

Mechanisms of Oxidative Degradation. II. Effect of Metallic Salts and Metal Deactivators on the Oxidation of Polybutadiene*

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Synopsis

The metal-catalyzed oxidation of polybutadiene is further discussed. The mild catalytic effect of stearic acid on the oxidation was shown due to the synergism of the acid and a stearate. The synergism was also found for the mixture of two different stearates. The results of the preliminary study on the stabilization are given. For both iron and copper stearates, zinc diethyldithiocarbamate (ZDC) was found to be the best metal deactivator, and the chelated mixture behaved as an oxidation inhibitor. Tetramethylthiuram disulfide (TMT), phenyl- β -naphthylamine, and oxamide were less effective.

INTRODUCTION

In the first part of this paper,¹ the effect of metallic ions on the oxidation of synthetic rubbers was reported. It was concluded that the mechanism of the metal-catalyzed oxidation of rubbers is, in general, similar to that of the metal-catalyzed oxidation of hydrocarbons in the liquid phase. In this part, we confined the study of the mechanism to one rubber, polybutadiene.

In the previous study, a catalytic effect of stearic acid on the oxidation of rubber was noted. No explanation was obtained during the previous work. Further study revealed a possible synergistic effect of stearic acid with other metallic ions. Results on synergism are discussed in this paper. Preliminary results on stabilization with metal deactivators are also discussed.

In general, the art of stabilization precedes the knowledge of the degradation mechanism. Occasionally stabilizers have been discovered before the inhibition mechanisms were known. This occurred in the case of metal deactivators. For example, with copper deactivators for gasoline, many patents were issued between 1939 and 1945. A summary of the deactivators was made by Watson and Tom² in 1949. The theory of coordina-

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tion-complex formation was employed to explain the relation of chemical structures to activities of metal deactivators.

Although the number of known chelating and complexing agents is very large, the donor atoms which undergo combination with the metal are restricted to strongly nonmetallic elements of Group V and VI. Of these, nitrogen, oxygen, and sulfur are the only common examples where the unpaired electrons are donated to the metal ions to form mostly covalent bonds. The formation of the chelate is in nearly every case accompanied by a decrease in ionic activity.³

Walling⁴ suggests that the role of metal deactivators such as ethylenediaminetetraacetic acid in a system is either to remove the metal entirely by precipitation or to modify the oxidation-reduction potential of the metal to the point where one of the metallic ion-hydroperoxide reactions is suppressed.

A systematic study of the chelation of metallic ions in the nonpolar medium was carried out by Chalk and Smith.⁵ They found that copper could be sequestered by a variety of oxygen- and sulfur-containing chelates, and cobalt could be sequestered by sexidentate chelating agents. The work of Leyland and Stafford⁶ and Kuzminskii⁷ regarding the suppression of metallic ions in rubbers has been mentioned previously.

EXPERIMENTAL

Materials

The polybutadiene rubber tested was a commercial product (Diene, Firestone) which was prepared in solution. This rubber did not contain stearic acid. A minimal amount of antioxidant was used by the manufacturer.

Other chemicals used for this study were all reagent grade. The metal deactivators were obtained commercially; the abbreviations for the deactivators are as follows: ZDC, zinc diethyldithiocarbamate (Ethyl Zimate, R. T. Vanderbilt Co.); TMT, tetramethylthiuram disulfide (Pennsalt Organic Chemicals); Age Rite HP, phenyl- β -naphthylamine (R. T. Vanderbilt Co.); oxamide, (CONH₂)₂. Structurally, ZDC and TMT contain sulfur and nitrogen atoms; Age Rite HP contains nitrogen, and oxamide contains nitrogen and oxygen. These three elements are known to be the key donor atoms involved in chelation.

Oxygen Absorption Study

The experimental procedure for oxygen absorption and reproducibility of test data were described in Part I of this study.¹

Sample Preparation

Polybutadiene was dissolved in methylene chloride. Aliquots, equivalent to 10 g. polymer, were withdrawn and mixed with solutions of the additives containing 0.01 g. of additive (0.1% concentration based on poly-

mer weight). After thorough mixing, the solutions were cast in 1.5-in. diameter aluminum dishes and dried. The additives were all compatible in the dried films.

