JOURNAL OF POLYMER SCIENCE VOL. VI, NO. 1, PAGES 13–20

Tetramethylthiuram Disulfide Vulcanization of Extracted Rubber. IV. Behavior of Rubber as an Acid

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The retarding effect of organic acids on vulcanization as well as the activating effect of certain acids on certain accelerators is well recognized. The activating and accelerating effects of bases and metallic oxides is also well recognized. In this connection, the mild activating effect of palmitic acid on vulcanization with TMTD in the presence of zinc oxide was described in the first paper of the present series. With the behavior of acids and bases during vulcanization as a background, the study of rubber itself as an acid has been undertaken. This paper sets forth a description of two reactions investigated during the study. These are the reaction of rubber with zinc palmitate and of TMTD with acids.

REACTION OF EXTRACTED RUBBER WITH ZINC PALMITATE

The short path still technique of paper III is well suited to the study of this reaction which forms palmitic acid and apparently a zinc salt of rubber. When varying amounts of the zinc palmitate were milled on a warm mill into extracted crepe containing 1 PHR of phenyl-beta-naphthylamine and the resulting clear mixtures (40 g. of each) short path distilled, the amount of palmitic acid liberated approached a limiting value of about 1.0 PHR as the amount of zinc palmitate added to the rubber was increased. The results are plotted in Figure 1. The equivalent weight of rubber calculated from 1.0 PHR (0.0039 equivalent) of palmitic acid is 25,700. An idea of the efficiency with which zinc palmitate reacts with rubber may be had by noting that 0.0039 equivalent equals 1.12 g. of zinc palmitate. According to Figure 1 the yield of palmitic acid resulting from mixing this amount of zinc salt into rubber is 0.56 PHR or 56%. In order to drive the reaction to completion, that is, to realize a recovery of palmitic acid equivalent to the acid groups in the rubber, about 5 PHR of zinc palmitate must be added to the rubber.

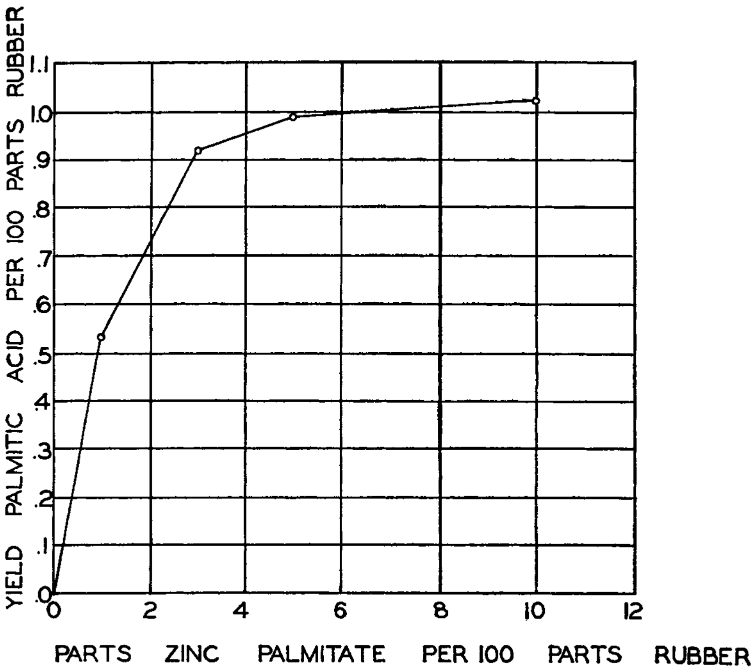
This reaction can be understood on the basis of reaction I, followed by

$$\mathrm{RC(O)OH} + \mathrm{Zn(OC(O)C_{15}H_{31})_2} \rightleftharpoons \mathrm{HOC(O)C_{15}H_{31}} + \mathrm{RC(O)OZnOC(O)C_{15}H_{31}} \quad \text{(I)}$$

