Stability of Butadiene

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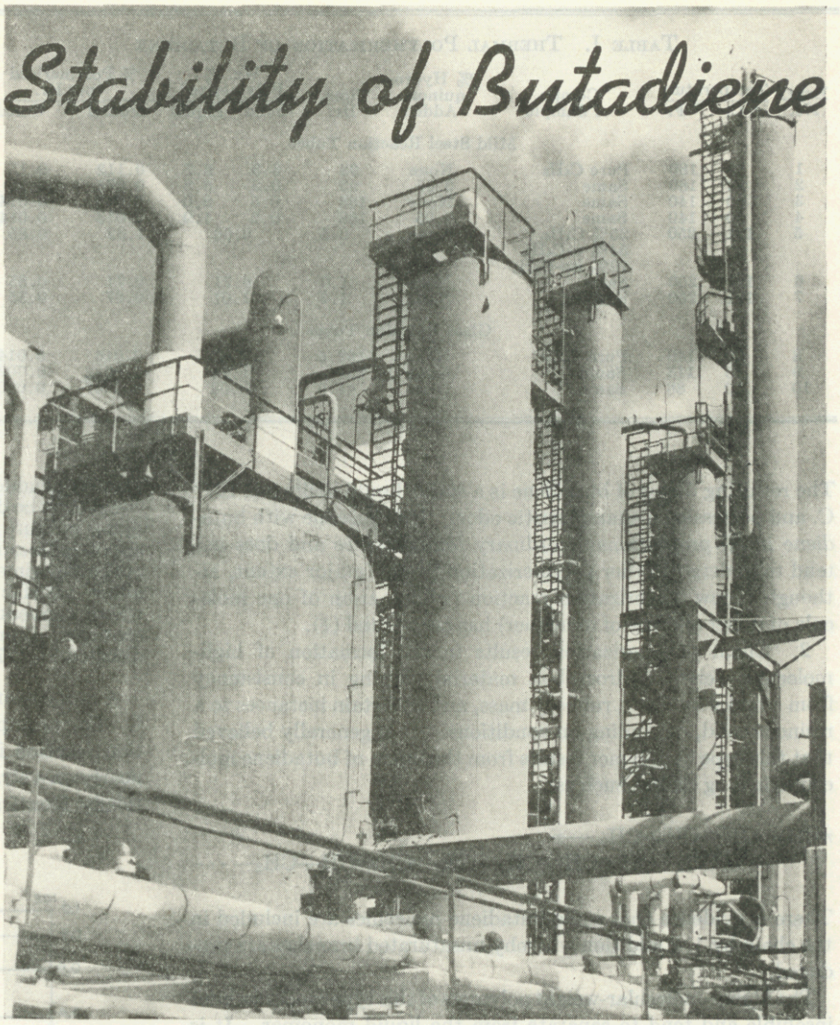


Reactions which butadiene undergoes during storage and plant processing have been studied. The two reactions of most interest are as follows: (1) dimerization by a Diels-Alder type condensation, and (2) polymerization to plastic materials of high molecular weight. The first reaction is bimolecular and homogeneous in the liquid phase under a variety of conditions. Bimolecular reaction rate constants have been determined for a range of temperatures and compared with the constants for the gas phase reaction. The magnitudes of these constants are quite close. The formation of higher-molecular-weight polymers is peroxide-catalyzed. For a number of peroxide catalysts the rate of polymerization to plastic substances is proportional to the square root of the peroxide concentration. Data on the rate of peroxidation of butadiene are also given.

THE urgency for the expansion of synthetic rubber production involves a number of problems, not the least of which are the storage and handling of the hydrocarbon raw materials. Although butadiene possesses a certain degree of instability, the goal of this investigation was to obtain more detailed insight into the chemical reactions occurring during storage and handling. This information will permit a more intelligent selection of the conditions under which the diolefin can be handled or stored safely and with a minimum loss of valuable material.

From a broad point of view, butadiene can be considered unstable from two aspects: (*a*) With respect to its elements; that is, butadiene reverts to its elements, carbon and hydrogen, under an effective impulse and appropriate conditions, and results in the evolution of considerable heat:

$$C_4H_6 \longrightarrow 4C + 3H_2 + \text{approx. } 27{,}000 \text{ cal.}$$

At least one report (*4*) states that this reversion apparently took place under high hydrostatic pressure.

