone for 24 hours and then vacuum-dried.

The peroxide vulcanizate used in some of the auxiliary experiments was prepared in the same mold using the recipe: deproteinized crepe, 100 parts; dicumyl peroxide, 3 parts. Vulcanization was for 30 minutes at 140°C., and the sheet was then extracted for 24 hr. in hot acetone.

Stress-Relaxation Measurements

The techniques involved in the stress-relaxation measurements have been fully described previously.⁷⁻⁹ In all cases the initial extension was 100%.

The theory of rubber elasticity shows that

$$\frac{f}{f_0} = \frac{N}{N_0}$$

where f is the force exerted by an extended rubber sample and N is the number of network chains supporting the stress. In continuous measurements

TABLE I

Values of the Volume Fraction of Rubber Swollen in *n*-Decane at 25°C. (v_r) for Unaged Vulcanizates and for Vulcanizates Aged to a Stress Ratio $(f/f_0)_{final}$ in air at 100°C.

Thiuram	Vulcanization time (min.)	Unextracted vulcanizates			Extracted vulcanizates		
		v_r (unaged)	v_r (aged)	$(f/f_0)_{final}$	v_r (unaged)	v_r (aged)	$(f/f_0)_{final}$
TMT	6	0.143	0.260	0.410	—	0.255	0.504
	8	0.164	0.287	0.553	0.188	0.258	0.524
	10	0.188	0.314	0.658	0.203	0.255	0.591
	10	0.204	0.303	0.630	0.202	0.227	0.650
	15	0.251	0.304	0.774	0.238	0.235	0.584
	20	0.267	0.288	0.788	0.256	0.240	0.590
	30	0.282	0.299	0.936	0.267	0.217	0.462
	40	0.290	0.298	0.926	0.272	—	0.431
	60	0.292	0.289	0.940	0.278	0.243	0.353
TET	90	0.289	0.285	0.941	—	—	—
	15	0.162	0.293	0.744	0.156	0.239	0.444
	20	0.214	0.292	0.807	0.202	0.242	0.511
	30	0.245	0.279	0.841	0.234	0.236	0.747
	40	0.268	0.287	0.870	0.245	0.235	0.729
	60	0.288	0.281	0.876	0.261	0.207	0.421
	75	0.280	0.282	0.913	0.263	0.236	0.476
	90	0.283	0.280	0.893	0.260	0.232	0.466
	120	0.283	0.254	0.917	—	0.241	0.578
TBT	180	0.289	0.277	0.913	0.260	0.245	0.714
	30	0.237	—	0.743	0.213	0.228	0.755
	40	0.246	0.289	0.865	0.229	0.227	0.722
	60	0.272	0.294	0.933	0.256	0.247	0.753
	90	0.290	0.293	0.954	0.262	0.241	0.631
	120	0.286	0.292	0.871	0.256	0.245	0.755
	180	0.284	0.292	0.875	0.259	0.235	0.707

only the N_r chains remaining from the original network support stress, while in intermittent measurements these are supplemented by N_f chains formed by crosslinking reactions in the unextended strip, i.e.,

$$(f/f_0)_{continuous} = N_r/N_0$$

and

$$(f/f_0)_{intermittent} - (f/f_0)_{continuous} = N_f/N_0$$

Thus continuous stress measurements provide a direct means of following network degradation, while a comparison of the results of intermittent and continuous stress relaxation gives a direct measure of the amount of crosslinking occurring during aging.