reaction II. Here, R is the portion of the rubber molecule attached to a single acid group which is assumed to be C(O)OH. In the presence of excess zinc palmitate, reaction I can go to completion to the right and reaction II will be repressed. When the palmitic acid is allowed to volatilize

$$RC(O)OZnOC(O)C_{15}H_{31} + RC(O)OH \rightleftharpoons RC(O)OZnOC(O)R + HOC(O)C_{15}H_{31} \quad (II)$$

in the short path still, both reactions will shift to the right. Reaction II requires that two acid groups be sufficiently near each other. With a macromolecular weight acid such as rubber it would seem that this condition would not always be met. If this condition does not exist then the probability of the existence of the mixed salt formed by reaction I is increased and the probability of a "zinc salt cross-link" is decreased.



1. **Palmitic acid recovered by distillation of rubber–zinc palmitate mixtures.**

The reaction of rubber (a hydrophilic substance) with zinc palmitate was at first thought to involve only the hydrolysis (reaction III) of the salt

$$Zn(OC(O)C_{15}H_{31})_2 + HOH \rightleftharpoons Zn(OH)OC(O)C_{15}H_{31} + HOC(O)C_{15}H_{31} \quad (III)$$

of a weak acid and a weak base. Doubt was cast on this view when it was found that zinc palmitate could be recrystallized from a boiling mixture of toluene and water with nearly quantitative recovery of the salt, m.p. 131–132°. That hydrolysis is involved in the formation of palmitic acid in a rubber stock (originally containing 1.5 PHR of zinc palmitate), however, was shown by remilling it after short path distillation. Water was absorbed from the atmosphere, even on a warm mill, and then, when the stock was again short path distilled, a further amount of palmitic acid was collected. The first distillation produced 0.92 PHR and the second 0.04 PHR, a total of 0.96 PHR. This is nearly the limiting amount of 1.0 PHR of palmitic acid. In another experiment 4.6 PHR of zinc palmitate was compounded. After short path distillation, the stock was placed over water in a humidifier for three days. During this period it increased in weight by about 1%. When it was short path distilled the total yield of palmitic acid from both distillations amounted to 2.93 PHR.

The possibility of reactions (reactions IV and V) of the zinc salts produced by reactions I and II with water should also be considered.

$$\mathrm{RC(O)OZnOC(O)C_{15}H_{31} + HOH \rightleftharpoons HOC(O)C_{15}H_{31} + RC(O)OZn - OH} \qquad \text{(IV)}$$

$$\mathrm{RC(O)OZnOC(O)R + HOH \rightleftharpoons RC(O)OZnOH + RC(O)OH} \qquad \text{(V)}$$

The products RC(O)OZnOH formed in these reactions would not be stable in the presence of excess zinc palmitate in the short path still because reaction VI would occur. The products of reactions VI and I are identical.

$$\mathrm{RC(O)OZnOH + Zn(OC(O)C_{15}H_{31})_2 \longrightarrow RC(O)OZnOC(O)C_{15}H_{31} + HOC(O)C_{15}H_{31}} \qquad \text{(VI)}$$

The palmitic acid liberated by I, II, III, IV, and VI should repress the hydrolytic reactions, however, while the nonvolatile rubber acid RC(O)OH tends to release water (reaction V) which can either volatilize or enter into reactions III, IV and V. Only when large amounts of both zinc palmitate and water are present would reaction III seem to be important.

