[Contribution from the Noyes Chemical Laboratory, University of Illinois]

OXIDATIVE HYDROLYSIS OF THE OZONIDES OF POLYBUTADIENES. II. ISOLATION OF 1,2,3-PROPANETRICARBOXYLIC ACID[1,2]

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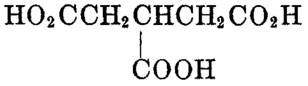
The present investigation was initiated to determine whether chromatographic separation (1) of the oxidative cleavage products of the ozonides of various polybutadienes would indicate the nature and degree of branching in the polymer. It was also hoped that the chromatograms might be characteristic for different polymers.

Preliminary work on a highly gelled polybutadiene (S1, Table I) made without modifier led to the isolation of 1,2,3-propanetricarboxylic acid (I), a product which would not be expected from any of the structural units in an unbranched polybutadiene. This offered promise that the method could be used to determine branching in these polymers.



$$\mathrm{HO_2CCH_2\underset{\displaystyle COOH}{\underset{|}{C}}HCH_2CO_2H}$$

I

In this communication are presented the results of the examination of eleven polymers and copolymers of butadiene made under different conditions. The polymers are described in Table I.

The acid mixtures from the oxidative decomposition of the polymer ozonides were separated by the use of a modification of the partition chromatographic technique reported by Marvel and Rands (1). The chromatographic separation worked well and some of the results are shown in Figures 1 through 11 and Table II. Slightly different systems, such as size of column and developing solutions, were used at different times in conducting this investigation, due to improvements in the technique as the work progressed. Therefore, it is not possible to assign standard peak effluent volumes (1) to the peaks appearing in one graph and to expect these to hold for the others. Consequently a standard numbering system will be used in this discussion. In the chromatograms, I marks the complex mixture of acids of which formic, β-formylpropionic, levulinic, and acetic acids have been identified (2). II marks the succinic acid portion; III the 1,2,4-butanetricarboxylic acid portion; and IV the 1,2,3-propanetricarboxylic acid portion. The identifications were made first by comparing the peak effluent vol-

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the U. S. Government Synthetic Rubber Program.

[2] This is the second paper on oxidative-ozonolysis of polymers and copolymers of butadiene. For the first see C. S. Marvel and R. E. Light, Jr., *J. Am. Chem. Soc.*, **72**, 3887 (1950).

TABLE I

POLYMERS USED IN OXIDATIVE-OZONOLYSIS STUDY

OUR IDENTIFICATION	TEMP. OF POLYMERIZATION, °C.	CONVERSION, %	STATIC SOLUBILITY, %	TYPE	REMARKS
S1 polymer	50	95 (approx.)	13.5	E.P.[a][e]	Trace of DDM[c]
H14R5D4[b]	100	73	21	E.P.	Modified with 1.25 parts t-C-16SH[d]
H778[a]	27	75	100	E.P.	Modified with DDM
1044[a] series	50	20.5	100	E.P.	Modified with DDM
	50	40.0	—	E.P.	Modified with DDM
	50	60.5	—	E.P.	Modified with DDM
	50	81.0	—	E.P.	Modified with DDM
	50	97.0	—	E.P.	Modified with DDM
GLSVES-3[b]	−10	59	96	GR-S	Modified with DDM
GLSVES-1[b]	50	61	83	GR-S	Modified with DDM
B 318	30	93	92	Sodium BD/S	No modifier

[a] We are indebted to Dr. B. L. Johnson of the Firestone Tire and Rubber Company for these samples. [b] We are indebted to Mr. W. K. Taft of the Government Laboratories, University of Akron, for these samples. [c] DDM is dodecylmercaptan. [d] t-C-16-SH is a mixture of tertiary mercaptans containing sixteen carbon atoms. [e] Emulsion polybutadiene.

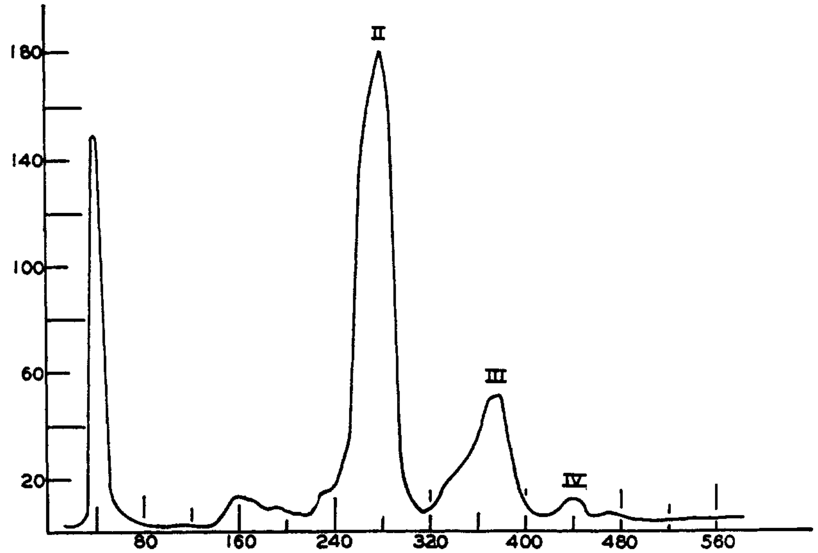


FIG. 1. CROSS-LINKED POLYBUTADIENE (S 1)

umes of the oxidation products with those of authentic acids using identical chromatographic conditions. Further identification was made in the case of the crystalline acids by melting points, mixture melting points, and carbon-hydrogen analytical data.