Equilibrium Swelling

A convenient measure of the extent of crosslinking in a vulcanized network was obtained by measurement of the equilibrium swelling at 25°C. in *n*-decane. Pieces cut from the sheet of vulcanizate were weighed and then allowed to swell in the liquid for 24 hr. at 25°C. They were then removed, rapidly surface-dried, and reweighed. Knowledge of the densities at 25°C. of rubber

(0.910) and of *n*-decane (0.726) enabled the volume fraction of rubber, v_r , in the swollen vulcanizate to be determined. The elastic constant C_1 , a direct measure of the extent of crosslinking, could be obtained from v_r if desired by means of a previous calibration.¹⁰

EXPERIMENTAL RESULTS

Measurements of the volume fraction of rubber, v_r , when the various vulcanizates before aging are swollen to equilibrium in *n*-decane (Table I) bear out the technological observations that tetramethylthiuram disulfide gives more rapid vulcanization than the tetraethyl or tetrabutyl compounds, the respective times required to reach maximum crosslinking being 40, 60, and 90 minutes although equimolecular amounts of the three compounds were used. The extents of crosslinking attained after these vulcanization times were similar for all the three compounds. However, since zinc dimethyldithiocarbamate, which is formed during vulcanization with TMT, has a low solubility in rubber, the stocks which were cured fully with this compound bloomed badly; the tetraethyl and tetrabutyl compounds give much more soluble dithiocarbamates and have an advantage in this respect.

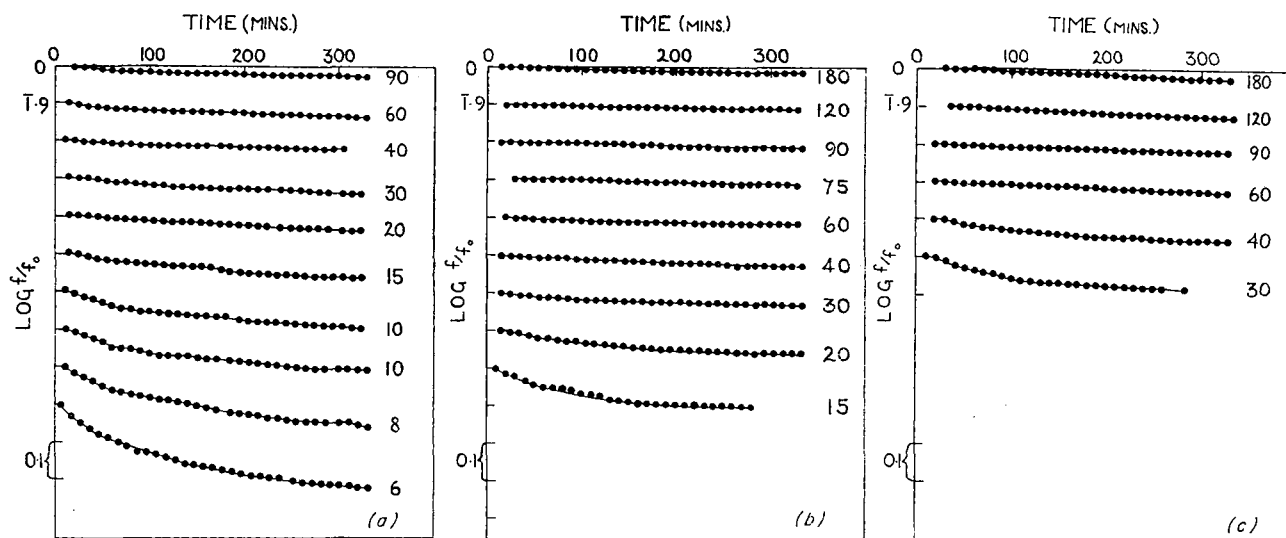


Fig. 1. Stress relaxation at 100°C. in air of unextracted tetraalkylthiuram disulfide vulcanizates: (a) TMT; (b) TET; (c) TBT. Times of vulcanization at 140°C. are included on the diagrams, and successive graphs are vertically displaced by 0.1 unit.