A reaction bearing on the hydrolysis of zinc palmitate is the synthesis of the zinc salt from zinc oxide and palmitic acid. It was at first postulated that the reaction would be aided by reduction of the pressure. However, at 0.2 mm. pressure equivalent amounts of reagent grade zinc oxide and palmitic acid did not react completely at 160° during two hours. When 0.815 g. (0.01 mole) of ZnO, 5.37 g. (0.021 mole) of palmitic acid, 30 ml. of toluene and 5 ml. of water were refluxed at 94° for 40 minutes a transparent two-phase liquid system was obtained. The mixture was cooled to room temperature and the colorless crystals which formed were filtered with suction and washed with 20 ml. of benzene. The yield of air-dried zinc palmitate melting at 129–131° amounted to 5.595 g. or 97%. An experiment differing from the one described in that the water was omitted and also in that 20 ml. of benzene were added in order to get refluxing at 95° was next conducted. The starting materials were recovered quantitatively. Whitmore and Lauro[1] reported that zinc palmitate prepared from sodium palmitate and zinc acetate melted at 129° but gave no analytical data. Our product recrystallized from toluene melted at 133° and was found to contain 11.34% Zn which is the calculated value for $\mathrm{Zn(OC(O)C_{15}H_{31})_2}$.

The possible reaction of zinc oxide with palmitic acid in extracted rubber during milling was examined briefly. The stock used was rubber 100, ZnO 6.25, and palmitic acid 2.00. When mixed at room temperature and then short path distilled for one hour at 133° at 0.0007 mm., an 89.4% recovery of the palmitic acid was realized. The same stock, except that excess water was added before sheeting off the mill was distilled in the same way. The recovery of palmitic acid amounted to 93.4%. Little reaction appeared to have occurred, wet or dry, during the mixing.

The reaction of zinc oxide with palmitic acid is thus seen to be inhibited by a moderate degree of desiccation and failed to occur even in wet rubber on the mill. It would be classified by Smith[2] as ionic in nature and therefore requiring a dissociating medium. It is interesting to note that zinc oxide, zinc palmitate, and palmitic acid are not water-soluble and do not absorb water in more than small amounts. The reaction of zinc palmitate with rubber is also ionic in nature and whether or not water is necessary it has always been present. The effects of water on the yield of palmitic acid from zinc palmitate-rubber mixtures are difficult to evaluate because these substances codistill from rubber in the short path still. However, the experiments described show that rubber *at least in the presence of water* acts as an acid toward zinc palmitate. It may not be amiss to point out that water acts as an acid in the hydrolysis of any salt. Thus, rubber could be acting merely as a solvent for the hydrolysis. Independent evidence that rubber is an OH acid is supplied by a comparison of the reaction of fatty acids with TMTD, which forms dimethylamides, and the reaction of rubber with TMTD. These reactions are discussed in the following section.

The palmitic acid values of Figure 1 were determined by titration of the short path distillates. Palmitic acid recovered in similar experiments from phenyl-beta-naphthylamine-free stocks has been found to melt at 62–63°. In such cases the acid is usually determined by weighing. Figure 1 seems to be reproducible to within about 10% from one batch of rubber to another. The rubber removed from the short path still containing the zinc salts of rubber and zinc palmitate was tacky. It lost a part of this tackiness by being allowed to absorb moisture. Crystallization (blooming) did not take place on long standing of the stocks containing up to 5 PHR of zinc palmitate.

FORMATION OF DIMETHYLAMIDES FROM TMTD

Dimethylamide formation from TMTD, a new reaction, was first investigated with palmitic acid. Equimolecular amounts of this acid and TMTD were heated for 30 minutes at 130–140°. By crystallization of the reaction mixture from alcohol an 80% recovery of the TMTD was secured. Longer periods of heating were found to produce dimethylpalmitamide, sulfur and CS_2.