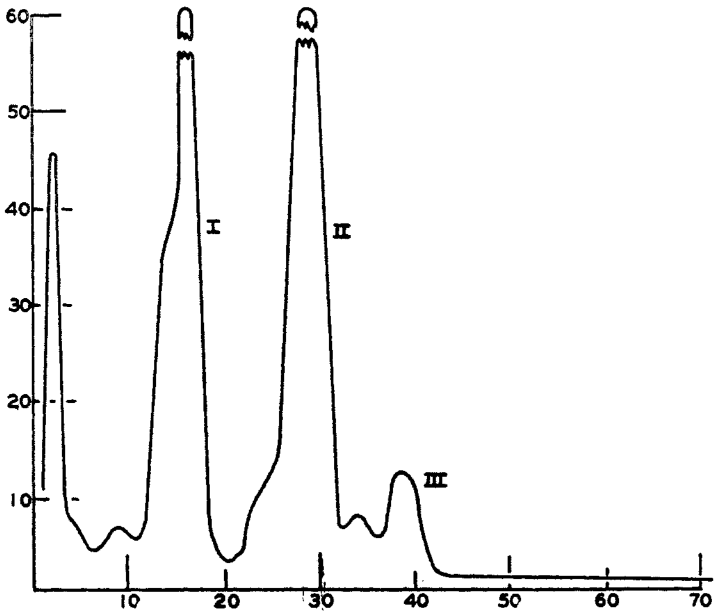


FIG. 2. WATER-SOLUBLE ACIDS FROM H14R5D4, SMALL COLUMN EXAMINATION TO LOOK FOR TRICARBALLYLIC ACID

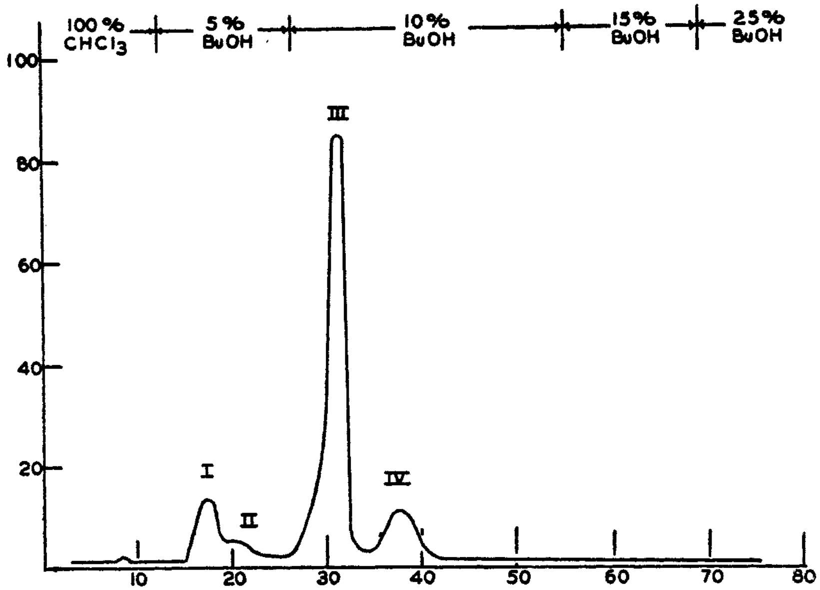


FIG. 3. WATER-SOLUBLE ACIDS FROM FIRESTONE POLYBUTADIENE H 778

In Table II only the milliequivalents of the base used to neutralize the fractions corresponding to sections I, II, III, and IV of the chromatograms above are recorded in order to conserve space.

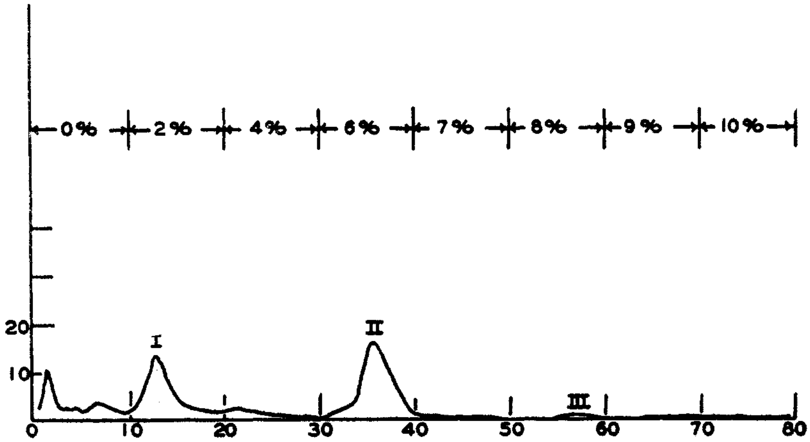


FIG. 4. NO. 1044—20.5% CONV. OXIDIZED 3% H_2O_2 3 HRS. AT 60°C.

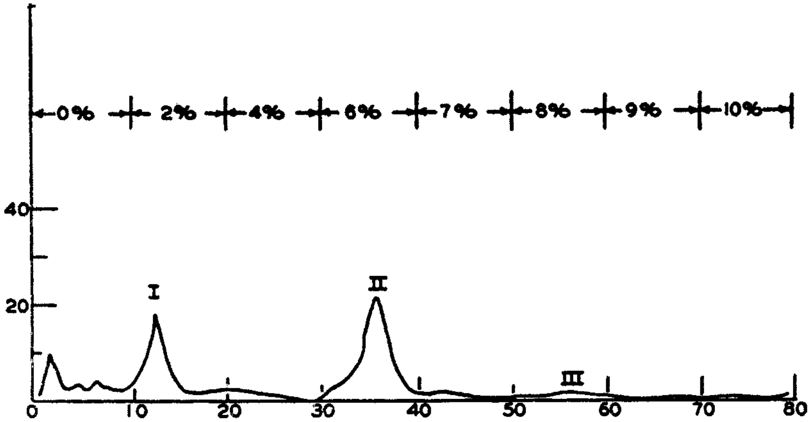


FIG. 5. NO. 1044—40.0% CONV. OXIDIZED 3% H_2O_2 3 HRS. AT 60°C.

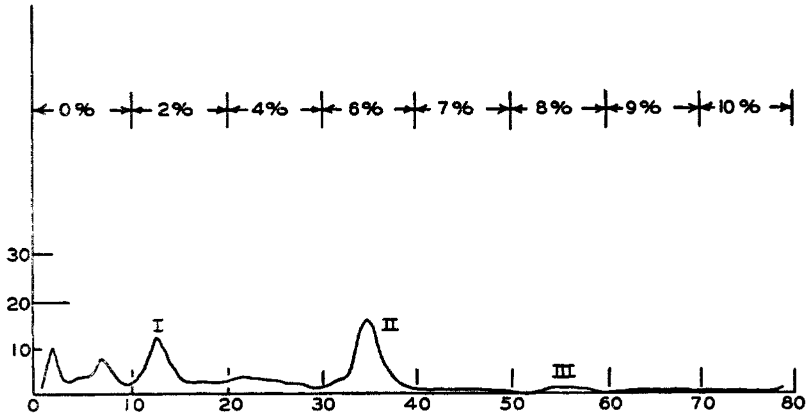


FIG. 6. NO. 1044—60.5% CONV. OXIDIZED 3% H_2O_2 3 HRS. AT 60°C.

