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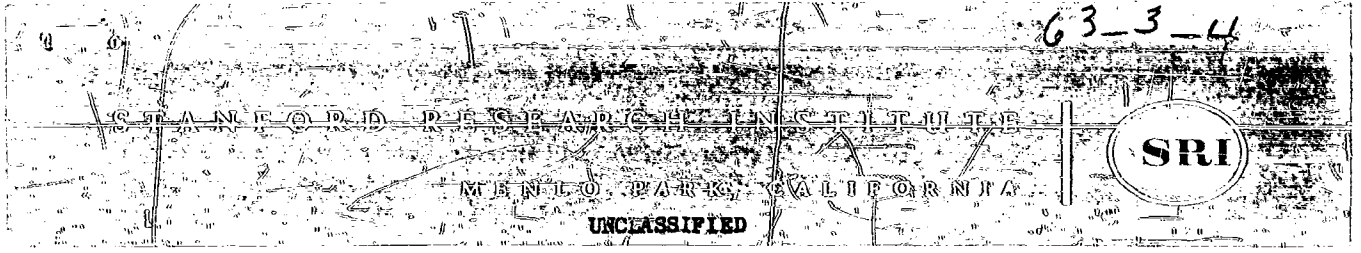
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Covering the Period

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Title: ACCELERATED DETERIORATION OF ELASTOMERS

Prepared by

Frank R. Mayo, Kurt Egger, Jorge Heller, and Katherine Crawford

Date: May 8, 1963

Prepared for

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Edgewood Arsenal, Maryland

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<p>AD STANFORD RESEARCH INSTITUTE, Menlo Park, California</p> <p>ACCELERATED DETERIORATION OF ELASTOMERS Frank R. Mayo, K. Egger, K. Crawford, Jorge Heller and R. L. Walrath Third Quarterly Progress Report May 10, 1963, 19 pp., 6 figs., 4 tables. Contract DA18-108 OML-7216-CP3-90</p> <p>The effects of possible catalysts on the oxidation of polyisoprene in chlorobenzene solution have been studied at 50°C. Soluble metal salts of transition metals decompose rubber peroxides, causing various amounts of chain cleavage and chain initiation. The metal salts may also terminate oxidation chains, but they appear not to affect chain propagation. Infrared analyses for hydroxyl and carbonyl groups and titrations for peroxides suggest that most of the oxygen must be in cyclic peroxide, epoxide, or ether groups. Oxygen is required for the rapid degradation of rubber by phenylhydrazine. The rates of degradation by three hydrazines and <i>p</i>-thiocresol are compared. Preliminary data on oxygen consumption are given.</p>	<p>UNCLASSIFIED</p> <p>1. Elastomers - Oxidation, Degradation Contract DA18-108 OML-7216-CP3-90</p> <p>2. Contract DA18-108 OML-7216-CP3-90</p>	<p>Accession No. STANFORD RESEARCH INSTITUTE, Menlo Park, California</p> <p>ACCELERATED DETERIORATION OF ELASTOMERS Frank R. Mayo, K. Egger, K. Crawford, Jorge Heller and R. L. Walrath Third Quarterly Progress Report May 10, 1963, 19 pp., 6 figs., 4 tables. Contract DA18-108 OML-7216-CP3-90</p> <p>The effects of possible catalysts on the oxidation of polyisoprene in chlorobenzene solution have been studied at 50°C. Soluble metal salts of transition metals decompose rubber peroxides, causing various amounts of chain cleavage and chain initiation. The metal salts may also terminate oxidation chains, but they appear not to affect chain propagation. Infrared analyses for hydroxyl and carbonyl groups and titrations for peroxides suggest that most of the oxygen must be in cyclic peroxide, epoxide, or ether groups. Oxygen is required for the rapid degradation of rubber by phenylhydrazine. The rates of degradation by three hydrazines and <i>p</i>-thiocresol are compared. Preliminary data on oxygen consumption are given.</p>	<p>UNCLASSIFIED</p> <p>1. Elastomers - Oxidation, Degradation Contract DA18-108 OML-7216-CP3-90</p> <p>2. Contract DA18-108 OML-7216-CP3-90</p>
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Third Quarterly Progress Report

ACCELERATED DETERIORATION OF ELASTOMERS

1. Object

The object of this research is to find ways to degrade elastomers rapidly at or near room temperature. This work has led us to study the effects of soluble metal salts, hydrazines and thiols on the rates of oxidation and chain scission of polyisoprene.

2. Summary

The metal compounds examined have no significant pro-oxidant effect in the absence of oxidation products (peroxides). With partially oxidized polyisoprene, however, these same metal compounds show pronounced pro-oxidant effects, giving rates of oxygen absorption several times that of 0.01 M ABN [2,2'-azobis(2-methylpropionitrile)].

Most of the metal octanoates and naphthenates catalyze the decomposition of rubber hydroperoxides. In this process the proportion of chain cleavage and the rate of chain initiation vary with the metal. Thus, cobalt and manganese salts cause most rapid disappearance of peroxides but the former strongly accelerates oxidation while the latter does not. Iron gives the most chain scissions for the peroxide decomposed, and about double the oxidation rate with 0.005 M ABN. Nickel, copper, lead, zinc, and calcium salts have little or no effect on the rate of oxidation. Cobaltous salts show marked color changes indicating conversion to cobaltic compounds and complexing with oxidation products. After extensive oxidation of the rubber, precipitation of cobalt compounds may occur. This separation may account for the progressive decrease in catalysis by this metal.

Infrared analyses for hydroxyl and carbonyl groups and peroxide titrations account for less than half of the oxygen in the polymer. Much of the bound oxygen must be in ether, epoxide, or cyclic peroxide groups.