The reaction of 48 g. (0.2 mole) of TMTD with 60 g. (1 mole) of acetic acid was conducted for five hours at 125°. The products which distilled during this period included water, CS_2, COS, and a small amount of H_2S. Sulfur separated from the reaction mixture on cooling to room temperature. The mixture was filtered to supply a yield of 6.01 g. of sulfur or 94% of the amount calculated from the reaction:

$$[(CH_3)_2NC(S)S]_2 + 2\,HOC(O)CH_3 \longrightarrow H_2O + CS_2 + COS + 2\,(CH_3)_2NC(O)CH_3 + (S)$$

The distillation at 10 mm. of the filtrate provided a series of fractions, the lowest boiling one being recovered acetic acid. The higher boiling fractions were refractionated at atmospheric pressure to give a main fraction distilling at 167–169° at 740 mm. This fraction contained 23.5% acetic acid as shown by its titration with sodium hydroxide. Pure dimethylacetamide (b.p. 163.5°, 740 mm., m.p. −19°) and acetic acid were found to form a maximum boiling mixture containing 24.5% acetic acid which distilled at 168° at 740 mm. Based on the titration of the acetic acid-dimethylacetamide fractions and their weights, the dimethylacetamide yield amounted to 35 g. or 0.40 mole. This is the theoretical yield based on the above equation. That acetic acid was present in the 167–169° boiling fraction was shown by its piperazine hydrate derivative which we have found to melt at 235–240° with decomposition. Addition of the derivative which melted at the same temperature and which was prepared from an authentic specimen of acetic acid produced no change in the melting point. The value given in the literature for this derivative, 208.5–209°,[3] we believe to be in error.

The reaction of equimolecular amounts of TMTD with acetic anhydride at 140–145° during five hours formed the following substances: sulfur (74%), dimethylacetamide (93.5%), COS (68%), CS_2 (110%), and small amounts of tetramethylthiourea. The percentages given are based on the equation:

$$[(CH_3)_2NC(S)S]_2 + [CH_3C(O)]_2O \longrightarrow (S) + 2\,(CH_3)_2NC(O)CH_3 + COS + CS_2$$

The yield of CS_2 of over 100%, the formation of tetramethylthiourea, and the recovery of about 6.5% of the acetic anhydride started with, show that this is not the only reaction that occurred, though it is the main one.

Since TMTM is a reaction product of TMTD vulcanization in the presence of zinc oxide, a mixture of 0.01 mole TMTM, 0.01 atom sulfur, 0.02 mole of palmitic acid, and 0.01 mole of ZnO was heated for two hours at 1 mm. to 0.3 mm. pressure. The products which were separated and identified included ZnDMDC, zinc palmitate, dimethylammonium dimethyldithiocarbamate, and dimethylpalmitamide. About one-third of the sulfur and one-half of the ZnO remained. No ZnS could be detected. The TMTM and palmitic acid were almost completely consumed. This reaction is similar to the reaction of palmitic acid, TMTD, and zinc oxide which, therefore, will not be described.

The formation of dimethylpalmitamide in an extracted rubber-zinc palmitate (10 PHR) stock was demonstrated by an experiment that will be described in some detail. As a preliminary step this stock was short path distilled to remove palmitic acid. Then 5 PHR of zinc oxide and 4 PHR of TMTD were added on the mill. A 42.5 g. sample 0.010 in. thick was cured in the short path still at atmospheric pressure for 1.5 hours at 133°. The distillate amounted to 0.235 g. from which 0.05 g. of TMTD was recovered by crystallization from hexane. Gaseous products were not identified. The rubber was severely overcured. It was left in place in the still and distilled for two hours at 0.001 to 0.0005 mm. The distillate, amounting to 1.09 g., was removed and distillation conducted for a second period of 2.5 hours. The distillate (total = 1.42 g.) was separated into alcohol-soluble and -insoluble fractions. One of the insoluble fractions weighed 1.09 g.