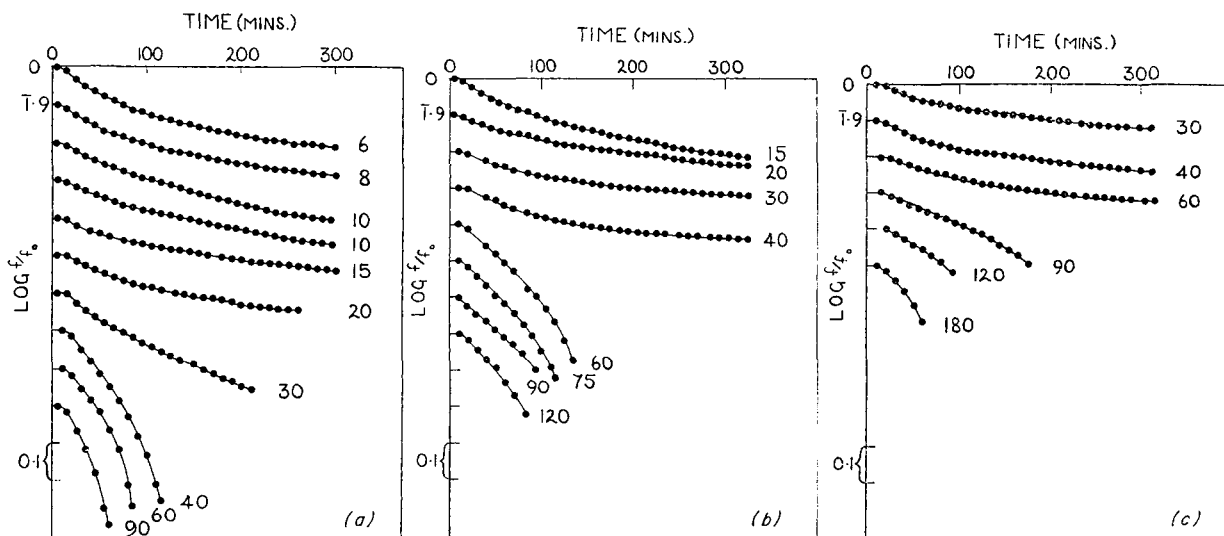


Fig. 2. Stress relaxation at 100°C. in air of extracted tetraalkylthiuram disulfide vulcanizates: (a) TMT; (b) TET; (c) TBT. Times of vulcanization at 140°C. are included on the diagrams, and successive graphs are vertically displaced by 0.1 unit.

Figures 1 and 2 show the course of stress relaxation in air at 100°C. for the three thiuram vulcanizates before and after extraction, the results being shown as plots of $\log(f/f_0)$ against t , where f is the force exerted by the strip at time t and f_0 is the initial force. Figures 3 and 4 show the results obtained during relaxation in oxygen at 25°C. under the influence of ultraviolet light of wavelength 365 $m\mu$. The fully cured stocks showed excellent resistance to aging before extraction, the nature of the alkyl groups making little difference although the tetraethyl compound did give

marginally better results. In the early stages of aging of grossly undercured stocks the relaxation was more rapid but later decreased in rate.

The aging of the extracted vulcanizates showed a very different pattern. In accordance with previous observations¹ on TMT vulcanizates, the fully cured materials aged very rapidly both thermally and photochemically. During thermal aging of extracted, under-cured vulcanizates, however, the rate of degradation, initially rapid, quickly decreased and finally assumed a steady value similar to that obtained with unextracted vulcanizates.