Further experiments with phenylhydrazine and rubber solutions in chlorobenzene show that oxygen (not peroxides in the rubber) is required for the very rapid degradation observed. The amount of oxygen consumed is comparable to the amount of phenylhydrazine used. In one experiment at 50° the degradation was complete within four minutes. Other hydrazines cause slower but more extensive degradations.

Further experiments with p -thiocresol show that many molecules of oxygen are absorbed per molecule of thiol originally present. How long the catalysis would continue is not yet known.

3. Experimental

3.1. Rubber Solutions

For most of the experiments in Section 4, 72.8 g of Shell polyisoprene, purified as described in Section 3.1 of the Second Quarterly Progress Report, was dissolved in 2993 ml chlorobenzene. All of this solution was then stirred with oxygen and 24.4 mg of ABN for 94 hours at 63°C. During this period, 99% of the ABN is calculated to have reacted. This solution was then concentrated by distillation at 15-20 mm pressure to 90.96 g of nonvolatile material per liter of solution at 25°. At this point the titratable peroxide content (Section 3.3) was 52.6 mmol/liter, and the number-average molecular weight (M_n) was 1351. The carbon and hydrogen analysis on the solvent-free residue corresponded to $(C_5H_8.08O.45)_{17.8}$. This solution is designated "oxidized polymer 1351."

Since the molecular weight of this polymer was rather low and the oxygen content rather high, this oxidized polymer may not be a suitable model for undegraded polyisoprene. A second oxidized solution was therefore prepared without added initiator. Here 88.92 g of purified cis-polyisoprene in 3100 ml chlorobenzene was stirred with oxygen for 10.5 hours at 63°C. M_n was found to be 4082 and the carbon and hydrogen analysis on the solvent-free residue corresponded to $(C_5H_7.98O.213)_{57.06}$. This solution ("oxidized polymer 4082") contained 26.3 g of nonvolatile material per liter, but no titratable peroxides. The infrared absorption showed only one-tenth as much carbonyl and hydroxyl groups as the "oxidized polymer 1351."

3.2. Procedure

For the experiments in Section 4, the reaction vessels were long-necked 100-ml round-bottom flasks with ground joints and capillary stopcocks. In general, 25 ml of rubber solution was added to the measured metal compound or ABN. The reaction vessel was then cooled, degassed, and put in a water bath at $50 \pm 0.1^\circ$. After equilibrating for about one hour, oxygen was admitted to the system and its consumption was measured with time, following the procedure described in Section 3.2 of the previous quarterly report. Number-average molecular weights were determined with the vapor phase method described in Section 3.4 of that report.

3.3. Peroxide Analysis

In determining hydroperoxides in chlorobenzene solutions of oxidized polyisoprene by an iodometric method, a homogeneous reaction mixture is at least desirable, if not essential. Standard methods employing isopropanol or acetic acid as solvents were found to be unsuitable, but

a variation of the procedure of Nozaki¹ gave homogeneous solutions and reproducible results. A stock solution of 9 g of dry sodium iodide in 105 ml of fresh reagent acetic anhydride and 35 ml of chlorobenzene is prepared and kept under nitrogen. A 1-ml aliquot of the solution of polyisoprene in chlorobenzene and 14 ml of the stock solution are then heated together for 70 minutes at 50°. Neither the sodium iodide nor the rubber should precipitate. After heating, 50-75 ml of water is added and the mixture is shaken for about 2 minutes. The liberated iodine is then titrated with N/100 thiosulfate, with vigorous shaking of the mixture. Near the endpoint, 1 ml of 1% starch solution is added to sharpen the endpoint. The number of moles of peroxide found is equal to the number of moles of iodine liberated.

Our modified method has been compared with other methods with known amounts of tertiary butyl hydroperoxide, with the results listed in Table I. Three published methods give results varying by as much as 20%. While our method finds only 81% as much hydroperoxides as the average of the three others, it is reproducible and suitable for semi-quantitative comparisons.

Table I
TITRATION OF A SAMPLE OF t-BUTYL HYDROPEROXIDE
BY DIFFERENT METHODS

% t-BuO ₂ H in sample			
Wibaut et al. ²	Nozaki ¹	Hargrave et al. ³	Egger
71.2	64.3	78.7	58.5
70.4	64.1	78.3	57.2
		77.7	57.7
70.8 av.	64.2 av.	78.2 av.	57.8 av.

¹K. Nozaki, *Anal. Chem.*, 18, 583 (1946)

²J. P. Wibaut, H. B., van Leeuwen and B. van der Wal, *Rec. trav. chim.*, 73, 1033 (1954)

³D. Barnard and K. R. Hargrave, *Anal. Chim. Acta* 5, 476 (1951)

3.4. Infrared Analysis

We have tried to determine the concentrations of carbonyl and hydroxyl groups in our degraded rubber solutions by comparing their infrared absorptions with those of di-n-heptylketone and 2-octanol through the use of potassium thiocyanate as standard. For this purpose 0.08 ml of a solution of 3.041 g KCNS in 50 ml of methanol was added to 1 ml of the oxidized polymer 1351 or its oxidation products. To this mixture methanol was added to give a homogeneous solution which was evaporated in a rotating evacuated flask. The polymer-KCNS mixture was then pressed between NaCl plates and its infrared absorption measured on a Perkin-Elmer 221 Spectrophotometer. All the measured peak heights were related to the KCNS peak at 4.85 μ .

3.5. Oxidations with Hydrazines and Thiols

The apparatus used in following viscosity changes and oxygen uptake was described in Section 3.2 of our Second Quarterly Progress Report. For the present work the reaction vessel was fitted with a neoprene serum cap (never in contact with solution) so that the catalyst solution could be injected into the vessel without disconnecting the viscosimeter from the burette.