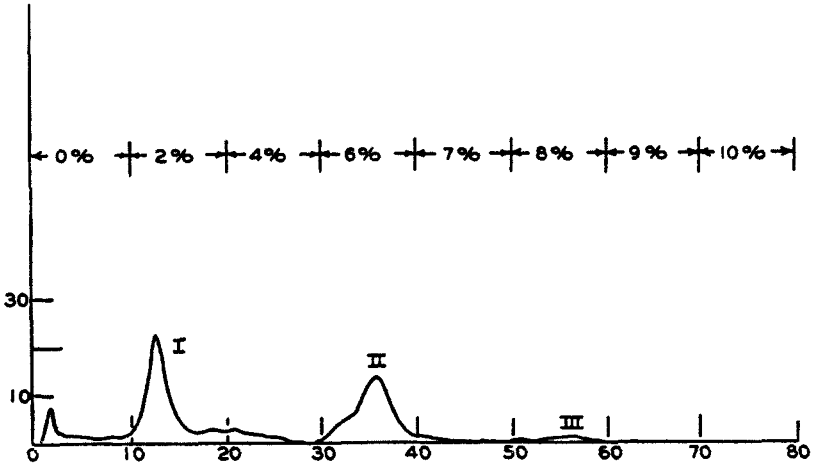


FIG. 7. No. 1044—81.0% CONV. OXIDIZED 3% H_2O_2 3 HRS. AT 60°C.

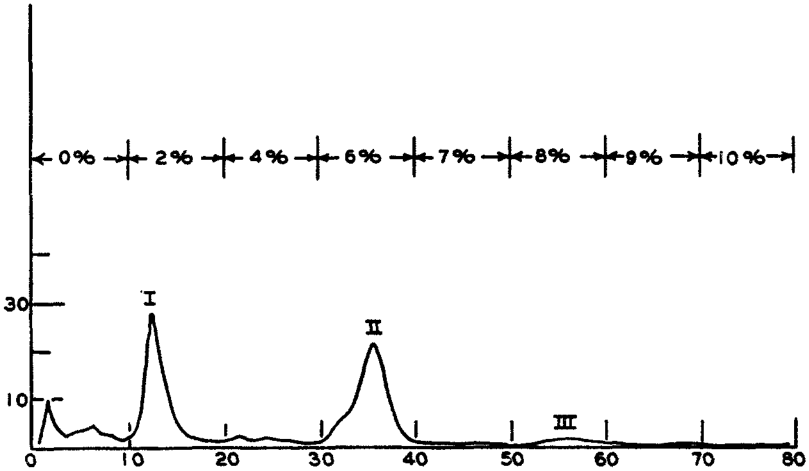
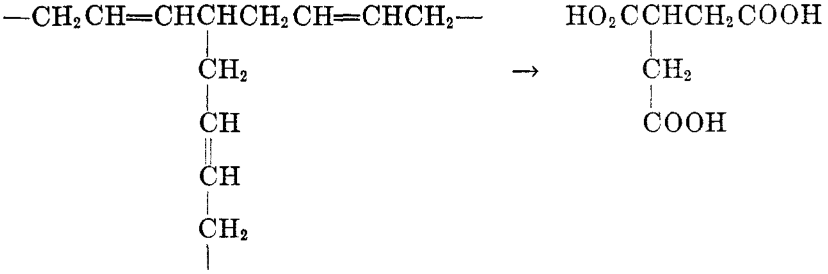


FIG. 8. No. 1044—97.0% CONV. OXIDIZED 3% H_2O_2 3 HRS. AT 60°C.

It was originally thought that the isolation of 1,2,3-propanetricarboxylic acid (I) as an oxidation product of polybutadiene indicated the presence in that



$$\mathrm{-CH_2CH{=}CH\underset{\begin{array}{c}|\\ CH_2\\ |\\ CH\\ \|\\ CH\\ |\\ CH_2\\ |\end{array}}{C}HCH_2CH{=}CHCH_2-} \longrightarrow \mathrm{HO_2C\underset{\begin{array}{c}|\\ CH_2\\ |\\ COOH\end{array}}{C}HCH_2COOH}$$