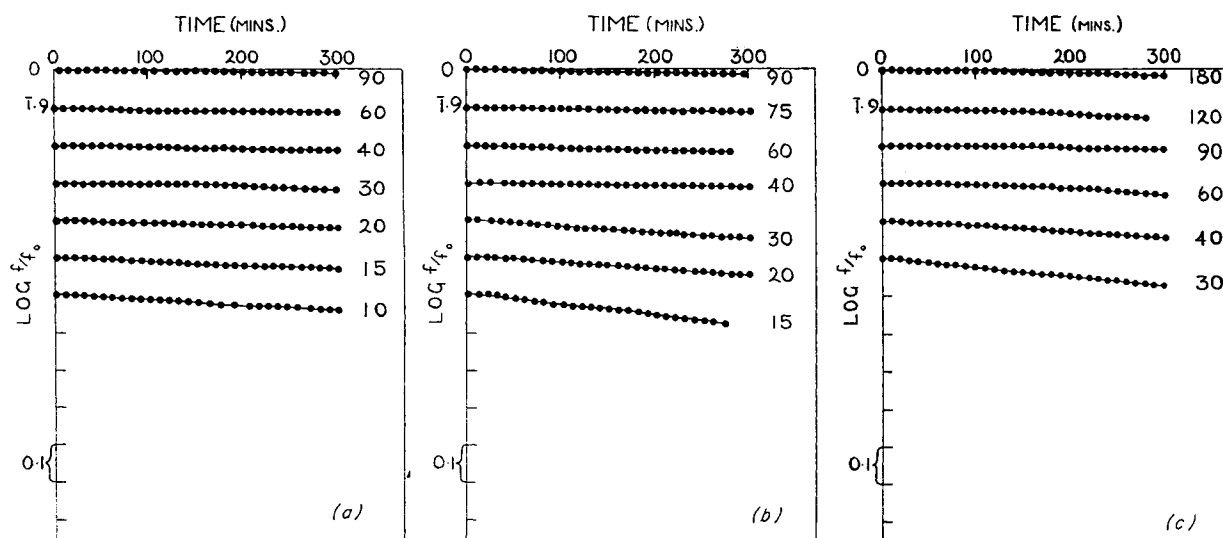


Fig. 3. Stress relaxation under $365\text{ m}\mu$ irradiation in oxygen of unextracted tetraalkylthiuram disulfide vulcanizates: (a) TMT; (b) TET; (c) TBT. Times of vulcanization at 140°C . are included on the diagrams, and successive graphs are vertically displaced by 0.1 unit.

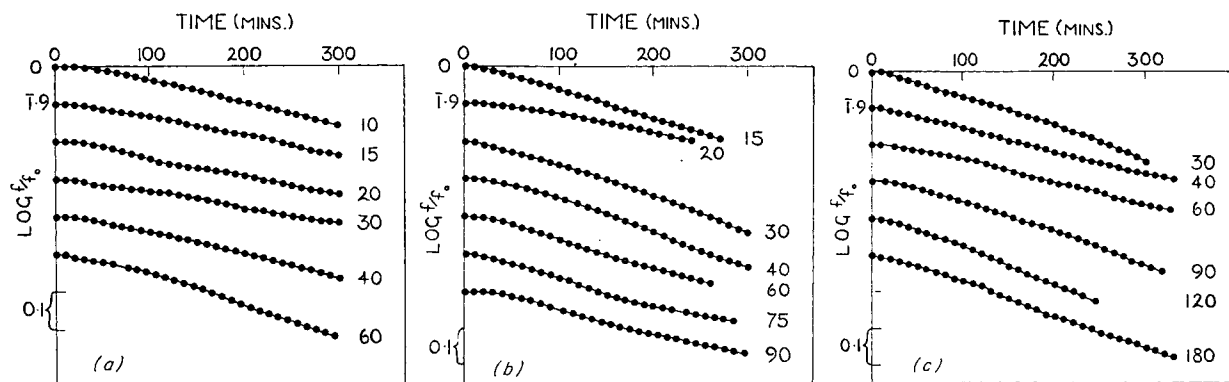


Fig. 4. Stress relaxation under $365\text{ m}\mu$ irradiation in oxygen of unextracted tetraalkylthiuram disulfide vulcanizates: (a) TMT; (b) TET; (c) TBT. Times of vulcanization at 140°C . are included on the diagrams, and successive graphs are vertically displaced by 0.1 unit.

In ultraviolet light, on the other hand, the behavior of the extracted stocks did not depend greatly on the state of cure.