(*b*) Polymers are also formed with the evolution of heat:

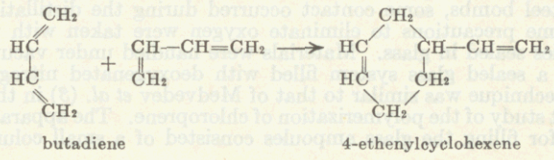
$$nC_4H_6 \longrightarrow (C_4H_6)_n + \text{approx. } n\ 19{,}000 \text{ cal.}$$

Thus the lower conjugated dienes, in general, can be considered as compounds existing at a high level of chemical energy with a tendency to drop to lower levels, on the one hand, by decomposition to elements and, on the other, by polymerization. Under conditions affording poor dissipation of heat, these reactions can produce high localized temperatures and thus spontaneously proceed with extreme rapidity, since they have positive temperature coefficients.

Another type of instability results when the diolefin reacts with other available substances, such as oxygen of the air, to form peroxides which are per se unstable. However, polymerization is the most important degradation reaction likely to be encountered in storage and handling, and hence considerable emphasis is placed on it in this discussion.

For years it has been known that butadiene and homologous conjugated diolefins undergo spontaneous polymerization to liquid polymers even at ordinary temperatures. Higher temperatures are known to result in the formation of relatively larger quantities of the polymer. Occasionally the formation of plastic rubbery polymers has been noted. In the latter cases some substances known to act as polymerization catalyst—e.g., peroxides or active metal—were generally known to be present. It has thus become clear in recent times that butadiene is capable of at least two types of polymerization which may occur separately or concurrently depending on conditions:

1. Cyclic polymerization or thermal dimerization results when two molecules of butadiene unite to form a ring type compound by Diels-Alder condensation:



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A portion of the first full-scale butene dehydrogenation plant for the manufacture of butadiene is shown above. To the left is one of the reactors through which butene-rich gases are passed for contact with a dehydrogenation catalyst.

Table I. Thermal Polymerization of Butadiene

Expt. No.	Temperature ° C.	Temperature ° F.	Compn. of Sample	% Hydroquinone Added	Time, Hr.	Wt. % Polymerized Solid	Wt. % Polymerized Liquid	% Polymerized per Hr. Found	% Polymerized per Hr. Calcd.
Mild Steel Reaction Tubes									
1	82	180	Pure C_4H_6	None	93	3.8	6.7	0.112	0.15
2	82	180	Same	0.05	93	0.2	6.8	0.075	0.15
3	60	140	Same	None	168	0.5	2.0	0.015	0.014
4	60	140	Same	0.05	168	0.2	1.9	0.013	0.014
5	121	250	25% C_4H_6, 54% n-C_4H_8, 19% iso-C_4H_8	None	0.5	0.66		1.32	0.85
6	121	250	Same	None	1.0	0.71		0.71	0.85
7	121	250	Same	None	1.5	1.01		0.67	0.85
Glass Reaction Tubes									
8	60	140	Pure C_4H_6	None	162.5	2.43		0.016	0.014
9	45	113	Same	None	790	1.72		0.0022	0.0025
10	30	86	Same	None	41.5	0.03		0.0007	0.0004

The resulting dimer of butadiene is a stable liquid boiling at 127° C. and possessing a characteristic odor. It is miscible with butadiene in all proportions at ordinary temperatures and does not tend to undergo further polymerization to any major extent, although a slow trimerization reaction (combination of one molecule of dimer and one of monomer) has been noted (*1*).

2. Chain polymerization results in the formation of high-molecular-weight hydrocarbon material varying in consistency from a tacky fluid to a rubbery mass, and in certain instances to a resinous solid, depending on conditions. It is generally believed that this type of polymer results from the union of butadiene molecules in long chains, such as:

$$nCH_2{=}CH{-}CH{=}CH_2 \longrightarrow$$
$$\cdots{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}\cdots$$

There is evidence that some butadiene molecules are included in the chain by 1, 2 addition whereby unsaturated branches are produced.