In a typical experiment, 50 ml of rubber solution was placed in the viscosimeter and thoroughly degassed at room temperature. The viscosimeter was then filled with nitrogen. After equilibration in the thermostat the initial flow time was measured. The nitrogen was next removed with a water aspirator and replaced with oxygen. After equilibration had again taken place (~ 10 min), the flow time was measured and 0.25 ml of a chlorobenzene solution of catalyst was injected by means of hypodermic syringe. This addition caused a slight decrease in flow time, due to a dilution effect, and a slight rise in gas volume. The maximum volume of oxygen in the gas burette was taken as the zero point for determining oxygen consumption.

In current experiments (not in this report) evacuations are limited to pressures about 5 mm above the vapor pressure of the solvent, to minimize solvent losses.

4. Effects of Metal Catalysts on Oxidations of Polymer Solutions at 50^o(K. Egger and K. Crawford)

4.1. Effect of Metal Octanoates (O) and Naphthenates (N) on Rates of Oxidation

For these experiments, summarized in Table II and Fig. 1, we used the oxidized polymer 1351, characterized in Section 3.1 and Table II. The first group of experiments in Table II shows that this solution oxidized slowly with oxygen alone (1.2 mmol/liter/hr without additional ABN, 2.7 mmol/liter/hr with 4.8 mmol/liter of ABN). The increase in peroxide titer corresponded to 10-25% of the oxygen consumed and there was one net chain scission per 14-15 molecules of oxygen absorbed.

Table II
EFFECTS OF SOLUBLE METAL SALTS ON THE OXIDATION OF A CHLOROBENZENE
SOLUTION OF DEGRADATED POLYISOPRENE (1.335 M in C₅H₈ units) AT 50°C

Expt. No.	Catalyst ^a	mmol ^b liter	Reaction time, hours	M _n ^c	O ₂ absorbed, ^d mmol liter	Chain scissions, ^e mmol liter	O ₂ scissions	RO ₂ H, ^f mmol liter
Oxidized Polymer	-	-	(0)	(1351)	-	-	-	(52.6)
20/1	-	-	26	-	27.52	-	-	-
22/4	-	-	95.1	1217	114.4	7.4	15.4	78.0
22/5	ABN	4.79 ^g	94.9	1110	206.5	14.6	14.1	73.5
22/2	Co-O	2.0	6.6	1146	133.3	12.0	11.1	38.3
22/1	Co-O	2.0	29.9	961	295	27.3	10.8	62.0
20/2	Co-O	2.0	36.1	928	337.5	30.7	11.0	66.0
20/5	Co-N	2.0	36.1	950	360.5	28.4	12.7	80.5
23/5	Co-O	7.89	75.8	715	781	59.9	13.0	71.5
22/3	Co-O	20.0	19.0	523	631	106.6	5.9	64.5
20/3	Fe-O	1.95	36.1	977	197.3	25.8	7.7	84.0
20/4	Mn-O	2.1	46.6	970	155.2	26.4	5.9	38.0
20/6	Mn-N	2.1	46.9	1000	132.1	23.6	5.6	37.5
23/4	Cu-N	2.0	75.8	976	151.5	25.9	5.9	56.3
23/1	Ca-N	2.0	75.2	1040	80.5	20.1	4.0	37.4
23/2	Zn-N	2.0	76.3	1120	64.7	13.9	4.7	34.0
23/3	Pb-N	2.0	76.3	1100	50.0	15.4	3.3	33.3
Oxygen absent during reaction at 50°								
21/4	-	-	43.8	1347		0.0	-	51.0
21/1	Co-O	2.0	43.8	1159		11.2	3.7 ^h	11.0
21/2	Fe-O	1.95	43.8	1081		16.8	1.5 ^h	27.0
21/3	Mn-O	2.1	43.8	1166		10.7	3.7 ^h	13.3
21/5	Pb-N	0.54	43.8	1230		6.6	1.2 ^h	45.0
Oxygen absent during reaction at 0°								
24/2	Co-O ⁱ	7.89	0.03	708		61.1	0.3 ^h	36.0

^a N = naphthenate; O = octoate

^b Based on the metal content, certified by the manufacturer, Nuodex Products Company, New York

^c Number-average molecular weights after oxidation determined as described in Section 6.3.4; based on the weight of rubber hydrocarbon in solution.

^d During the indicated reaction time.

^e Based on decrease in M_n.

^f Based on iodometric titrations (heating under N₂ for 70 minutes at 50°C).

^g 2.50 mmole/liter decomposed during 95 hours

^h Decrease in peroxide titer, chain scissions.

ⁱ Addition under N₂ to the frozen solution and warming up to room temperature for 2 minutes, then kept at 0°C until the RO₂H and M_n measurements were made.

The next six experiments in Table II show the effect of cobalt on the further oxidation of the solution of oxidized polymer 1351. First, there is little difference between the octanoate and the naphthenate. With 2 mmol/liter of cobalt ion, there is an initial rapid absorption of oxygen, accompanied by a net decrease in peroxide titer and color changes from blue to olive to brown. Subsequently, the rate of oxidation slows; the peroxide titer recovers, and after several hours a cobalt compound begins to precipitate. Eleven to 13 oxygen molecules are absorbed per chain scission, significantly fewer than in the absence of cobalt. We take these results to mean that on addition of cobalt to oxidized rubber, the cobalt causes decomposition of accumulated peroxides with accompanying chain cleavages, and effects a higher rate of chain initiation. Thereafter, the effect of the cobalt decreases and most of the chain scissions take place in the standard ratio during the oxidation process. Larger proportions of cobalt give higher initial rates of oxidation and permit less titratable peroxide to accumulate. The initially large effect of the cobalt gradually wears off as it probably becomes complexed and precipitated.