With undercured materials, both extracted and unextracted, considerable crosslinking occurred during thermal aging as is indicated by the equilibrium swellings in *n*-decane, v_r , (Table I) and shown in greater detail for the TMT vulcanizates by the intermittent stress-relaxation measurements (Figs. 5 and 6). The effect is larger for the unextracted cures and even the fully cured materials showed a small amount of crosslinking. During photolytic aging there is a small amount of crosslinking, the extent of which does not vary with the state of cure.

DISCUSSION

It has previously been demonstrated¹ that the resistance to aging of unextracted fully-cured

thiuram vulcanizates is due to the presence in them of powerful antioxidants, the zinc dialkyldithiocarbamates, which are formed during vulcanization.³

The somewhat lower initial resistance to thermal aging of the unextracted but undercured materials does not appear to be due to the lower concentration of dithiocarbamate in these materials, since very low concentrations of dithiocarbamate (0.2%) have previously been found to give excellent protection over periods of time comparable to those investigated here.¹ Extraction of an undercured TMT vulcanizate and subsequent replacement of zinc diethyldithiocarbamate by swelling from a saturated ethyl acetate solution did not prevent this initial rapid relaxation. Consequently this behavior is not due to the presence of an extractable prooxidant and must be a property inherent in the network. Furthermore, TMT itself acts as a

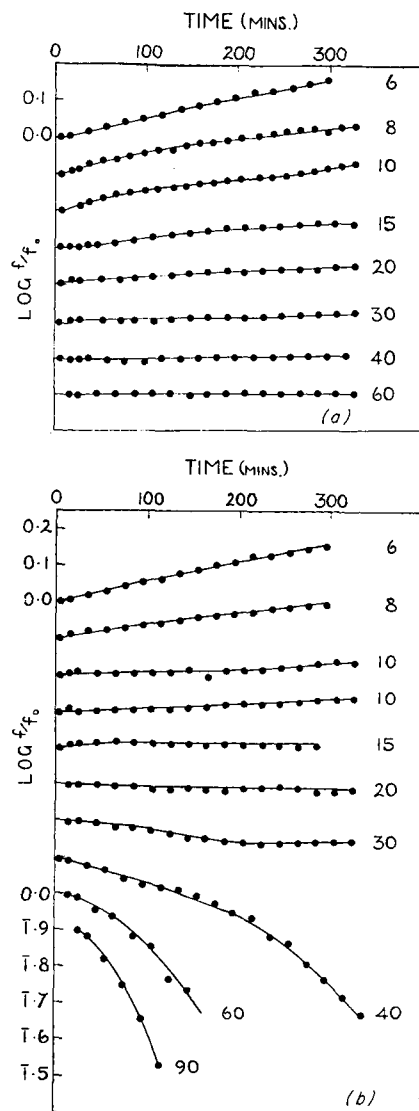


Fig. 5. Intermittent stress relaxation at 100°C. in air of TMT vulcanizates: (a) unextracted; (b) extracted. Times of vulcanization at 140°C. are included in the diagrams, and successive graphs are vertically displaced by 0.1 unit.

fairly good antioxidant in a peroxide vulcanizate (Fig. 7).

The decreasing rate of thermal relaxation in extracted undercured materials suggests that an antioxidant can be formed by heating them at 100°C., even in the absence of the vulcanizing agent. Scheele and co-workers¹¹ have measured the rate of formation of zinc dithiocarbamates during vulcanization with thiuram disulfides and have deduced that a two-stage process is involved. In order to explain the present results it is necessary only that the intermediate product, still present in undercured vulcanizates, is not extracted from the rubber by hot acetone, for then dithiocarbamate