II I

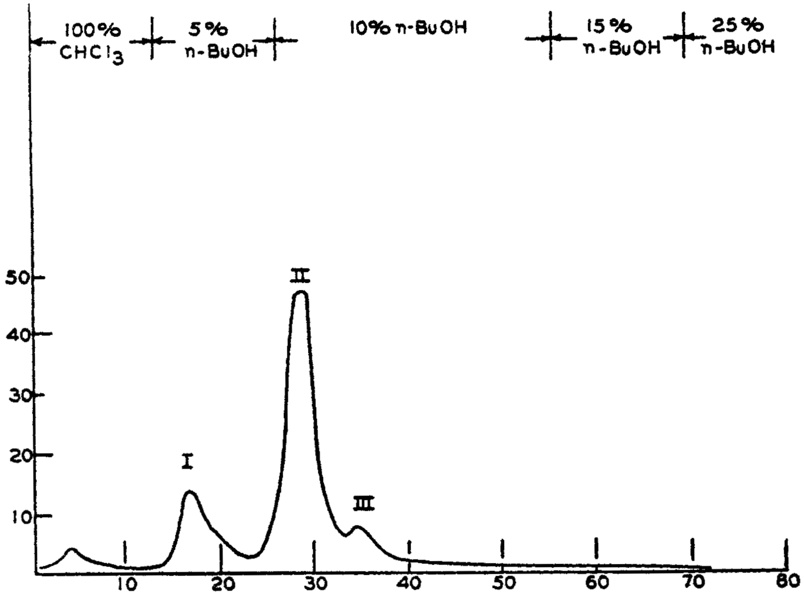


FIG. 9. GLSVES-3 WATER-SOLUBLE ACIDS

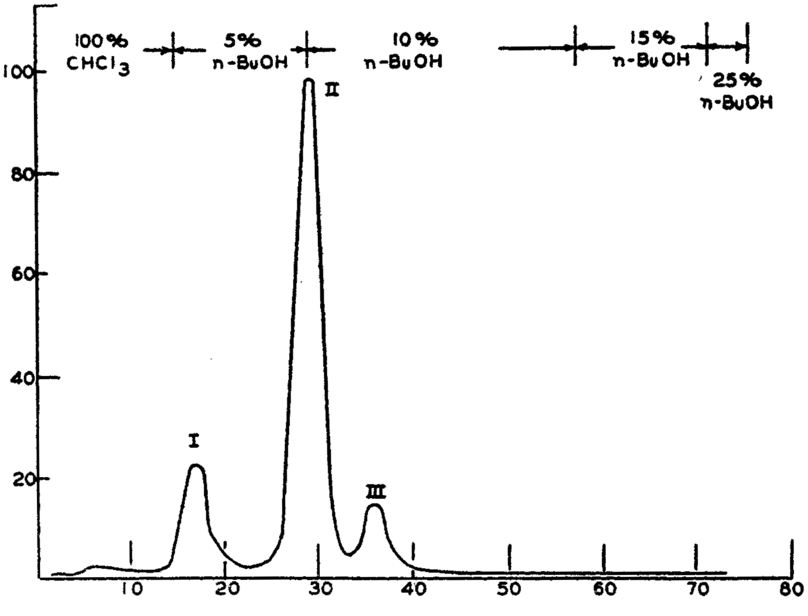


FIG. 10. GLSVES-1 WATER-SOLUBLE ACIDS

polymer of a branched structural unit (II). Such a structural unit could be formed readily by a branching process at an allyl position between two adjacent

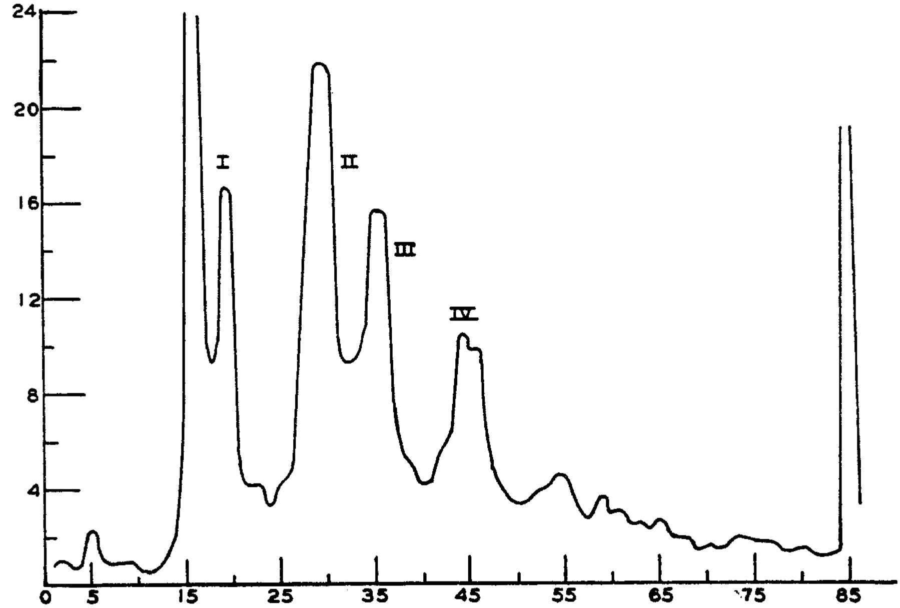


FIG. 11. WATER-SOLUBLE ACIDS FROM SODIUM CATALYZED POLYBUTADIENE (B 318) 0.35 ML. AQUEOUS SOLN. CONTAINING ABOUT 35 MG. SOLIDS

TABLE II

PRODUCTS OF OXIDATIVE CLEAVAGE OF 1044 SERIES BY PROCEDURE C

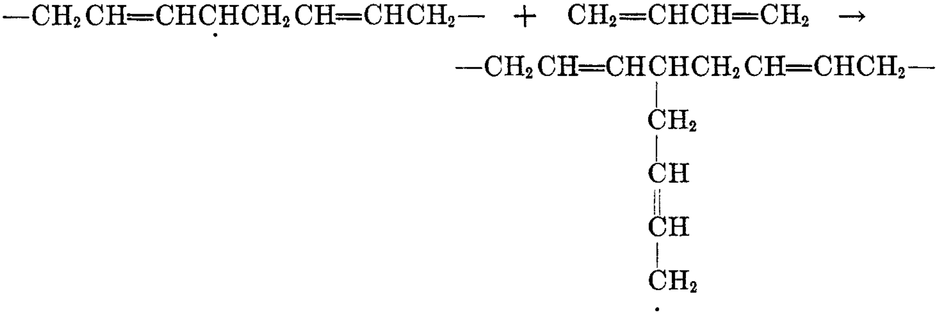
POLYMER CONVERSION, %	MEQ. BASE × 10^3			
	Peak I	Peak II	Peak III	Peak IV
20.5	55.2	281.1	47.8	2.6
40.0	47.4	325.5	58.1	2.6
60.5	34.1	337.6	65.0	3.8
81.0	38.9	316.2	58.3	3.5
97.0	20.2	318.2	52.4	6.2

1,4-butadiene units in polybutadiene and could be accounted for by the following series of reactions.

1. Chain transfer between a growing polymer chain and a preformed polymer chain.

$$\mathrm{P\cdot\ +\ -CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2-\ \rightarrow}$$
$$\mathrm{PH\ +\ -CH_2CH{=}CH\underset{\cdot}{C}HCH_2CH{=}CHCH_2-}$$
$$\mathrm{III}$$

2. Growth of the new free radical by addition of monomeric butadiene in a 1,4-manner.



$$-CH_2CH{=}CH\underset{\bullet}{C}HCH_2CH{=}CHCH_2- + CH_2{=}CHCH{=}CH_2 \rightarrow -CH_2CH{=}CHCH(CH_2CH{=}CH\underset{\bullet}{C}H_2)CH_2CH{=}CHCH_2-$$

IV

The intermediate free radical (III) could also rearrange to give different isomers before the addition of the butadiene.