RESULTS AND DISCUSSION

Effect of Synergism

Since most rubbers contain many metallic impurities,¹ it might be possible to detect a synergistic effect after a foreign metallic ion is added to the rubber. The results on synergism (Table I) are shown in Figures 1 and 2. In Figure 1 the results with mixtures of stearates are compared with those with each individual stearate. First, it should be noted that the increase in the concentration of the catalyst affects the induction time to a much larger extent than the rates. Both cupric and ferric stearates show the same trend. Second, the synergistic effect of cupric and ferric stearate is notable. For instance, by using 0.05% of ferric stearate in combination with 0.05% cupric stearate, the induction time becomes equal to that with 0.1% of cupric stearate. Furthermore, the rate becomes faster than that of 0.1% of cupric stearate or 0.1% ferric stearate alone. It is also interesting to note that on addition of a less active catalyst, e.g., zinc stearate, a similar synergistic effect is noted.

During the preceding study on various rubbers,¹ it was found that in many instances stearic acid functions as a mild catalyst for the oxidation

TABLE I
Effect of Metallic Salts on the Autoxidation of Diene Rubber at 120°C., 760 mm.

Expt. no.	A		B		Induction time, min.	Rate of oxygen absorption, ml./hr.
	Chemical	Wt., mg.*	Chemical	Wt., mg.		
1	Ferric distearate	10.0	—	—	170	20.5
2	Ferric distearate	5.0	—	—	20	19.9
3	Ferric distearate	5.0	Stearic acid	5.0	120	49.5
4	Ferric distearate	4.0	Copper stearate	5.0	54	81.0
5	Copper stearate	10.0	—	—	53	71.0
6	Copper stearate	5.0	—	—	72	72.0
7	Copper stearate	5.0	Stearic acid	5.0	57	74.5
8	Copper stearate	5.0	Zinc stearate	5.0	60	90.0

* The weight of additive is based on 10 g. of Diene rubber.

of rubber. It could be postulated that stearic acid activates or forms a synergistic mixture with one or several of the metallic impurities in the rubbers. The obvious one is, of course, the ferric ion. In order to substantiate this, we ran a series of experiments in which stearic acid was added

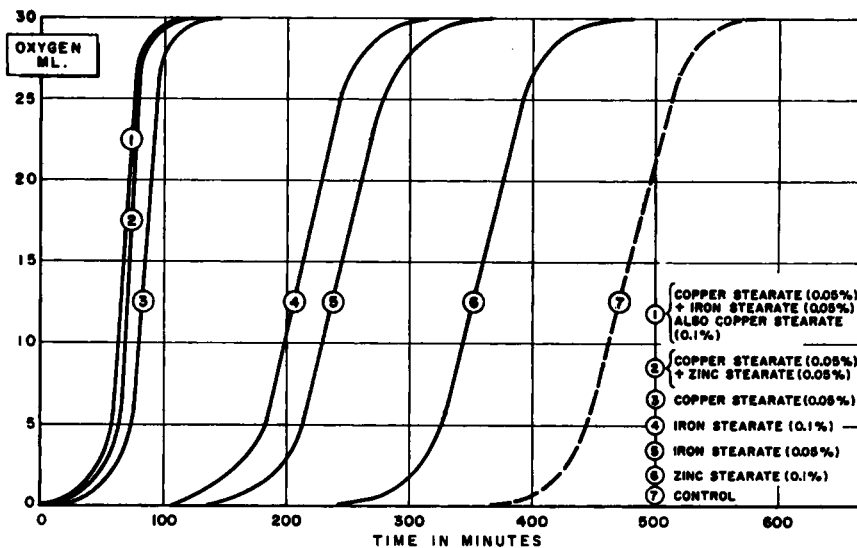


Fig. 1. Effect of synergism on oxygen absorption with zinc stearate and other stearates for cold-flow Diene rubber (Firestone), 120°C., 760 mm. Hg.

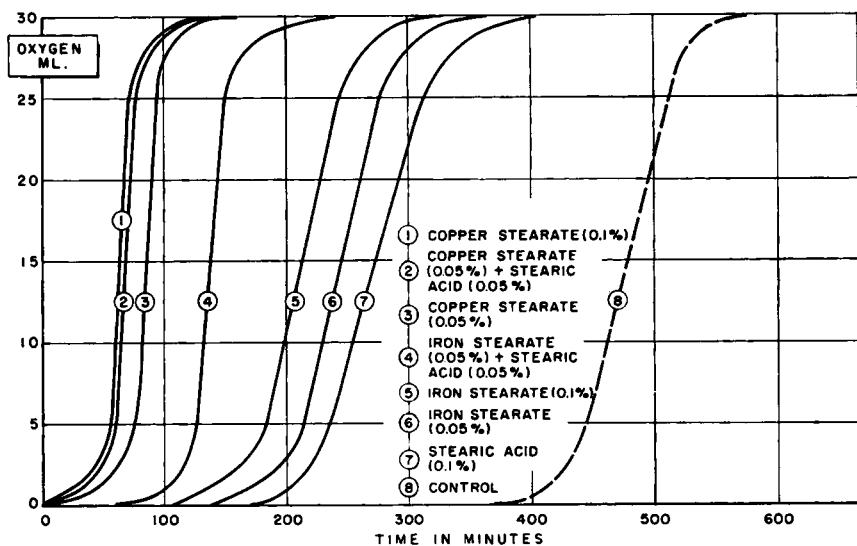


Fig. 2. Effect of synergism on oxygen absorption with stearic acid and other stearates for cold-flow Diene rubber (Firestone), 120°C., 760 mm. Hg.

in combination with metallic stearates. Results comparing the mixtures with the single components are shown graphically in Figure 2.