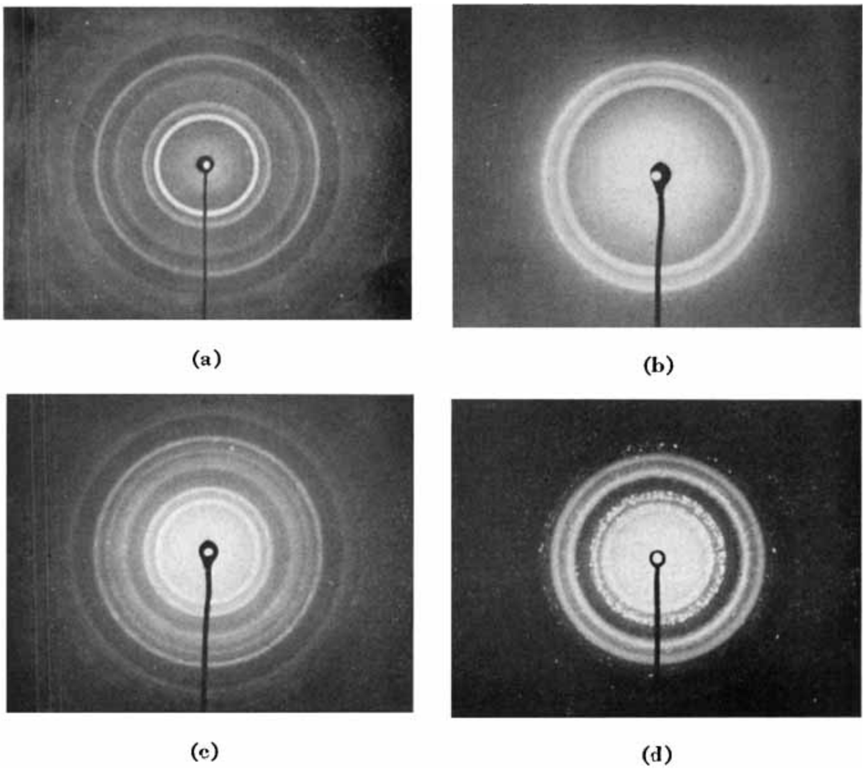

(a) (b) (c) (d)

Fig. 2. (*a*) Zn DMDC; (*b*) zinc palmitate; (*c*) specimen melting 238–243°; and (*d*) specimen melting 130–240°. All patterns made utilizing CuK x-radiation. Sample-film distance 5 cm.

and melted at 238–243°. A second insoluble fraction melted at 130–240° and weighed 0.22 g. These fractions were identified by x-ray diffraction studies. The patterns are shown in Figure 2 along with the patterns for ZnDMDC and zinc palmitate. The diagrams for the two fractions correspond to superpositions of the patterns for the two pure substances. A study of the patterns for artificial mixtures of the two pure substances permits us to say that the high melting fraction is about 80% ZnDMDC, while the 130–240° melting sample is about 20% ZnDMDC. Since zinc palmitate is nonvolatile, its appearance in the distillate is without doubt due to the reaction of palmitic acid with ZnDMDC after these substances have distilled from the vulcanizate.

The presence of dimethyl palmitamide as a double compound with palmitic acid in the alcohol-soluble fraction was established by infrared absorption, x-ray diffraction, and melting point techniques. The alcohol-soluble fraction also contained TMTM.

The formation of dimethylamides as just described suggests that if rubber is an OH acid it too should react with TMTD to form a dimethylamide. The nitrogen analysis of extracted crepe rubber before and after vulcanization with 4 PHR of TMTD and 5 of ZnO is given in Table I. The cured stock was short path distilled to remove ZnDMDC before analysis. The difference between the N content before and after vulcanization amounts to 0.053%, or to 0.0038 equivalent PHR. This value checks the 0.0039 equivalent of palmitic acid liberated from zinc palmitate in the short path still, thus confirming the presence of an OH acid group in rubber.

