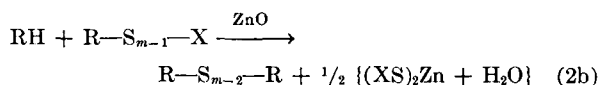
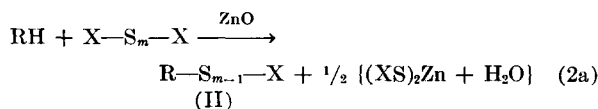
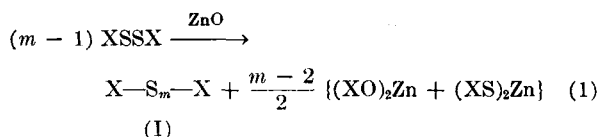


An Interpretation of Acceleration by Thiourea and Related Compounds of the Tetramethylthiuram Disulfide Vulcanization of Natural Rubber

It has recently been discovered that thiourea and certain of its *N*-derivatives¹ and chemically related compounds,² accelerate the vulcanization of natural rubber (NR) by tetramethylthiuram disulfide (TMTD)-zinc oxide combinations to such an extent that excellent vulcanizates can be produced at 100°C. or lower.

A reasonable explanation of this acceleration is now offered, based on a theory of vulcanization by TMTD and related "sulfurless" curing systems currently being developed here. This theory recognizes the importance of polysulfidic intermediates (I, $m > 2$), formed during the vulcanization process, which subsequently react with the polyisoprene to yield further intermediates (II) which finally react to yield sulfurated crosslinks.

The process is broadly schematized as follows:

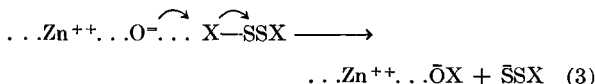


where $\text{X} = \text{Me}_2\text{N}\cdot\text{C}(\text{:S})-$; RH = rubber hydrocarbon.

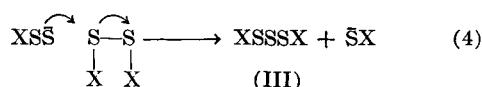
Since the crosslinking reaction (2b) follows from the products of reaction (2a) which itself requires the thiuram polysulfides (I) produced in reaction (1), it follows that any acceleration of the latter must lead also to a corresponding increase in overall vulcanization rate.

The accelerative effect of thiourea is attributed to its interaction with TMTD offering, under the prevailing basic reaction conditions, a particularly easy route for the formation of thiuram polysulfides (I). This view is perhaps more clearly understood if we inspect the mechanism of polysulfide formation in a simple TMTD-zinc oxide reaction.

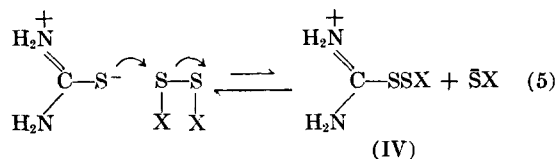
Recent fundamental studies³ on the reactivity of basic oxy-anion type nucleophils suggest that oxygen atoms of zinc oxide prefer to attack the thiocarbamyl carbon atoms of TMTD causing the following polar substitution:



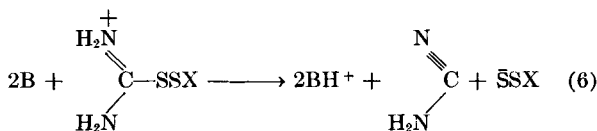
Reaction (3) yields a *perthioanion* (XSS^-) which will rapidly effect the heterolysis of an S—S bond in another TMTD molecule to give the *trisulfide* (III):



Participation of (III) in processes similar to (3) and (4) will lead to the formation of higher polysulfides (I , $m \geq 4$). It is believed that the slow steps in this propagation of thiuram polysulfides are reactions, exemplified by (3) above, in which the perthioanions are released during relatively difficult X—S bond fissions. If thiourea is added to the system it will engage in a thioanion-disulfide interchange reaction of the type:



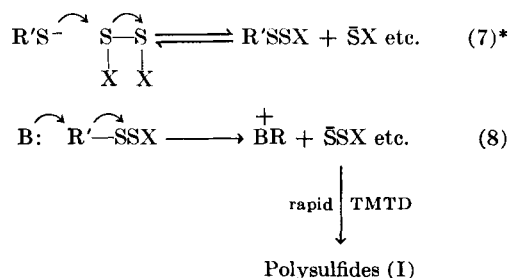
to give a supply of (IV) which would lose a proton to a suitable base and thence decompose rapidly to a perthioanion:



where B = base.

Thus the relatively easy processes (5) and (6) lead to a rapid production of perthioanion precursors of the thiuram polysulfides required in the ultimate crosslinking reactions. Our contentions as to the ease of reactions such as (6) gain support both from the early observations of Werner⁴ that dithioformamidinium salts readily eliminate sulfur on treatment with aqueous sodium acetate, or on boiling with water, and from our own unpublished experiments which show that although TMTD slowly gives sulfur (ca. 0.7 g. atoms S per g. mole TMTD) on refluxing with excess sodium methoxide solution, the addition of thiourea results in an immediate liberation of sulfur.