The higher-molecular-weight polymers of this type are sometimes insoluble and tend to separate from the liquid monomer. It is believed that resinous properties and insolubility result from cross linking between polymer chains.

In the present investigation an endeavor was made to study these two types of polymerization independently and to determine the effects of variables, such as temperature, catalysts, extent of surface, and type of surface.

THERMAL POLYMERIZATION

The rate of conversion of butadiene and other conjugated dienes to their respective dimers was studied in the gas phase by Kistiakowsky and co-workers (*1*). A brief study of the rate in the liquid phase was made by Lebedev *et al.* (*2*), but only at somewhat elevated temperatures. No systematic investigation under commercial storage, handling, and distillation conditions has been made to the authors' knowledge.

Several experiments were carried out in which liquid butadiene was sealed in tubes of steel or glass and maintained at a given temperature for a known length of time. Ultimately the tubes were opened and analyzed for the presence of polymer. The results of some of these experiments are presented in Table I.

The tests in steel bombs were made on freshly distilled (in a fifty-plate Stedman column), 97–99 per cent pure diolefin derived from the cracking of petroleum. The main impurity was 1-butene. The α-acetylene content was not more than 0.05–0.1 per cent. Although care was taken to exclude air while filling the steel bombs, some contact occurred during the distillation. Extreme precautions to eliminate oxygen were taken with the samples sealed in glass. Materials were handled under vacuum or in a sealed glass system filled with deoxygenated nitrogen. The technique was similar to that of Medvedev *et al.* (*3*) in their recent study of the polymerization of chloroprene. The apparatus used for filling the glass ampoules consisted of a small column from which a sample in contact with pyrogallol was distilled into a flask connected to a reflux condenser. Here the sample was allowed to reflux for about 30 minutes before it was drawn into the evacuated ampoule. The sample was then frozen with liquid nitrogen and the ampoule sealed with a torch. The sealed ampoule was placed in a constant-temperature bath for a definite time.

Polymer was determined in the sample, after removal from the bath, by opening the ampoule, allowing the unreacted butadiene to boil off under room conditions, and weighing the polymer left behind. In some cases precipitated solid polymer was separated first. To make certain that no dimer was carried over with the vapors, the butadiene was recondensed and distilled in a small fractionating column in the presence of a small amount of added isooctane to act as carrier. The amount of dimer could then be determined by the refractive index of the isooctane-dimer mixture left as the residue in the fractionating column. No appreciable amount of dimer was found in this portion. In most of the experiments dimer was produced in too small a quantity to allow satisfactory characterization. However, in experiments where conversion was permitted to proceed to considerable percentages, a product was formed at least 95 per cent of which distilled at 127° C.

A number of important conclusions can be drawn from Table I. For example, the temperature coefficient of the polymerization reaction is quite high (Figure 1). The plotted points fall nearly on a straight line, and the lower portion of this line is practically identical with a calculated curve. This curve was ob-