However, 1,2,3-propanetricarboxylic acid has been obtained from all the polymers examined by using more strenuous conditions of oxidative hydrolysis of the ozonide (compare Figure 1 with Figure 2).

Of particular interest are the results obtained upon examination of a sample of sodium rubber. Inspection of Figure 11 shows a large peak representative of 1,2,3-propanetricarboxylic acid. Calculation indicates that approximately 3.4 mg. of 1,2,3-propanetricarboxylic acid or 9.7% of the solids put on the column is represented by this peak. This was quite unexpected since sodium rubbers were believed to be essentially linear polymers. Of considerable significance is the fact that this type of polymer contains about 60% 1,2-addition as compared with about 20% for the emulsion polymers. It was suspected that the appearance of 1,2,3-propanetricarboxylic acid could be largely tied in with the units formed by 1,2-addition of butadiene.

It is of interest to examine the results obtained by ozonolysis of polybutadiene made at different conversions when different methods of oxidative hydrolysis were used. The 1044 Firestone Series in Table I represents such a series. Inspection of the results (see Table III) obtained by the oxidative cleavage of this series shows that in our experiments, the ratio of succinic acid to 1,2,4-butanetricarboxylic acid is greatest at 20.5% conversion. This ratio decreases to 60.5% conversion and again increases after that. This indicates that 1,4 addition of butadiene units must occur to a greater extent during the first and last part of the polymerization process.

When the oxidative hydrolysis of the ozonides was carried out by Method B, which consists of a three-hour treatment with 3% hydrogen peroxide at 60° and then at 100° for 30 minutes, followed by decomposition of the excess peroxide with platinum oxide (3), none of these samples yielded 1,2,3-propanetricarboxylic acid. When the oxidative hydrolysis of the ozonide was done by Method C which consists of an eight-hour treatment with 3% hydrogen peroxide at gentle boiling temperature, followed by decomposition of the excess peroxide as before, all samples gave 1,2,3-propanetricarboxylic acid and the samples of highest conversions gave the most of this acid.

In Table IV are collected results of the oxidative hydrolysis of the ozonides of different polybutadienes (1044 series) under a variety of conditions. Here it is significant that a longer treatment of the ozonide from a 20.5% conversion polybutadiene with 6% hydrogen peroxide gave more 1,2,3-propanetricarboxylic acid than did a shorter treatment of the ozonide of the 97% conversion polymer with the same strength of hydrogen peroxide solution.

TABLE III

OXIDATIVE OZONOLYSIS OF POLYBUTADIENE OF DIFFERENT CONVERSIONS

% CONV.[a]	OXIDATIVE HYDROLYSIS PROCEDURE	PER CENT OF TOTAL MIXTURE (BY WEIGHT)			RATIO: SUCCINIC TO 1,2,4-BUTANETRICARBOXYLIC AICD
		Succinic Acid	1,2,4-Butanetricarboxylic Acid	Propane 1,2,3-Tricarboxylic Acid	
20.5	Method B	9.3	0.95	0	9.8
40.0		11.7	1.5	0	7.8
60.5		8.7	1.3	0	6.7
81.0		9.1	1.1	0	8.3
97.0		12.0	1.5	0	8.0
20.5	Method C	36.4	4.8	0.24	7.6
40.0		45.3	8.7	.22	5.2
60.5		46.3	9.7	.41	4.8
81.0		44.3	7.2	.45	6.2
97.0		37.5	6.6	.76	5.7

[a] These are the Firestone 1044 Series in Table I.

TABLE IV

OXIDATIVE HYDROLYSIS OF POLYBUTADIENES

1044 SERIES POLYBUTADIENES % CONVERSION	METHOD OF OXIDATIVE HYDROLYSIS	SUCCINIC ACID (g.)	1,2,4-BUTANETRICARBOXYLIC ACID (g.)	1,2,3-PROPANETRICARBOXYLIC ACID (g.)	RATIO: SUCCINIC TO 1,2,4-BUTANETRICARBOXYLIC ACID
97.0	3% H_2O_2, 55°, 10 Hrs.	0.00213	0.0003	0	7.2
60.5	3% H_2O_2, 85°, 10 Hrs.[a]	.0089	.00115	0	7.7
20.5	B + 6% H_2O_2, 11.5 Hrs., 105°	.0192	.0035	0.00096	5.5
97.0	B + 6% H_2O_2, 8.75 Hrs., 105°	.0190	.00405	.00078	4.7
20.5	B + $Na_2Cr_2O_7$	.0043	0	0	—
20.5	B + HIO_4	.00337	.00365	0	9.2
20.5	B + HIO_3	.0054	.00070	0	7.7
97.0	F + HIO_3	.00271	.00036	0	7.4
20.5	B + Ag_2O	.0173	.0028	.00016	6.2

[a] This is called Method F for oxidative hydrolysis.

This certainly is evidence that the method of oxidative cleavage can change the yield of 1,2,3-propanetricarboxylic acid and this acid cannot be regarded entirely as a primary oxidative product of polybutadiene.

In order to investigate the possible source of the 1,2,3-propanetricarboxylic acid, a model olefin, carefully purified 4-vinylcyclohexene (V), was ozonized and the resulting ozonide hydrolyzed with 10% hydrogen peroxide. This would be expected to yield only 1,2,4-butanetricarboxylic and formic acids by ozonolysis and oxidative cleavage. When a large scale chromatographic separation of the oxidative products was carried out (see Figure 12), a small amount of 1,2,3-propanetricarboxylic acid was isolated and identified conclusively by its melting point, mixture melting point, analysis, and neutral equivalent. This formation of 1,2,3-propanetricarboxylic acid from 4-vinylcyclohexene shows that during oxidative ozonolysis the allyl positions of such an olefin may be attacked.