At the indicated end of Expt. 23/5, an additional 7.9 mmol/liter of cobalt salt was added and reaction was continued for 54 hours. During the first 5 hours the rate of oxidation was about one-half the initial rate, but it again leveled off; 207 mmol/liter of oxygen was absorbed and the molecular weight decreased to 442. During this 54-hour interval, only 2.7 molecules of oxygen were absorbed per chain cleaved. This experiment supports the suggestions above.

A single experiment with iron octanoate suggests that iron does not destroy peroxides as rapidly as cobalt and that it does not cause as rapid chain initiation, but that the number of chain scissions per oxygen consumed is higher. Manganese causes considerable peroxide decomposition without accelerating oxidation very much; possibly manganese is a retarder as well as an initiator of oxidation. Copper slightly accelerates the rate of oxidation, but calcium, zinc, and lead salts are without much effect on rates. However, salts of these metals cause the highest number of cleavages per oxygen absorbed, probably because they decompose peroxides without causing much oxidation.

One experiment with nickel octanoate (prepared from $\text{Ni}(\text{OH})_2$ and octanoic acid) is shown in Fig. 2 and was carried out with a solution of oxidized polymer 4082. This experiment is not entirely comparable with those with the oxidized polymer 1351. However, this experiment indicates an oxidation rate with nickel about half that with 0.01 M ABN, a rate of no special interest.

Experiment 22/5 in Table II indicates that 82 molecules of oxygen reacted and six chains were cleaved per ABN decomposed at 50°. This result conflicts sharply with those of Tobolsky and Mercurio.⁴ In experiments with natural rubber in benzene at 60-80°, they found only

⁴A. V. Tobolsky and A. Mercurio, J. Am. Chem. Soc. 81 5535 (1959)

about one cleavage per ABN or peroxide decomposed. The high vapor pressure of benzene may have kept their oxygen concentration too low, and their molecular weights, determined from viscosities, are suspect.

At this writing, we propose tentatively that various metal salts have little or no effect on the propagation of oxidation chains. All metals seem to cause decomposition of peroxides, and the efficiencies of the associated chain cleavage reactions may vary with the metal. The abilities of metals to catalyze chain oxidations vary considerably, but we cannot now distinguish between a low efficiency of chain initiation and a high efficiency of initiation associated with chain-terminating properties as well. All of these effects are complicated by uninvestigated changes in the valence and coordination states and in solubilities of the metal compounds.

4.2. The Effects of Metal Catalysts in the Absence of Oxygen

In four of the last five experiments in Table II, to determine the effects of the metals on peroxide stability, degassed solutions of oxidized polymer 1351 were shaken at 50° for 44 hours in evacuated vessels. In all cases, significant amounts of peroxides were lost in the presence of metal salts. Comparison of "oxidized polymer 1351" and Expt. 21/4 shows that little peroxide decomposed in the absence of metal salts, but that peroxides disappeared relatively fast in the presence of manganese and cobalt, slower in the presence of iron or lead. Iron seems to be more efficient in producing chain scissions for a given amount of peroxide decomposed (the data with lead are not as accurate or strictly comparable).

In the last experiment in Table II, the color change indicated that extensive reaction occurred rapidly at 0°. Prompt work-up showed that more chain cleavages than decompositions of titratable peroxide had occurred. Comparison of this experiment with Expt. 21/1 raises the question of whether cross-linking or condensation may follow rapid initial cleavage.

4.3. Oxidation Products

With increasing oxidation, infrared absorption shows progressively stronger absorptions near 2.9 μ and 5.8 μ for hydroxyl and carbonyl groups, respectively. At the same time general absorption increases at 6 to 15 μ , obscuring detail in this region. Very similar infrared absorption spectra are obtained by oxidation of films of natural rubber⁵ or synthetic cis-polyisoprene. Infrared does not distinguish between alcohols and hydroperoxides, the difference between the 2.9 μ absorption maxima being only about .05 μ .⁶ The oxidized polymer 1351 contains

⁵V. Ke. 3, A. Tkac and J. Hrivikova, Chem. Listy, 49, 1433 (1955); Translation in Rubber Chem. and Technology, 29, 1245 (1956)

⁶H. R. Williams and H. S. Mosher, Anal. Chem., 27, 517 (1955)

hydroxyl and carbonyl compounds by infrared and hydroperoxides by titration. The main carbonyl absorption at 5.83μ is tentatively assigned to ketone groups and the shoulders at 5.7 and 5.9μ to aldehydes and acids, respectively, by analogy with studies on oxidation products of polyethylene.⁷ The oxidized polymer 4082, however, shows only about one-tenth as much hydroxyl and carbonyl absorptions as the oxidized polymer 1351, despite the fact that its oxygen content is nearly half that in the 1351 polymer. The carbonyl absorption maximum is still at 5.83μ , but the shoulders are not obvious. Further, no titratable peroxides are found in the 4082 polymer.

When we heated the oxidized polymer 1351 for 48 hours at 160° the titratable peroxides disappeared but both the hydroxyl and carbonyl absorption increased. If alcohols and hydroperoxides have comparable absorption intensities, this result must mean that the additional hydroxyl (and maybe some carbonyl) groups arose by decomposition of nontitratable (cyclic or dialkyl) peroxides.

When the 1351 polymer is oxidized further, the increase in its oxygen content, from carbon and hydrogen analyses, accounts for only 70 to 80% of the volume of oxygen absorbed. These results are listed in Table III; if they are confirmed by direct oxygen analysis on the polymers, they indicate loss of highly oxidized, low-molecular-weight material during isolation of the analytical samples.

Efforts at quantitative infrared studies are also summarized in Table III. A known proportion of potassium thiocyanate was used as standard in each sample. The hydroxyl concentration estimated in this way is only 5-10% of the hydroperoxide found by titration. Although reproducible and sharp absorptions were obtained with potassium thiocyanate in oxidized polymers, sharp absorptions were not obtained with the alcohol and ketone standards. In any event, the hydroxyl and carbonyl contents indicated by infrared absorption fall far short of accounting for the oxygen contents of the polymers.