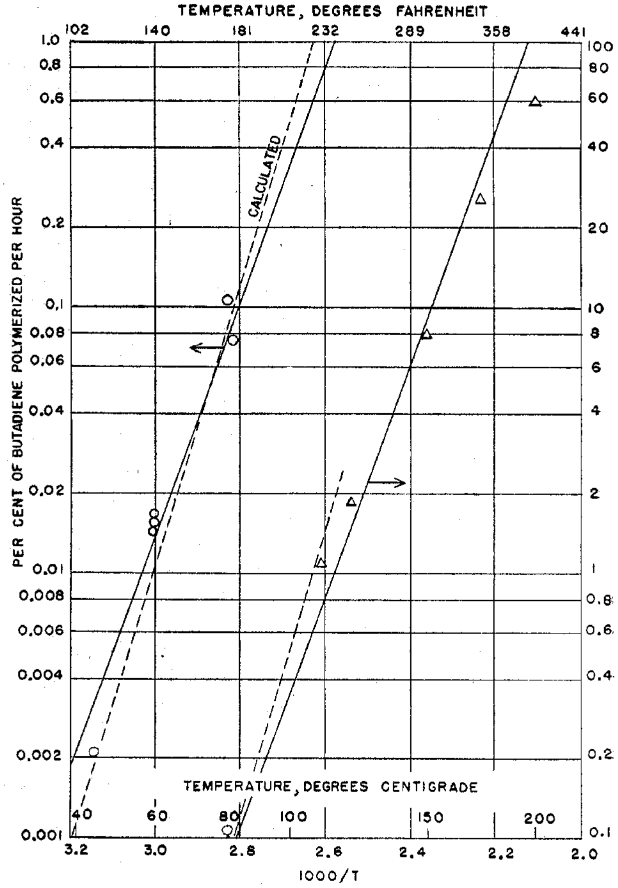

Figure 1. Rate of Dimerization of Pure Butadiene in Liquid Phase as a Function of Temperature

○ = this investigation; △ = Lebedev *et al.* (2)

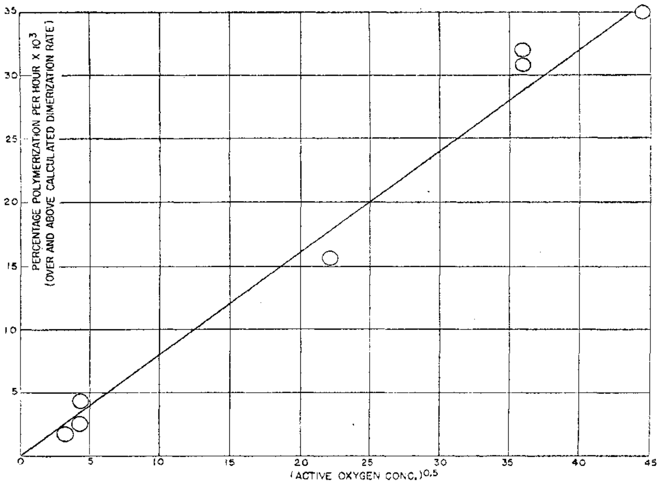

Figure 2. Rate of Formation of High-Molecular-Weight Polymer in Pure Butadiene as a Function of Active Oxygen Concentration at 45° C.

tained by substituting liquid-phase concentration in the equation of Kistiakowsky *et al.* (*1*) for the vapor-phase dimerization reaction. The dimerization of butadiene in the vapor phase is a rather clean-cut bimolecular reaction, the rate of which can be expressed by the equation:

$$\text{rate (moles cc.}^{-1}\text{ sec.}^{-1}) = 9.20 \times 10^9 \exp.\ (-23{,}690/RT)\ [C_4H_6]^2$$

Barring the first run in Table I, the amount of solid polymer produced was insignificant, and the remarkable agreement between the observed rates of dimerization (liquid polymer formation) and those calculated by substitution of liquid-phase concentrations in the equation can be seen in the last two columns. The calculated rates of dimerization in the vapor phase under these conditions are negligible.

Deviation of the experimental data from the calculated curve in Figure 1 is greater at higher temperatures. This is probably due to the greater conversions to which the reactions were permitted to proceed in Lebedev's work. Adherence to a linear plot of log rate against $1/T$ in Figure 1 would be expected only when the concentration of monomer remains virtually constant. Deviation is therefore observed as appreciable amounts of polymer product dilute the monomer.

A further point of interest is that the data for runs in various types of vessels fall on the same curve, indicating that the types of surface studied have no pronounced catalytic influence on the dimerization reaction.

TABLE II. POLYMERIZATION OF BUTADIENE IN PRESENCE OF PEROXIDES[a]