On adding 0.05% of stearic acid to 0.05% cupric stearate, the resultant catalytic activity is equal to that of 0.1% cupric stearate. This indicates that one of the functions of stearic acid could be the synergistic effect upon the activities of other metallic ions. The sample containing stearic acid was less stable than the control. Furthermore, in the case of ferric stearate

TABLE II
Stabilization with Metal Deactivators for the Metal-Catalyzed
Autoxidation of Diene Rubber at 120°C., 760 mm.

Expt. no.	A		B		Induction time, min.	Rate of oxygen absorption, ml./hr.
	Chemical	Wt., mg. ^a	Chemical	Wt., mg.		
1	—	—	—	—	430	18.3
2	Ferric distearate	10.0	—	—	170	20.5
3	—	—	ZDC	34.8	188	10.1
4	Ferric distearate	10.0	ZDC	34.8	1790	5.5
5	—	—	TMT	23.1	180	46.7
6	Ferric distearate	10.0	TMT	23.1	109	51.2
7	Ferric distearate	10.0	Age Rite HP	21.3	465	6.8
8	Ferric distearate	10.0	Oxamide	8.4	176	19.5
9	Copper stearate	10.0	—	—	53	71.0
10	Copper stearate	10.0	ZDC	22.9	2700	3.1
11	Copper stearate	10.0	TMT	15.2	843	21.4
12	Copper stearate	10.0	Age Rite HP	14.0	86	38.8
13	Copper stearate	10.0	Oxamide	8.4	176	19.5

^a The weight of additive is based on 10 g. of Diene rubber.

the synergistic effect is strongly accentuated by stearic acid. Since synergistic effects are detected in the above two instances, it may be worthwhile to investigate many other combinations of metallic ions and perhaps other substances needed to be investigated.

It should be pointed out that the fatty acid content in the three stearates involved in the above discussion are low. The stearic acid contents are: 3.9% in copper stearate, 4.5% in iron stearate, and 0.5% in zinc stearate.

Stabilization of the Metal-Catalyzed Autoxidation of Polybutadiene

Another interesting area of research regarding the metal-catalyzed autoxidation of rubbers is the aspect of stabilization. The theoretical background of this aspect has been summarized in the earlier section. Some preliminary results are shown in Table II.

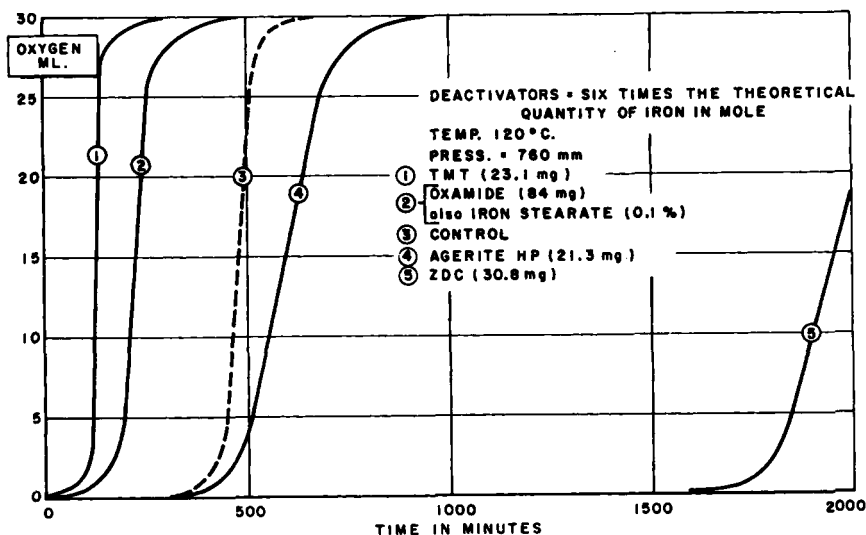


Fig. 3. Effect of metal deactivators on the iron stearate-catalyzed oxidation of Diene rubber (Firestone), containing 0.1% iron stearate.