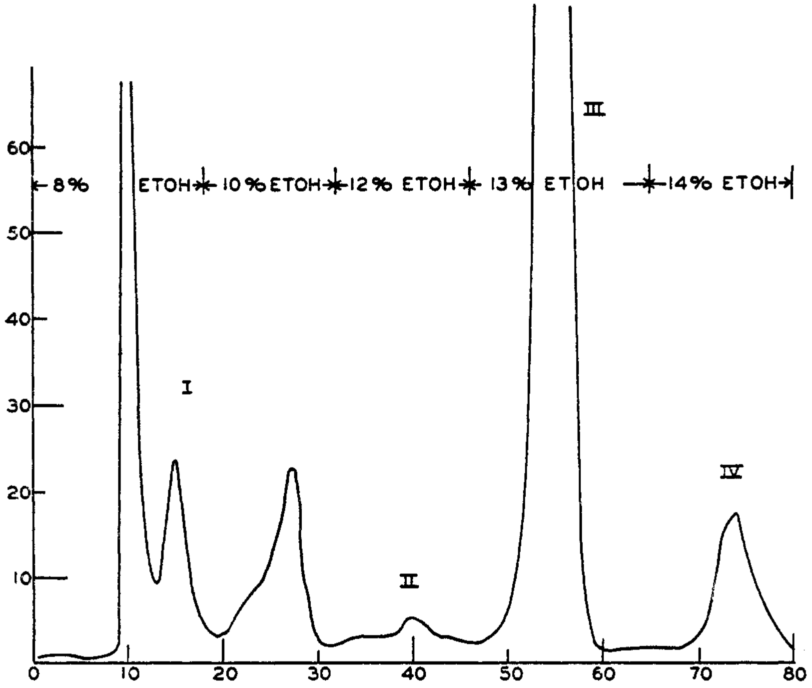
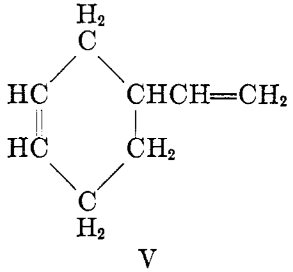


FIG. 12. VINYL CYCLOHEXENE LARGE SCALE SEPARATION



V

Thus it appears that the 1,2,3-propanetricarboxylic acid obtained from the degradation of the polymer can be a secondary product; however, this does not eliminate entirely the possibility of branching occurring at the allylic position. That a portion of the 1,2,3-propanetricarboxylic acid found in the acid mixtures is from the unit (IV) postulated, is supported by the discovery that reoxidation of an acid mixture, resulting from mild hydrolysis of the ozonides, with silver oxide produced a small amount of 1,2,3-propanetricarboxylic acid (Table IV, last line).

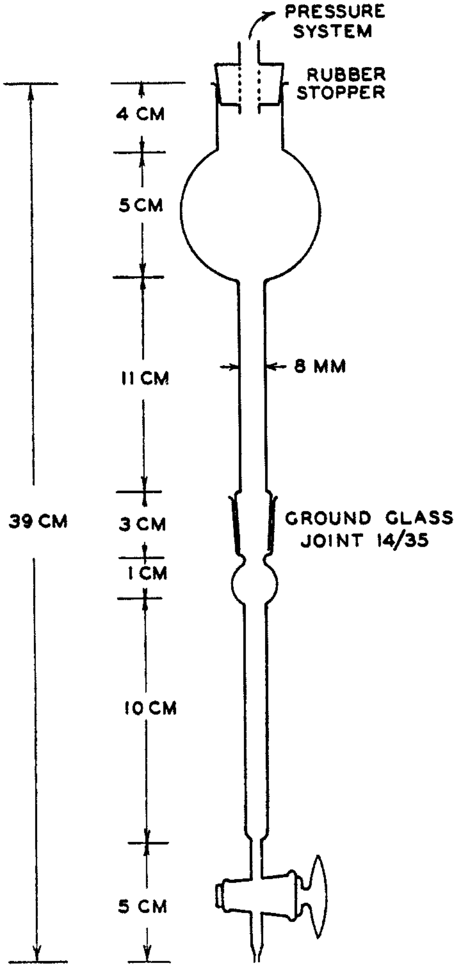


FIG. 13

Another interesting result of this study is that the ratio of succinic acid to 1,2,4-butanetricarboxylic acid obtained in the oxidative ozonolysis of GLSVES-3, a −10° GR-S sample, is 9.5. Under the same conditions of cleavage GLSVES-1, a 50° GR-S, gave a ratio of about 5.4. This is evidence for a greater amount of 1,4-addition of the butadiene units in the polymerization at the lower temperature. This is chemical evidence supporting the infrared results of Hart and Meyer (4).

In the chromatographic separations of the acids obtained by the hydrogen peroxide hydrolysis of all the ozonides studied in this series, a large amount of acidic material which was not completely oxidized was isolated. The examination of these products and the identification of these unexpected constituents is to be considered separately.

EXPERIMENTAL

Purification of polymers to be ozonized. Ten grams of polymer was dissolved in 750 ml. of benzene. The solution was poured slowly with vigorous stirring into 1500 ml. of 0.2% ethanolic phenyl-β-naphthylamine. This was repeated two times and after the third precipitation the polymer was broken into small pieces and dried under a vacuum of less than 10 mm. overnight.

Polymers of high gel content were swollen in benzene, dispersed in the solvent in a Waring blender, precipitated and dried as above.

Ozonization. Three grams of dry, purified polymer was dissolved in 750 ml. of chloroform, cooled to −5° to 0° in an ice-salt mixture, and a stream of oxygen containing 2% ozone was passed through the solution until the exit gas turned two successive 20-ml. portions of 5% potassium iodide red in color. The average time of ozonization was approximately three hours. To assure complete ozonization the chloroform suspensions of polymers of high gel content were ozonized six hours.

Oxidative decomposition of ozonides. After removal of the chloroform at room temperature under a vacuum, the ozonides were decomposed by one of the following methods:

Method A: To the ozonides was added 67 ml. of 3% hydrogen peroxide and the mixture was boiled gently under reflux for three hours.

Method B: To the ozonides was added 67 ml. of 3% hydrogen peroxide, the mixture was heated at 60° under reflux for three hours, and finally at 100° for 30 minutes.