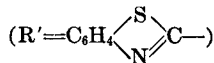
On the basis of the present theory it is predicted that easy production of perthioanions (XS_2^-) and hence polysulfides and a consequent acceleration of vulcanization in the NR-TMTD-ZnO system will result upon the addition to the system of any thioanion ($\text{R}'\text{S}^-$) wherein the group R' is more susceptible than X to nucleophilic attack by bases:



The requirement for acceleration, namely that R' is attacked more readily than X by basic nucleophils, is fulfilled in the case of thiourea ($\text{R}' = \text{H}_2\text{N}\cdot\text{C}\cdot\text{NH}_2$, easy N-proton removal) but not in its *N*, *N'*-tetraalkyl derivatives ($\text{R}' =$

* This reaction will be promoted by the removal of $\text{R}'\text{SSX}$ by eq. (8) and SX^- as $\text{Zn}(\text{SX})_2$.

$\text{Me}_2\text{N}^+\text{C}^-\text{NMe}_2$). The anions of thioacetic acid ($\text{R}' = \text{MeCO}$) which have a marked accelerative effect also meet the theoretical requirement. Conversely, one would expect retardation of vulcanization where the group R' is less reactive towards basic nucleophils than is the thiocarbonyl center, X. This has recently been demonstrated by Swift⁵ who has shown, first, that the rate of crosslinking in a NR-TMTD-ZnO system is decreased when mercaptobenzothiazole



is included, and second, that there is complete inhibition of cure when naphthalene-2-thiol is added to the system.

References

1. Fletcher, W. P., and S. G. Fogg, *Rubber J. and Intern. Plastics*, **135**, 687 (1958).
2. Philpott, M. W., unpublished.
3. Saville, B., unpublished.
4. Werner, E. A., *J. Chem. Soc.*, **1912**, 2166.
5. Swift, P. M., unpublished.

C. G. MOORE
B. SAVILLE
A. A. WATSON

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

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Particle Identity Point in Suspension Polymerization

One important parameter which should be known for the understanding and control of the suspension polymerization process is the per cent conversion after which the particles

retain their identities for the rest of the polymerization. In all cases the monomer was styrene, the suspending agent was a combination of polyvinyl alcohol and a sodium salt of an alkyl-aryl sulfonic acid used in 0.7 wt.-% based on the monomer, and the oil-to-water weight ratio was one-to-one. The polymerization conditions were 0.22 wt.-% of benzoyl peroxide, 95°C. for 10 hours duration, followed by 3 hours at 120°C. under nitrogen pressure. The procedure was as follows: A batch of clear polystyrene beads were made under the standard conditions and the -18 +20 screen fraction isolated as Material I. Another batch was made with the monomer saturated with a high molecular weight dye (National Carbanthrene Printing Golden Orange G Double Powder). The -18 +20 screen fraction of these deep orange beads was isolated as Material II. Appropriate weights of I and II were then suspended together in water, equilibrated under agitation with styrene monomer (containing the appropriate amount of catalyst) at room temperature for 48 hours, to yield the equivalent of the standard suspension polymerization at 25% or at 50% conversion. The temperature was then raised to 95°C. and the appropriate remainder of the polymerization cycle completed. To establish the "0% conversion" behavior, the standard polymerization was conducted with the only variation being that the monomer was added in two equal successive increments, the latter containing the orange dye.

From each of the last three polymerizations described, the beads were recovered, dried, randomly sampled, and each sample completely categorized. Results are given in Table I.

The discrepancy between the half-count and the full count is attributed to the very large number of tiny clear beads which sifted to the bottom of the sampler; these beads are presumably formed from the small amount of monomer reflux returned to the kettle. Unfortunately, the counted beads were not weighed as then the influence of these small clear beads could have been shown to be negligible.

From the data in Table I it is concluded that, under the specific conditions employed, almost all the particles in these suspension polymerizations of styrene retain their identities after 50% conversion. Further, at 25% conversion about one-half of the particles will continue to retain their identities throughout the rest of the polymerization.

TABLE I

Run No.	% conversion at which color was added	Number of beads in sample	One-half count ^a				Full count			
			% orange	% yellow	% clear	% $1/2 \times 1/2^b$	% orange	% yellow	% clear	% $1/2 \times 1/2^b$
3	0	ca. 5000	0	100	0	0	0	100	0	0
4	25	6062	31.3	29.3	36.3	3.1	22.1	29.6	46.7	1.6
5	50	4493	45.1	2.2	48.0	4.7	40.4	2.1	53.9	3.6

^a Score after counting one-half of the total sample.

^b Any bead containing clear and colored portions was placed in this category.

retain their identities for the rest of the polymerization. This "particle identity point," PIP, has not been explicitly determined insofar as this writer is aware. This letter is to record an attempt to determine a PIP for a particular system.

The experimental equipment used was a standard laboratory glass stirred polymerization autoclave with a 1-liter ca-

E. H. MERZ

Plastics Division
Monsanto Chemical Company
Springfield, Massachusetts

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