An effort to use the 3.48μ C-H absorption as an internal standard in the polymer indicated still lower hydroxyl and carbonyl contents (but in similar relative proportions). Perhaps much of the oxygen is in cyclic peroxides, a possibility consistent with the disappearance of carbon-carbon double bonds during oxidation.

4.4. The Influence of Oxidation Products on the Rate Oxidation

In Fig. 3 we compare experiments with approximately the same concentration of cobaltous octanoate with three different solutions, the undegraded polymer, (25.45 g/liter, Section 3.1 of the last report) the oxidized polymer 1351, and the oxidized polymer 4082 (Section 3.1

⁷F. M Rugg, J. J. Smith and R. C. Bacon, J. Polymer Sci., 13, 535 (1954)

Table III

OXYGEN BALANCE ON CHLOROBENZENE SOLUTION OF OXIDIZED
POLYISOPRENE INITIAL SOLUTION 1.335 M IN C₅H₈ UNITS

Sample	M _n ^a	Av. composition of dry polymer by C + H ^c	Concentration in millimols of O ₂ /liter				
			O ₂ ^f uptake	Total O ₂ in ^c polymer	FO ₂ H ^d	Ketones ^e	Alcohols ^e
Original cis-poly- isoprene	~ 250,000 ^b	(C ₅ H ₈) _n	0	0	0	0	0
Oxid. pol. 1351	1351	(C ₅ H _{8.08} O _{.45}) _{17.8}	0	300	52.6	6.2	~2
Oxid. pol. 1351, 48 hr at 160° in vac.	1140	-	0	-	0	12.3	~4
Product of expt. 22/4	1217	(C ₅ H _{7.71} O _{.562}) _{15.7}	114.4	374.8	78.0	14.4	~7.2
Product of expt. 22/5	1110	(C ₅ H _{7.78} O _{.70}) _{13.9}	206.5	466.8	73.5	15.9	~4.7
Product of expt. 22/3	523	-	631	-	64.5	25.7	~3.1

^aM_n = number average molecule weight

^bFrom intrinsic viscosity measurements

^cO by difference from C and H

^dBy titration in Section 3.3

^eMethod in Section 3.4. The alcohol content should equal or exceed peroxide content, but does not.

^fPast 1351 stage.

of this Report). To get comparable figures, results of all three experiments have been recalculated to 25 ml of a solution containing 0.625 g of polymer (25 g/liter). The catalytic effect of the cobalt salt depends on oxidation products in the polymer.

The two oxidized polymers show only small rate differences, even though the 1351 polymer contains considerable titratable peroxide and the 4082 polymer contains none. The remarkable color changes from blue (Co^{II}) to olive (Co^{II} + green Co^{III}) to brown (unknown complexed form) are the same with both 1351 and 4082 polymers. Since titratable peroxides seem to have little effect on catalysis or color changes, some other oxidation products may be important. With solutions of unoxidized polyisoprene the metal has little catalytic effect until enough oxidation products have been formed. After the induction period, the rate of oxidation and the color changes are the same as with preoxidized polymer solutions. Thus, the association of metal catalysis with hydroperoxides is less certain than it previously seemed.

4.5. Proposed Work on Metal Catalysis

In an effort to associate metal catalysis with oxidation products, an oxidation will be carried out with squalene as a model for polyisoprene. Experiments on further oxidation of 4082 polymer with cobalt complexes with octahedral, tetrahedral, and planar coordinations are under way and will be continued. The influence of the common antioxidants, phenyl- β -naphthylamine and 2,6-di-*t*-butyl-4-methylphenol, on metal-catalyzed oxidations will be determined.

Some oxidation products from experiments with oxidized polymer 1351 will be analyzed by NMR to estimate the double bonds consumed during oxidation.

A new cobalt-complex precipitate has been prepared and will be analyzed to give us some idea about the interaction of cobalt salts and polymer oxidation products.

A few oxidations of polybutadiene will be carried out.

5. Degradations by Hydrazines and Thiols (Jorge Heller and R. L. Walrath)

5.1. Corrections to Previous Phenylhydrazine Experiments

In our Second Quarterly Progress Report, the following corrections apply:

In Fig. 4, the time scale is in ten-minute (not 1-minute) intervals. In the first paragraph in Section 7, for "one minute," read "10 minutes," and for "two minutes," read "20 minutes."

In the first full paragraph on page 10, the marked decreases in viscosity on heating the rubber solution in the absence of oxygen are due to partial gellation of the rubber on the sides of the glass tubes and the formation of less concentrated solutions. These results and Sections 5.2 of the present report invalidate our conclusion about the interaction of phenylhydrazine and peroxides in the last paragraph of Section 7 of our Second Quarterly Report.

In our Monthly Letter Report for March, 1963, the last sentence in the next-to-last paragraph should be deleted.

5.2. Effects of Chlorobenzene and Phenylhydrazine on Rubber Solutions in the Absence of Oxygen

As noted in the correction above, our Second Quarterly Progress Report suggested that phenylhydrazine can catalyze the degradation of polyisoprene even in the absence of oxygen by utilizing some reactive groups, presumably peroxides, which are present even in carefully degassed rubber solutions. We have since found that the addition of even very small amounts of chlorobenzene alone produces a noticeable decrease in viscosity. This work, summarized in Table IV, clearly shows that the observed decrease in "reduced relative flow time" does not depend on the amount of phenylhydrazine but only on the amount of solvent. We conclude that the solutions chosen for our previous work are unexpectedly sensitive to concentration changes.