Expt. No.	Temperature ° C.	° F.	Peroxide Added	Active O, P.P.M.	Time, Hrs.	Wt. % Polymerized	% Polymerized per Hr.
10	30	86	None	0	41.5	0.03	0.0007
11			Benzoyl	13	19.5	0.015	0.0008
12			Benzoyl	330	19.5	0.11	0.0056
13			Benzoyl	1275	20.5	0.10	0.0049
9	45	113	None	0	790	1.72	0.0022
14			Benzoyl	13	24	0.118	0.0049
15			Benzoyl	13	788	4.38	0.0055
16			Tetralin	20	788	5.29	0.0067
17			Benzoyl	500	24	0.432	0.0180
18			Benzoyl	1275	24	0.81	0.034
19			Benzoyl	1290	783	26.98	0.0342
20			Tetralin	2000	788	30.0	0.0381
8	60	140	None	0	162.5	2.43	0.016
21			Benzoyl	13	162.5	4.89	0.030
22			Tetralin	20	162.5	4.21	0.026
23			Benzoyl	1155	162.5	34.49	0.212
24			Tetralin	2000	162.5	25.52	0.157
25			Benzoyl[b]	1290	162.5	8.32	0.0512
26			Tetralin[b]	2000	162.5	26.83	0.165
27			Benzoyl[c]	1290	162.5	10.68	0.0657
28			Tetralin[c]	2000	162.5	27.91	0.172
29	45	113	Peroxidation by air	49[d]	720	2.70	0.0038
30			Same	193[d]	720	5.75	0.0079
31	60	140	Same	60[d]	264	6.4	0.024
32			Same	171[d]	264	8.1	0.031

[a] 98–99% butadiene in sealed glass tubes.
[b] In presence of steel strips.
[c] In presence of glass beads.
[d] Determined by the ferrous thiocyanate colorimetric method (*5*).

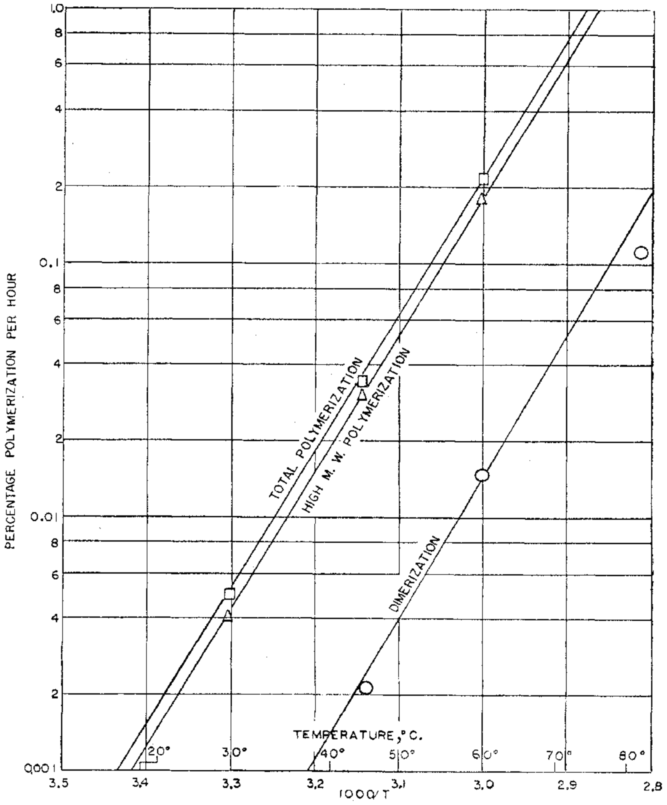

Figure 3. Rates of Conversion of Pure Butadiene to Dimer and to Chain Polymer as a Function of Temperature

(1200 p.p.m. active oxygen present)

Actually, the dimerization reaction was not the only type of polymerization in some of the runs. In experiments 1 to 4 (Table I) various amounts of a solid (rubbery) polymer were also obtained. However, the separation between the solid and liquid could not be made strictly quantitative because of the gel-like form of the solid; consequently the apparent proportion of solid polymer is probably somewhat high. In experiments 1 and 3, and 2 and 4, tests were made both in the absence and in the presence of the antioxidant, hydroquinone, at two different temperatures. Butadiene from the same distillation was used in these comparisons. Even casual inspection of the resulting data reveals that the presence of the antioxidant inhibits the formation of plastic polymer but has no appreciable effect on the rate of formation of dimer. In fact, so far as the authors know, no way has as yet been found for minimizing the dimerization reaction in concentrated butadiene other than the use of the lowest practical storage and handling temperatures.