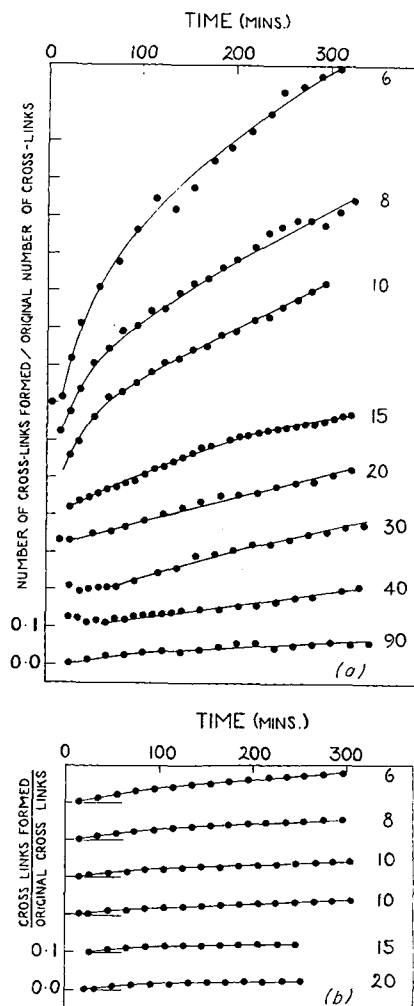


Fig. 6. Crosslink formation during aging in air of TMT vulcanizates at 100°C., derived from measurements of continuous and intermittent stress: (a) unextracted; (b) extracted. Times of vulcanization at 140°C. are included in the diagrams, and successive graphs are vertically displaced by 0.1 unit.

will be slowly formed at 100°C., by the further reaction of this intermediate. This mechanism explains also why extracted, under-cured vulcanizates are crosslinked considerably during aging while extracted, fully cured vulcanizates are not, if an intermediate which leads to dithiocarbamate formation is also an intermediate in the crosslinking reaction. These results give no evidence as to whether dithiocarbamate can be formed without crosslinks being formed, but indicate that the degree of cure affects both reactions in the same manner.¹² The absence of formation of antioxidant in undercured stocks under light-aging conditions is attributable to stability of the intermediate at the low temperature used.

As confirmation of the suggestion of an intermediate compound, the following simple observa-

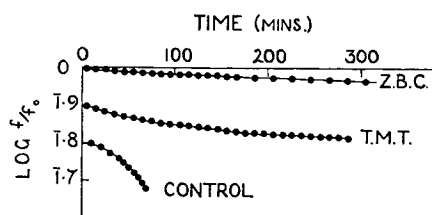


Fig. 7. Comparison of antioxidant effects of zinc diethylthiocarbamate and tetramethylthiuram disulfide at a concentration of 1% in a peroxide vulcanizate relaxed in air at 100°C.

tions may be quoted. A TMT vulcanizate was cured for 10 minutes at 140°C. and then thoroughly extracted with hot acetone, returned to the press in an evacuated mold, and heated at 140°C. for a further 60 minutes. This second heating reduced the equilibrium swelling of the vulcanizate in *n*-decane from a v_r -value of 0.202 to one of 0.257, indicating about a 76% increase in the number of crosslinks. Similarly, a 20-minute TBT cure after extraction and then a further 90 minutes curing showed an increase in v_r from 0.233 to 0.246.

The initial thermal relaxation of unextracted undercured vulcanizate is probably connected with the decomposition of the vulcanization intermediate. The stability of this intermediate under 365 μ irradiation would then mean that such materials should not differ from fully cured vulcanizates in photolytic stress relaxation as is, in fact, observed.