TABLE I

Sample	Extracted crepe, % N	Vulcanizate, % N
Sample A	0.388	0.439
Sample B	0.386	0.441
Average	*0.387*	*0.440*

A correlation of the zinc removal study of the preceding paper with dimethylamide formation also supports the conclusion that rubber is an OH acid. The vulcanizate just described was one used in the zinc removal study. Before the zinc removal treatment, it was found to contain 0.17% "ZnS" sulfur and 3.23% zinc. After the treatment it was not analyzed for sulfur but the zinc content was found to be 0.03%, equivalent to 0.015% zinc sulfide sulfur. Since the zinc removal treatment does not remove ZnS added as such, we feel that most of the 0.17% "ZnS" sulfur in reality may be a zinc hydrosulfide or a more than usual reactive form of zinc sulfide in which at least one valence of the zinc atom is bound to carbon through sulfur or oxygen. It should be emphasized that the low zinc content of 0.03% is to be expected if rubber contains —C(O)OH groups, which by the action of TMTD are converted to dimethylamide groups. If the acid groups of the rubber molecule are not hydroxylic, the treated stock should contain 0.0039 equivalent of zinc PHR or 0.125 PHR of Zn.

The acid equivalent of crepe rubber of 25,700, based on the liberation of 0.0039 equivalent of palmitic acid PHR from zinc palmitate, permits the calculation of the oxygen content of the rubber as 0.125% if we assume that the acid group is —C(O)OH and that no other oxygen containing group is present. This result is in agreement with the "general average" value of 0.13% calculated by Wing[4] from the carbon and hydrogen analyses of purified rubber. The correlation of the acid equivalent with Wing's figures is, of course, nonexistent if the view is taken that the 0.13% value represents impurity oxygen.

The extent to which rubber is acidic as shown by the experiments described here is slight and appears to disclose nothing about the nature of the vulcanization process.

Midgley and others[5] investigated the reaction of rubber with organic metallic compounds including thienyl Grignard reagents. These reagents failed to form a sulfur-containing reaction product and therefore it was concluded that rubber is neither ketonic nor carboxylic. The reversible vulcanization effects noted by these authors, however, are compatible with the liberation of palmitic acid by the reaction of rubber with zinc palmitate.

References

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English Synopsis, see Summaries, page S15, Vol. V, 1950.

Résumé

(*1*) La réaction du caoutchouc avec le palmitate de zinc libère de l'acide palmitique sous faible pression; le caoutchouc se comporte donc comme un acide. (*2*) La réaction de l'oxyde de zinc avec l'acide palmitique en solution toluénique est facilitée par la présence d'eau. (*3*) La faible augmentation de la teneur en azote dans le caoutchouc par suite de sa réaction avec le TMTD correspond à l'acide palmitique libéré par la réaction du palmitate zincique. (*4*) L'utilisation du TMTD comme réactif des acides organiques a été étudiée, et se base sur la transformation des groupes carboxyles en groupes diméthylamidés. Ce résultat suggère que la nature acide du caoutchouc est attribuable à des groupes carboxylés, présents dans la molécule de caoutchouc; cette suggestion est compatible avec l'enlèvement quasi total du zinc des vulcanisats TMTD par la technique d'élimination du zinc.

Zusammenfassung

(*1*) Es wurde gefunden, dass die Reaktion von Kautschuk mit Zinkpalmitat bei niedrigem Druck Palmitinsäure freimacht, und somit anzeigt, dass Kautschuk schwach sauer ist. (*2*) Die Reaktion von Zinkoxyd mit Palmitinsäure in Toluol wurde durch die Gegenwart von Wasser verstärkt. (*3*) Die geringe Zunahme des Stickstoffgehaltes von Kautschuk, die durch die Reaktion mit TMTD verursacht wurde, war mit der bei der Zinkpalmitatreaktion in Freiheit gesetzten Palmitinsäure äquivalent. (*4*) Die Verwendung von TMTD als Reagens für organische Säuren wurde untersucht und es wurde gefunden, dass es Carboxylgruppen in Dimethylamidgruppen umsetzt. Dieses Resultat lässt annehmen, dass die saure Natur des Kautschuks durch Carboxylgruppen im Kautschukmolekül bedingt ist. Diese Annahme ist vereinbar mit der nahezu vollständigen Entfernung von Zink aus dem TMTD Vulkanisat durch die Zinkentfernungstechnik.

Received September 12, 1949