It is not possible to state definitely at this time that the truly thermal reaction does not give rise to some plastic polymer, although it is certain that such material is produced only in very small amounts. This uncertainty is due to the difficulty in experimentally removing the last traces of peroxides from a test sample and hence in completely eliminating the second type of reaction discussed below.

POLYMERIZATION IN PRESENCE OF PEROXIDES

The second type of polymerization reaction occurring in butadiene is purely peroxide-catalyzed and is superimposed additively on the thermal reaction. The peroxide-catalyzed reaction produces largely the high-molecular-weight plastic type of polymer. Results so far available do not exclude the possibility of some dimer-like polymers also being formed in the peroxide-catalyzed reaction. Peroxide catalysts of different types were studied—benzoyl peroxide, Tetralin peroxide, and peroxidized butadiene.

The results of these experiments are summarized in Table II. It is apparent that the presence of peroxide does increase the rate of polymerization of butadiene at each of the temperature levels studied. Also, with the exception of experiments 25 to 28 which will be discussed later, there is no notable difference in the effects of benzoyl peroxide and Tetralin peroxide at 45° C. although a slight difference may exist at 60° C. Experiments 29 to 32, inclusive, made with the peroxide formed in butadiene on contact with air, showed considerably less activity.

The data in Table II indicate that the rate of formation of plastic polymer is very sensitive to small amounts of active oxygen (one active oxygen atom per molecule of peroxide), but the effect becomes less pronounced as the concentration is increased. More particularly it appears that the rate of formation of high-molecular-weight polymers varies directly as the square root of the concentration of active oxygen. This is shown by a plot of the data at 45° C. in Figure 2. The square root relation has been noted in many other polymerization reactions catalyzed by peroxides. This effect is in accord with the free radical concept of polymerization catalysis.

The polymer (including dimer) in all experiments was soluble in the monomer, with the possible exception of the runs in which no peroxide was added; in these some precipitation was observed.

Runs 25–28 (Table II) were made in the presence of peroxides and increased surface; in runs 25 and 26 several pieces of mild steel were present, and in runs 27 and 28 glass beads were added. This increase of surface had no effect on the rate of polymerization in the presence of Tetralin peroxide, but the rate in the presence of benzoyl peroxide was decreased about 80 per cent. This may be due to deactivation or recombination of free radicals on the surface.

The effect of temperature on the rate of polymerization of butadiene in the presence of peroxides is shown by the conventional plot in Figure 3. The curve for the rate of dimerization in Figure 1 is shown along with the curves for the rate of polymerization to high-molecular-weight polymer in the presence of 1200 p.p.m. of active oxygen and also total polymerization (dimer plus high-molecular-weight polymer). It can be seen that in the presence of this concentration of active oxygen the dimerization reaction furnishes only about 10 per cent of the total polymer. The fact that all the curves have nearly the same slope indicates that the energies of activation of chain and cyclic polymerization of butadiene are practically identical.

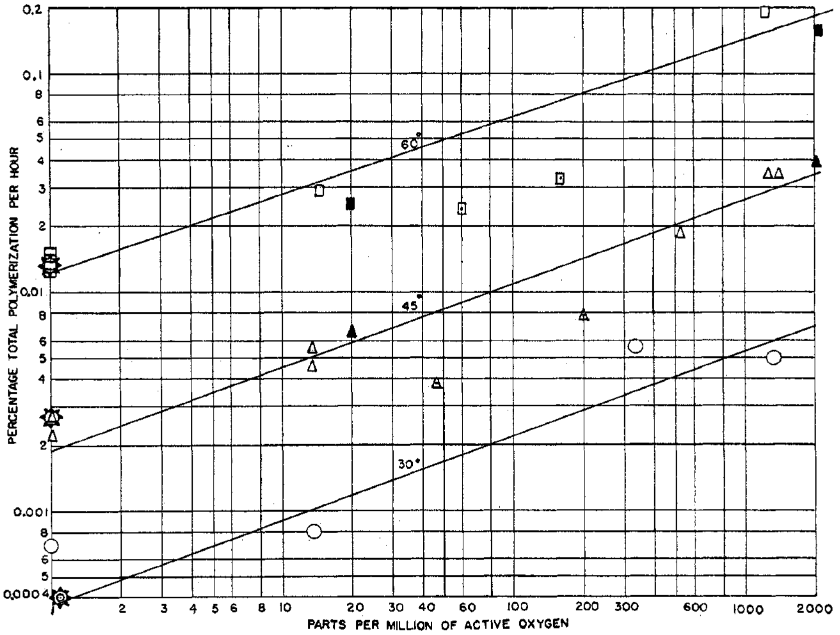

Figure 4. Rate of Polymerization of Pure Butadiene as a Function of Active Oxygen Concentration at Various Temperatures