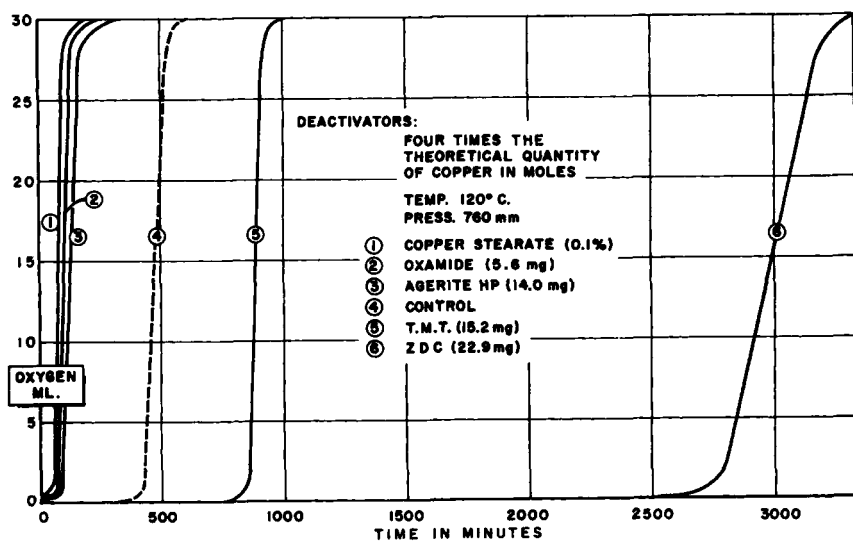


Fig. 4. Effect of metal deactivators of the copper stearate-catalyzed oxidation of Diene rubber (Firestone) containing 0.1% copper stearate.

Two commonly encountered catalysts or impurities are iron and copper. Most patent literature references on stabilization to metal ion catalysts are related to these two impurities. Previous work^{6,7} has revealed several types of metal deactivators. The work on the stabilization of the copper-catalyzed oxidation is well known.

For the stabilization of ferric stearate in polybutadiene rubber (Diene rubber), the results in Figure 3 show that zinc diethyldithiocarbamate (ZDC) is the best metal deactivator. For copper stearate (Fig. 4), ZDC is also the best deactivator. Tetramethylthiuram disulfide (TMT) shows some deactivating tendency. Oxamide, which is the best known inhibitor for polypropylene, was not active for polybutadiene under our experimental conditions.

CONCLUSIONS

A notable synergistic effect was found both for the mixture of stearates and for the mixture of a stearate and stearic acid. This synergistic effect could be one of the causes of a mild catalytic activity of stearic acid in several rubbers. The analyses indicated that most rubbers contained metallic impurities including iron and other transition metals which could form synergistic mixtures with stearic acid.

The results of the preliminary study on stabilization were given. For both iron and copper, zinc diethyldithiocarbamate was the best metal deactivator, and the chelated mixture behaved as an oxidation inhibitor as reported by others for natural rubbers.

The results of this study indicate that for cases where the metallic impurities cannot be removed from a rubber, it is feasible to add a metal deactivator to eliminate the catalytic effect of the metallic ions through chelation or other reactions.

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Résumé

L'oxydation du polybutadiène catalysée par les métaux est discutée. L'effet catalytique exercé par l'acide stéarique sur l'oxydation résulte du synergisme de l'acide et d'un stéarate. Le synergisme a également été trouvé pour un mélange de deux stéarates différents. On indique les résultats de l'étude préliminaire concernant la stabilisation. Aussi bien pour le stéarate ferrique que pour le stéarate de cuivre, le diéthylthiocar-

bonate de zinc (ZDC) est le meilleur désactivateur du métal, et le mélange chélaté se comporte comme un inhibiteur d'oxydation. Le disulfure de tétraméthylthiurame (TMT), la phényl- β -naphthylamine et l'oxamide sont moins efficaces.

Zusammenfassung

Eine weitere Diskussion der metall-katalysierten Oxydation von Polybutadien wird durchgeführt. Der milde katalytische Effekt von Stearinsäure bei der Oxydation konnte auf den Synergismus zwischen der Säure und einem Stearat zurückgeführt werden. Dieser Synergismus trat auch bei der Mischung zweier verschiedener Stearate auf. Die Ergebnisse einer vorläufigen Untersuchung der Stabilität werden mitgeteilt. Für Eisen- und Kupferstearat erwies sich Zinkdiäthylthiokarbonat (ZDC) als der beste Metalldesaktivator und die Mischung, in der Chelatbildung auftrat, bildete einen Oxydationsinhibitor. Tetramethylthiuramdisulfid (TMT), Phenyl- β -naphthylamin und Oxamid waren weniger wirksam.

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