Scheele, Lorentz, and Dummer originally proposed¹¹ a detailed mechanism for thiuram vulcanization which included an initial addition of thiuram disulfide across double bonds of the rubber, the addition compound then reacting with further polyisoprene to give crosslinking and formation of dithiocarbamate. Such a mechanism would have been completely in accordance with the present results but was later discarded by Scheele and Bielstein,¹² who proposed a more complicated mechanism involving the formation of a mercaptan intermediate which reacts with further thiuram disulfide to give crosslinking. This mechanism will not account for the present results, since it does not explain the formation of antioxidant after extraction. In any case, since, according to this mechanism, dithiocarbamate is always formed by reaction of $R_2N-C(S)-S$ radicals produced by decomposition of the disulfide, it cannot be formed more rapidly than the disulfide disappears, and this cannot be reconciled with the earlier kinetic results of Scheele's group, which show that, in general, a stage in the reaction is reached after which more dithiocarbamate is formed than is equivalent to the thiuram which disappears: e.g., at 160°C. after 20 minutes

only 3% of the original tetrapropylthiuram disulfide remains, but dithiocarbamate equivalent to at least 26% of original thiuram is later formed.

Similar critical comments can be made regarding Craig's¹⁴ mechanism of formation of dithiocarbamate and sulfur as intermediates in the vulcanization, since these will also be extracted by acetone.

Finally, it is suggested that the small amount of crosslinking which occurs during aging at 100°C. with the unextracted, fully cured vulcanizates in which there can be no thiuram disulfide or intermediate compound left is due to a reaction involving dithiocarbamate and oxygen. The results of continuous and intermittent stress-relaxation measurements on an extracted peroxide vulcanizate into which approximately 1% zinc, copper, nickel, or dibutylammonium dithiocarbamate had been introduced by swelling from ethyl acetate solution support this suggestion (Table II). Peroxide vulcanizates, after extraction, do not crosslink during aging, and it would thus appear that the presence of any one of the dithiocarbamates leads to a small amount of crosslinking during aging at 100°C. in air. This may account for the considerable compression set observed during the technological aging of thiuram vulcanizates.

TABLE II

Comparison of Continuous and Intermittent Stress Relaxation of a Peroxide Vulcanizate Containing 1% of Various Dibutylthiocarbamates after 1300 Min. in Air at 100°C.

Dibutylthiocarbamates	$(f/f_0)_{Int.}$	$(f/f_0)_{Cont.}$	$-(f/f_0)_{Cont.}$
Zinc	0.981	0.874	0.107
Copper	0.989	0.926	0.063
Nickel	1.012	0.880	0.132
Dibutylammonium	1.036	0.860	0.176

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Synopsis

The aging of sulfurless tetraalkylthiuramdisulfide vulcanizates has been studied by the stress-relaxation technique, the general behavior being independent of the nature of the alkyl group. The aging in air at 100°C. of fully cured vulcanizates is excellent before acetone extraction but rapid after it, due to removal of zinc dialkyldithiocarbamates which are powerful antioxidants. In undercured vulcanizates, the network breakdown at 100°C. after extraction is much less than in fully cured samples, and there is considerable crosslinking during the aging. This behavior is attributed to the presence of a vulcanization intermediate which, at 100°C., brings about crosslinking with formation of zinc dialkyldithiocarbamate and which cannot be removed by acetone extraction. The presence of such an intermediate is confirmed by the ability of extracted undercured thiuram vulcanizates to be further crosslinked in the press at 140°C. Previous theories regarding thiuram vulcanization are discussed in the light of these observations. The rapid initial relaxation of unextracted undercured vulcanizates may be due to the breakdown of this vulcanization intermediate. During the thermal aging of apparently fully cured samples, some crosslinking occurs which is considered to be due to a direct oxidative reaction of dithiocarbamates. Unextracted thiuram vulcanizates degrade very little on illumination with ultraviolet light (wavelength 365 m μ), but, after extraction, the photolytic aging becomes more rapid. There is no variation in the rate of this type of aging with degree of cure, presumably because the vulcanization intermediate is light-stable.