Table IV

IMMEDIATE EFFECT OF DILUTION ON THE RRFT^a
OF A DEGASSED SOLUTION OF 2.54% POLY-
ISOPRENE IN CHLOROBENZENE IN THE
ABSENCE OF OXYGEN
(Total volume of solution, 50 ml)

C ₆ H ₅ Cl Added, ml	φNHNH ₂ Added, mmoles	RRFT ^a After Addition
0.25	none	0.92
0.25	0.005	0.92
1.0	none	0.82
1.0	0.0092	0.82
1.0	0.0085	0.74
3.0	none	0.72
3.0	none	0.76
3.0	0.035	0.77
3.0	0.087	0.73

^aReduced relative flow time, defined in Section 3.3 of Second Quarterly Progress Report.

5.3. Phenylhydrazine in the Presence of Oxygen

The addition of small amounts of a chlorobenzene solution of phenylhydrazine to a solution of polyisoprene in the presence of oxygen causes a much greater decrease in viscosity. Changes in RRFT with time for different phenylhydrazine concentrations are shown in Fig. 4. As noted in our previous quarterly report, there is a very rapid viscosity decrease followed by little further change. The viscosity change increases with the amount of phenylhydrazine added.

The rapidity with which the RRFT value drops after oxygen is introduced is brought out by the following experiment. A rubber solution was carefully degassed and the flow time under nitrogen measured. Next phenylhydrazine solution was introduced and the flow time measured again to determine the dilution effect. The rubber solution was then briefly evacuated and the nitrogen replaced by oxygen. The usual sharp decrease in flow time occurred in less than four minutes.

These interesting data indicate that neither phenylhydrazine nor oxygen alone will cause rapid degradation of rubber, but that the combination causes very rapid but short-lived degradation. The amounts of oxygen absorbed during these degradations have been too small to measure accurately, usually less than 1 ml. To the extent that our numbers have any significance, they correspond to one to three molecules of oxygen reacting per molecule of phenylhydrazine added.

We shall try to obtain useful correlations between the amounts of phenylhydrazine added, the oxygen absorbed, and the number of chain cleavages. A few such experiments will also be carried out with polybutadiene.

5.4. Effects of Other Hydrazines

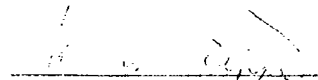
Figure 5 compares the effects of three hydrazines on the degradation of a 2.54% solution of polyisoprene in chlorobenzene. All experiments employed 5×10^{-6} mole of catalyst per 50 ml of solution. Unlike phenylhydrazine, 1,1-dimethylhydrazine has a slow but sustained action and produces an appreciably shorter ultimate flow time. Hydrazine hydrate has an intermediate effect. Again, correlations of hydrazine concentration, oxygen consumption, and chain scissions are desirable.

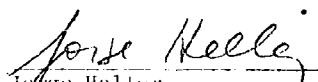
5.5. Effect of p-Thiocresol

Figure 6 shows decreases in RRFT and oxygen consumption for two p-thiocresol-catalyzed degradations of polyisoprene. Unlike phenylhydrazine, p-thiocresol seems to exert a catalytic action. In Expt. 2, 16 molecules of oxygen were absorbed per initial molecule of thiocresol when the reaction was discontinued. Correlations of thiocresol concentrations, oxygen consumption, chain scissions, and autocatalysis will be carried out. The action of thiocresol remains interesting and promising.

The action of thiocresol is compared with those of the three hydrazines in Fig. 5


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FRM:KWE:JD:LF

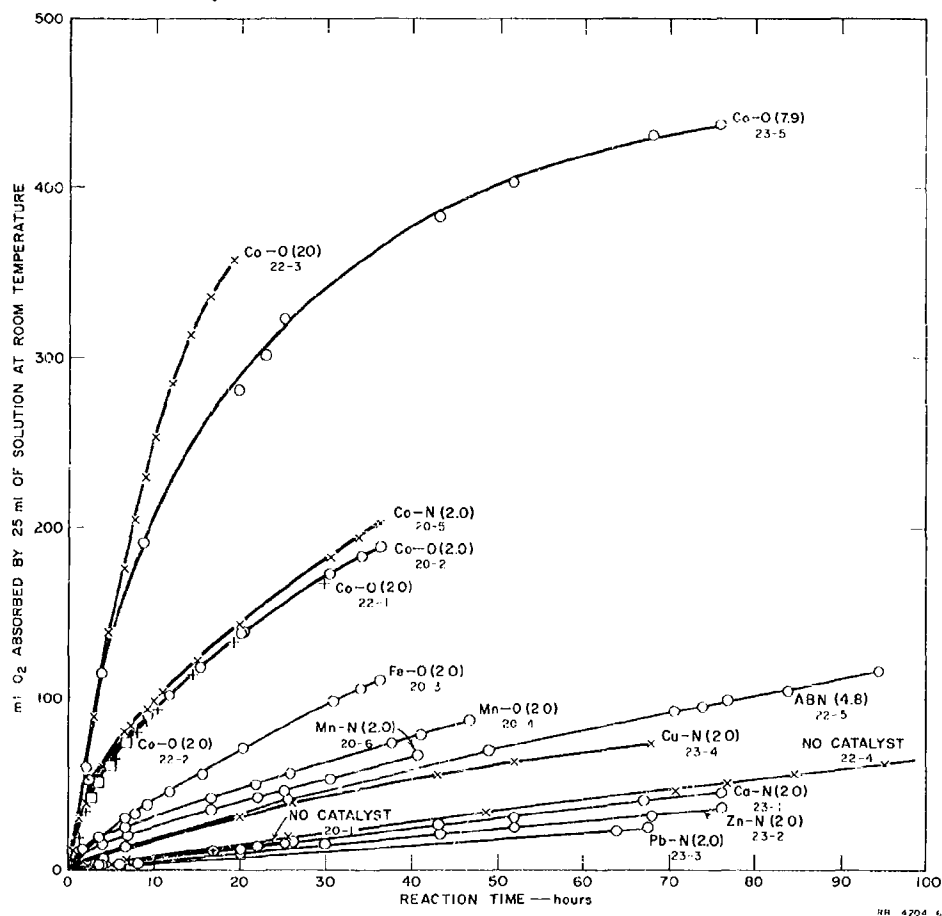


FIG. 1 RATE OF OXIDATION OF OXIDIZED POLYMER 1351 AT 50°C
 Identifications indicate the metal salt used, Octoate or Naphthonate,
 the concentrations of metals or ABN in millimoles/liter and the
 experiment number in Table II