Method C: To the ozonides was added 67 ml. of 3% hydrogen peroxide and the mixture was boiled gently under reflux for eight hours.

Method D: To the ozonides was added 75 ml. of 10% hydrogen peroxide and the mixture was boiled gently under reflux for five hours.

Method E: To the ozonides was added 60 ml. of 6% hydrogen peroxide. The mixture was heated slowly to 60° over a period of several hours and then rapidly to 100°. The heat source was removed when the temperature reached 100°.

Polymer	Ozonides Decomposed by
H14R5D4, H778 GLSVES-1, GLSVES-3	Method A
Firestone 1044 series	Method B
Firestone 1044 series	Method C
B 318	Method D
S 1	Method E

After cooling the solution, the excess hydrogen peroxide was decomposed by adding 50 mg. of Adam's platinum oxide catalyst (3) and finally warming at 100° for one hour. The acid mixture from butadiene-styrene copolymers was extracted with 75 ml. of chloroform. The platinum oxide was removed by filtration and the solution evaporated to dryness at 30–35° under a vacuum of less than 5 mm. The resulting acids were diluted with distilled water to a solids content of 100 mg. per milliliter and separated chromatographically.

Small standard column. Into a 50-ml. beaker was weighed 2.1 g. of silicic acid. (Mallinckrodt's Analytical Reagent, 100 mesh, for chromatography) and 1.1 ml. of distilled water was added dropwise, with stirring. The mixture was thoroughly ground against the sides of the beaker with a thick glass rod. Technical grade chloroform (10 ml.) was added in 1-ml. portions and thoroughly mixed after each addition. The resulting slurry was poured into the lower half of the apparatus illustrated in Figure 13 and the excess chloroform was forced out by applying a few centimeters of air pressure, until the material at the top of the column was firm but not cracked. If the latter event occurred, a new column was prepared.

Then 0.35 ml. of the aqueous acid solution was thoroughly mixed with 300 mg. of silicic acid in a 5-ml. beaker and packed uniformly on top of the column of silicic acid. The apparatus was assembled, the ground-glass joint first having been greased with silicone grease, and development started. The solutions were forced through the column under a pressure of approximately 450 mm. of mercury.

Two sets of developing solutions were used.

	SET A Weight per cent
50 ml.	100% $CHCl_3$
50 ml.	95% $CHCl_3$ + 5% *n*-BuOH[a]
100 ml.	90% $CHCl_3$ + 10% *n*-BuOH
50 ml.	85% $CHCl_3$ + 15% *n*-BuOH

	SET B Weight per cent
35 ml.	100% $CHCl_3$
35 ml.	98% $CHCl_3$ + 2% *n*-BuOH[a]
35 ml.	96% $CHCl_3$ + 4% *n*-BuOH
35 ml.	94% $CHCl_3$ + 6% *n*-BuOH
35 ml.	93% $CHCl_3$ + 7% *n*-BuOH
35 ml.	92% $CHCl_3$ + 8% *n*-BuOH
35 ml.	91% $CHCl_3$ + 9% *n*-BuOH
35 ml.	90% $CHCl_3$ + 10% *n*-BuOH

[a] The butanol was saturated with water at room temperature.

The eluant was collected in 3.5-ml. portions and titrated with dilute methanolic potassium hydroxide (0.005 *N*) using Bromthymol Blue as indicator. The amount of base consumed for each fraction was plotted against the number of the fraction and the curves, called chromatograms, were obtained. The figures at the top of the chromatograms indicate the amount of butanol and chloroform used to elute the acids.

The water-soluble acid mixtures from each of the polymers listed were examined. The acid mixtures from the Firestone 1044 series were separated using the developing solutions listed in Set B. The other acid mixtures were examined using Set A.

Since a small amount of 1,2,3-propanetricarboxylic acid had been indicated on the small column examination of the acids from the 50° polybutadiene of 95% conversion, it was decided to examine this mixture on a larger column prepared from 20 g. of silicic acid according to the directions of Marvel and Rands (1). The results of this separation are presented in Figure 1.

Isolation of 1,2,3-propanetricarboxylic acid from the 50° polybutadiene of 95% conversion. A slurry of 426 g. of silicic acid, 170 ml. of water, 28 ml. of glycerol (omitted in later experiments), and 1400 ml. of chloroform was added to a large column. The excess chloroform was removed by gravity, and a column of silicic acid 6.5 cm. in diameter and 25 cm. in height remained. To the surface of the column was added a solution of 3.0 g. of the acids from the gelled 50° polybutadiene in 10 ml. of ethanol. The following amounts of chloroform-ethanol developing solution were forced through the column and collected in 100-ml. portions.

ML. OF SOLVENT	PER CENT ETHANOL BY VOLUME
800	0
1600	5
2400	10
950	15
1400	20
2000	25

Aliquots of 5 ml. each were titrated. The results showed that 40 mg. of 1,2,3-propanetricarboxylic acid was present in the original 3-g. sample.

The portions containing the 1,2,3-propanetricarboxylic acid were combined and the solvent removed in a current of filtered air. The clear, viscous residue was dissolved in 10 ml. of water and passed through a column of freshly regenerated IR-4B anion exchange resin (5).

Water was flushed through the column to remove the glycerol. Excess 4% ammonium hydroxide was then percolated through the column and the eluant was concentrated *in vacuo*. The residual solution was passed through a column of IR-100 cation exchange resin (5) and an aqueous solution of the free acid was obtained. Evaporation yielded a small amount of solid material which was recrystallized with difficulty from dioxane.

The recrystallized acid had a melting point range of 153–155.5° on a micro-melting point apparatus. An authentic sample of 1,2,3-propanetricarboxylic acid melted from 157–158° on this same apparatus. A mixture melted from 153–158°.

Anal. Calc'd for $C_6H_8O_6$: C, 40.91; H, 4.58.
Found: C, 40.36; H, 4.48.