Résumé

Le vieillissement de vulcanisats au disulfure de tétraalcoylthiurame (sans soufre) a été étudié par la technique de tension-relaxation; le comportement général est indépendant du groupe alcoyle. Le vieillissement à l'air à 100°C de vulcanisats entièrement traités est excellent avant une extraction à l'acétone mais est rapide après celle-ci par suite de l'élimination des dialcoyldithiocarbamates de zinc qui sont des antioxydants énergiques. Dans les vulcanisats non-entièrement préparés la scission du réseau à 100°C après extraction est beaucoup plus faible que dans les échantillons entièrement prêts, et il y a un considérable pontage en cours de vieillissement. Ce comportement est attribué à la présence d'un intermédiaire en cours de vulcanisation, qui provoque à 100°C le pontage par formation

de dialcoyldithiocarbamate de zinc, et qui ne peut être éliminé par extraction à l'acétone. La présence d'un tel intermédiaire est confirmée par la possibilité de ponter ultérieurement à la presse à 140°C un vulcanisat au thiurame, non-entièrement traité et extrait au préalable. Les théories antérieures concernant la vulcanisation au thiurame sont discutées sur la base de ces observations. La relaxation initiale rapide de vulcanisats non-extraits peut être due à la rupture de cet intermédiaire de vulcanisation. Au cours du vieillissement thermique d'échantillons apparemment prêts il se passe quelques pontages qui sont considérés comme résultant de l'oxydation directe des dithiocarbamates. Les vulcanisats au thiurame non-extraits dégradent très peu par illumination sous la lumière ultra-violette (longueur d'onde 365 m μ), mais après extraction le vieillissement photolytique devient plus rapide. Il n'y a pas de changement de vitesse de ce genre de vieillissement en cours de traitement, vraisemblablement par suite de la stabilité à la lumière de cet intermédiaire de vulcanisation.

Zusammenfassung

Die Alterung von schwefelfreien Tetraalkylthiuramdisulfid-Vulkanisaten wurde mittels des Spannungsrelaxationsverfahrens untersucht, wobei das allgemeine Verhalten sich als unabhängig von der Natur der Alkylgruppe erwies. Das Verhalten von völlig ausvulkanisierten Proben bei der Alterung an Luft bei 100°C ist, vor der Acetonextraktion, ausgezeichnet, nachher erfolgt aber wegen der Entfernung der Zinkdialkyldithiocarbamate, die wirksame Antioxydantien sind, rasche Alterung. Bei nicht völlig ausvulkanisierten Proben ist die Zerstörung des Netzwerkes bei 100° nach der Extraktion viel geringer als bei den ausvulkanisierten und es tritt eine beträchtliche Vernetzung während der Alterung auf. Dieses Verhalten wird der Gegenwart eines intermediären Stoffes bei der Vulkanisation zugeschrieben, der bei 100°C eine Vernetzung unter Bildung von Zinkdialkyldithiocarbamat hervorruft und der nicht durch Acetonextraktion entfernt werden kann. Die Gegenwart eines solchen intermediären Stoffes wird durch die Fähigkeit extrahierter, mit Thiuram nicht völlig ausvulkanisierter Proben zur weiteren Vernetzung in der Presse bei 140°C bestätigt. Ältere Theorien über die Thiuram-Vulkanisation werden im Lichte dieser Beobachtungen besprochen. Die rasche anfängliche Relaxation von nicht extrahierten, nicht völlig ausvulkanisierten Proben ist vielleicht auf die Zerstörung dieses Vulkanisations-Zwischenproduktes zurückzuführen. Während der thermischen Alterung von offenbar völlig ausvulkanisierten Proben tritt eine gewisse Vernetzung ein, die als eine Folge einer direkten Oxydationsreaktion des Dithiocarbamats betrachtet wird. Nicht extrahierte Thiuram-Vulkanisate werden bei Bestrahlung mit ultraviolettem Licht (Wellenlänge 365 m μ) sehr wenig abgebaut; nach der Extraktion geht aber die photolytische Alterung rascher vor sich-Es besteht keine Abhängigkeit der Geschwindigkeit dieser Art von Alterung vom Vulkanisationsgrad, wahrscheinlich deshalb, weil der intermediäre Stoff der Vulkanisation lichtbeständig ist.

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