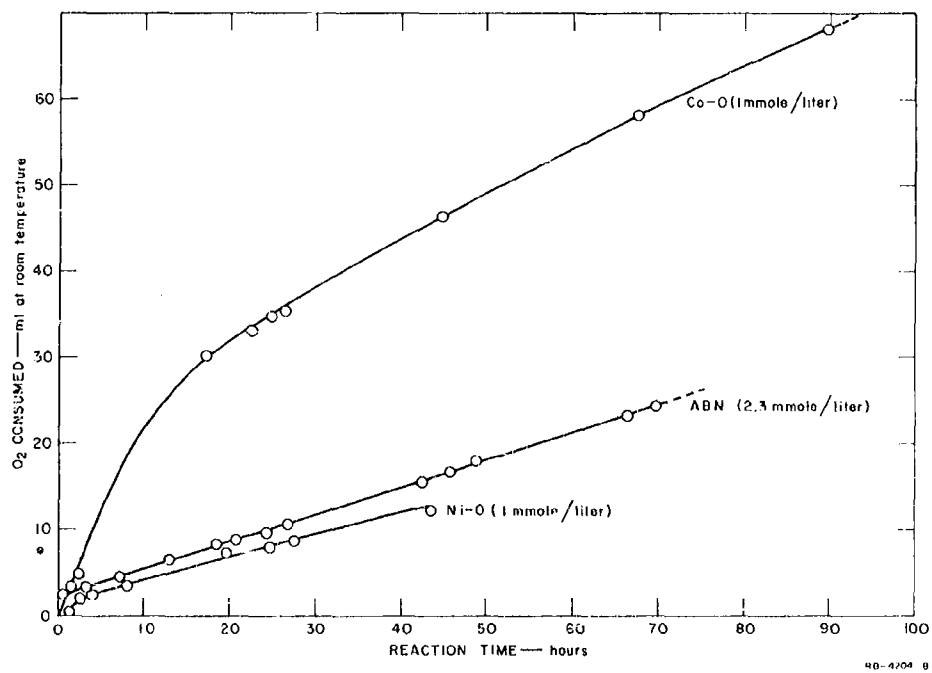


FIG. 2 OXIDATION OF 25 ml SAMPLES OF SOLUTIONS OF OXIDIZED POLYMER 4082 (0.3864 M in C₅H₈-units) AT 50°

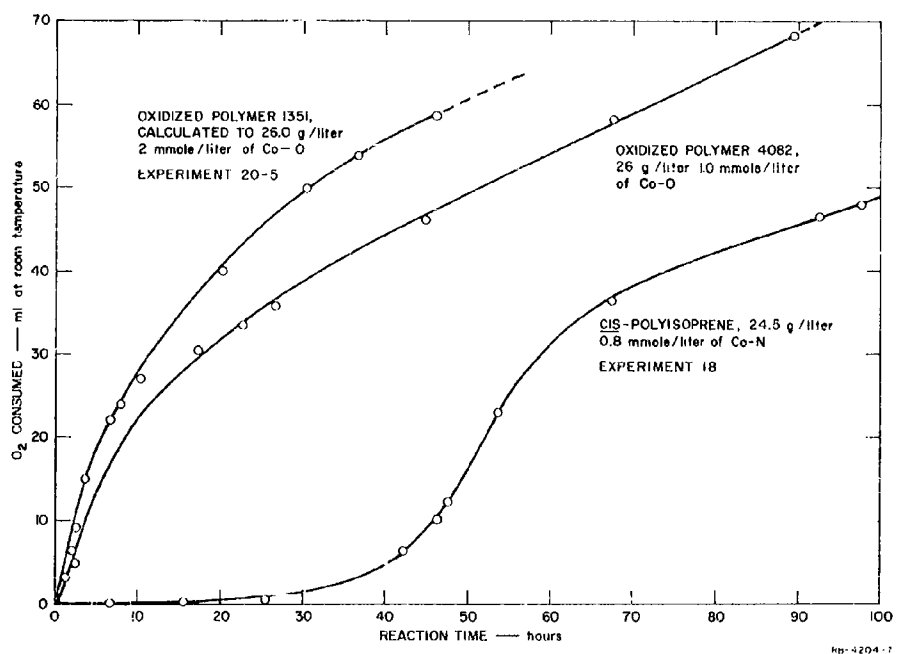


FIG. 3 COMPARISON OF RATES OF COBAL-T-CATALYZED OXIDATIONS OF RUBBER SOLUTIONS

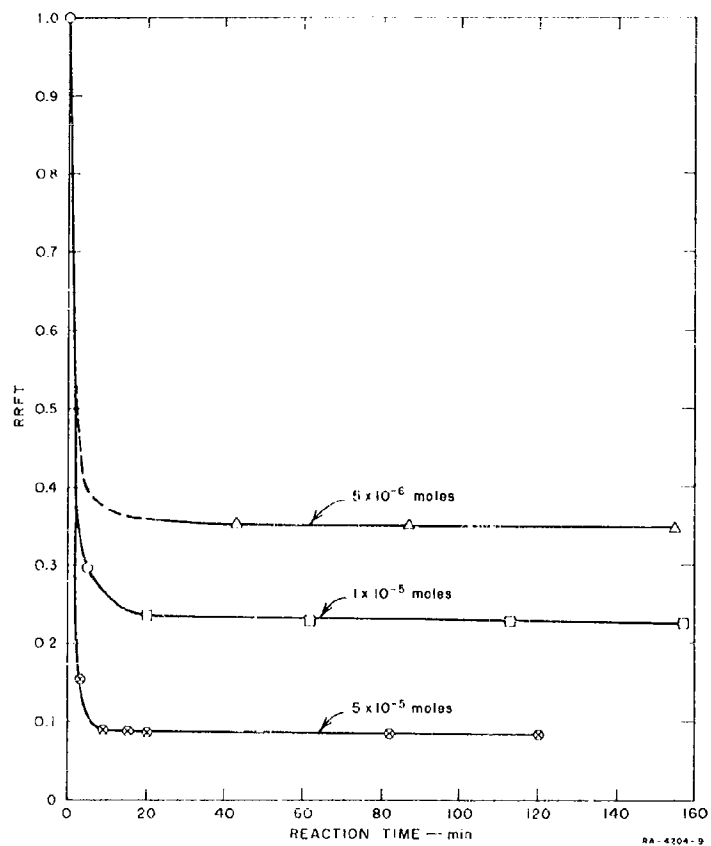


FIG. 4 CHANGE IN REDUCED RELATIVE FLOW TIMES DURING PHENYLHYDRAZINE-CATALYZED DEGRADATION OF 2.54% SOLUTION OF POLYISOPRENE IN CHLOROBENZENE UNDER OXYGEN AT 50°C