Ozonization of 4-vinylcyclohexene. 4-Vinylcyclohexene (15 ml.) fractionated through a Podbielniak column (b.p. 128.9° at 760 mm.; n_D^{20} 1.4652), in 350 ml. of chloroform was ozonized at 0° for 8½ hours with a stream of oxygen containing 2% ozone. The chloroform was removed under a vacuum at room temperature and the resulting ozonide treated with 350 ml. of 10% hydrogen peroxide. The mixture was held at room temperature for two hours and then slowly was brought to the boiling point. Boiling under reflux was continued for five hours. The excess hydrogen peroxide was decomposed with Adams's catalyst as before. Removal of the water at 40° under a vacuum left 18 g. of a brown, viscous oil.

The above oil (4 g.) was dissolved in 15 ml. of distilled water and thoroughly mixed with 30 g. of silicic acid. This was made into a slurry with 200 ml. of chloroform and placed on the surface of a column (6.5 cm. in diameter) prepared from 426 g. silicic acid, 200 ml. of water, and 1800 ml. of chloroform.

Development of the column was accomplished with the following distilled solvents:

2650 ml. of 92% $CHCl_3$— 8% C_2H_5OH[a]
2000 ml. of 90% $CHCl_3$—10% C_2H_5OH
2000 ml. of 88% $CHCl_3$—12% C_2H_5OH
2600 ml. of 87% $CHCl_3$—13% C_2H_5OH
2000 ml. of 86% $CHCl_3$—14% C_2H_5OH

[a] Per cent by volume.

and 125-ml. portions were collected. Aliquots of 5 ml. each were titrated (See Figure 12). Those portions corresponding to peak IV were combined, the solvent removed with a stream of filtered air, and the residue, a light tan solid, was dissolved in 15 ml. of water. The aqueous solution was boiled for a few minutes with decolorizing charcoal, filtered, and evaporated to dryness. The white residue was recrystallized four times from acetone-chloroform, m.p. 156.5–158°. The melting point of an authentic sample of 1,2,3-propanetricarboxylic acid on our apparatus was 157–158°. A mixture melting point showed no depression.

Anal. Calc'd for $C_6H_8O_6$: C, 40.91; H, 4.58; N.E., 58.7.
Found: C, 40.46; H, 4.58; N.E., 60.0.

Reoxidation with 6% hydrogen peroxide. To a measured quantity of solution, obtained after hydrolysis by Method B, enough 30% hydrogen peroxide was added to make the final concentration of hydrogen peroxide 6%. The mixture was boiled gently under reflux for the specified length of time. The solution was then treated in the same manner as those obtained directly from the ozonides.

Silver oxide reoxidation. A sample of 1.1 g. of freshly precipitated, moist silver oxide was added to 10.0 ml. of the solution from the 20.5% conversion rubber (Firestone 1044 series) resulting from decomposition of the ozonides by Method B. This mixture was shaken for 24 hours, filtered into a weighed flask, the residue of silver salts washed with hydrochloric acid and water, and the filtrate evaporated to dryness. The dark residue was dissolved and examined on the small standard column.

Sodium dichromate reoxidation. To 1.0 ml. of the solution from the 20.5% conversion rubber (Firestone 1044 series), resulting from oxidative hydrolysis by Method B, was added three drops of 1.7 *N* sodium dichromate. This was allowed to stand for one day and then examined on the small standard column.

Periodic acid reoxidation. Periodic acid (0.45 g.) was dissolved in 2.0 ml. of the solution obtained from the 20.5% conversion (Firestone 1044 series) rubber resulting from oxidative hydrolysis by Method B and the whole was allowed to stand for one hour. A concentrated solution of silver nitrate was added dropwise until one drop in excess caused no further precipitation. The precipitate was removed and the filtrate was examined directly on the small column.

Iodic acid reoxidation. To 5.0 ml. of solution (0.5 g. of solids), obtained from oxidative hydrolysis by Methods B or D, in a 500-ml. flask was added 250 ml. of iodic acid (5% potassium iodate in 40% sulfuric acid). The solution was heated under reflux to 100°. When the temperature reached 85° iodine began to form. Heating was continued for one hour. The mixture was steam-distilled until iodine could no longer be removed. To the cooled solution enough sodium bicarbonate (50 g.) was added to incompletely neutralize the sulfuric acid On standing, iodine was slowly liberated. This solution was then extracted with ether in a continuous liquid-liquid extraction apparatus for two days. The ether extract was dried over sodium sulfate. Evaporation to dryness left 0.19 g. of a dark residue which consisted mostly of iodine.

Attempts to convert 1,2,4-butanetricarboxylic acid to 1,2,3-propanetricarboxylic acid. Samples of carefully purified 1,2,4-butanetricarboxylic acid were boiled under refluxing conditions with 1%, 3%, and 10% hydrogen peroxide solution under the general conditions used for the oxidative cleavage of the polybutadiene ozonides. The excess hydrogen peroxide was destroyed with platinum oxide and the aqueous solutions were examined in the standard chromatographic procedure. No indications could be found that 1,2,3-propanetricarboxylic acid was present in any one of these experiments.

SUMMARY

The ozonolysis of emulsion polybutadiene followed by oxidative hydrolysis of the ozonide with hydrogen peroxide has given 1,2,3-propanetricarboxylic acid as one of the cleavage products. This is an indication that branching may occur at the allyl position in polybutadiene. The evidence is not conclusive since the amount of 1,2,3-propanetricarboxylic acid produced from a given polymer is dependent on the exact method of oxidative hydrolysis. While under mild conditions a highly gelled polybutadiene will give more 1,2,3-propanetricarboxylic acid than does a soluble polymer, changes in the methods of oxidative hydrolysis may reverse this situation.

It has also been found possible to produce 1,2,3-propanetricarboxylic acid by ozonolysis and oxidative cleavage of vinylcyclohexene although it has not been possible to degrade 1,2,4-butanetricarboxylic acid to 1,2,3-propanetricarboxylic acid by treatment with ozone and hydrogen peroxide.

By comparing the yields of succinic acid and 1,2,4-butanetricarboxylic acid which are produced by ozonolysis of polybutadienes of different conversions, it seems evident that more 1,4 addition than 1,2 addition occurs in the early stage of polymerization than is the case at about 60% conversion. There is also confirmatory evidence in this ratio of acids that polybutadiene formed at low

temperature contains a higher ratio of 1,4 to 1,2-butadiene units than occurs in 50° polybutadiene.

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