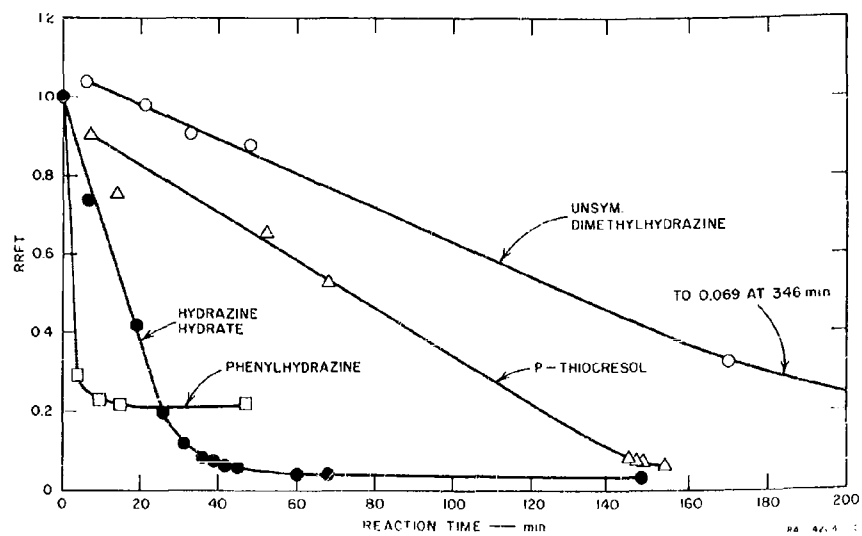


FIG. 5 EFFECT OF 5×10^{-6} MOLES OF VARIOUS AGENTS ON THE DEGRADATION OF 50 ml OF A 2.54% POLYISOPRENE SOLUTION IN CHLOROBENZENE UNDER OXYGEN AT 50°C

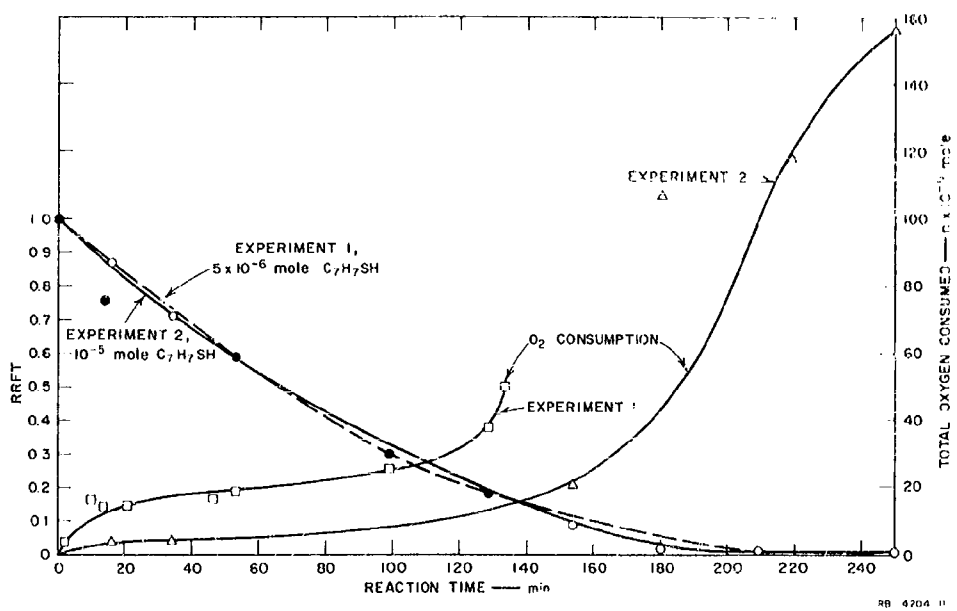


FIG. 6 CHANGE IN REDUCED RELATIVE FLOW TIME AND OXYGEN CONSUMPTION DURING A *p*-THIOCRESOL-CATALYZED DEGRADATION OF 50 ml OF A 2.54% SOLUTION OF POLYISOPRENE IN CHLOROENZENE AT 50°C

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