□, △, ○ = benzoyl peroxide; ■, ▲ = Tetralin peroxide; ⊡, ◬ = butadiene peroxide. Starred points at extreme left are calculated from dimerization rate equation.

A complete summary of the data obtained is presented in conveniently usable form in Figure 4. The data obtained in the absence of any significant amount of peroxides are plotted along the ordinate at 1 p.p.m. active oxygen, and they appear to fall quite well on the extrapolated curves for each temperature. Plotting these data at 1 p.p.m. may be justified on the grounds that this is about the minimum concentration which can be maintained with certainty in butadiene, even with the most careful technique.

The data of runs 2 and 4 (Table I) demonstrate that the peroxide-catalyzed reaction can be effectively subdued by the proper use of polymerization inhibitors. It should be emphasized, however, that no inhibitor can be expected to last indefinitely. For this reason, the periodic checking of the inhibitor content of stored butadiene appears desirable, especially under conditions affording exposure to air.

PEROXIDATION OF BUTADIENE

Since it has been shown that the presence of peroxides has considerable influence on the rate of polymerization, it is important to know whether butadiene will peroxidize in contact with oxygen, air, or other oxidizing substances. This has been answered in the affirmative.

Experiments were made in which freshly distilled butadiene was kept saturated with air at room temperature and at 50° C. under pressure. These showed active oxygen concentrations of 120 and 460 p.p.m. after 48 and 24 hours, respectively. When 25 ml. of the peroxidized butadiene obtained at the end of the room temperature run were permitted to evaporate to dryness under room conditions, 0.11 gram of an oily substance, having a sharp aldehydic odor and an active oxygen content of 18,000 p.p.m., remained as residue.

Compounds, such as hydroquinone, pyrogallol, catechol, etc., are quite effective as inhibitors of the peroxidation of the diene. For example, 300 cc. of butadiene containing 0.1 weight per cent of hydroquinone completely resists the peroxidizing action of a stream of air, at room temperature and 50 pounds per square inch pressure, for more than 120 hours.

INSTABILITY IN DISTILLATION

From the foregoing the extent of polymerization at the elevated temperatures of distillation can be predicted with considerable certainty. However, a more hazardous form of instability may be encountered. As pointed out above, there is a tendency for peroxides to accumulate as "bottoms". Distillation in batch to low bottoms, for example, may result in active oxygen concentrations in the residue so high that further heating produces an explosive autoxidation. The danger involved in distilling peroxidized butadiene to very low bottoms is emphasized by the following experiment: The peroxidized butadine produced in the 50° C. test was permitted to evaporate under room conditions. After all of the liquid hydrocarbon had disappeared from the flask and only a residue remained, the vessel was covered lightly and heated on a sand bath so that the temperature rose at the rate of 10° to 12° C. per minute. When 125° C. was reached, violent decomposition took place within the flask, the cover of the flask was displaced, and large volumes of white fumes were evolved. Further heating to 250° C. resulted only in the charring of the trace of residual material. Experience indicates that the explosion hazard may be eliminated by distilling in the presence of an adequate amount of peroxide-destroying substance and preventing air from returning to the distillation vessel after the heat is removed. In the case of batch distillation of butadiene-containing materials of high peroxide content, it is desirable that the peroxides be destroyed by the antioxidant before distillation is started. Since most peroxides require appreciable time for decomposition by antioxidants, the elimination can be conveniently effected by heating under pressure until the absence of peroxides is indicated by chemical test. In distillation the addition of a hydrocarbon boiling higher than butadiene is an added factor of safety since such a procedure limits the degree to which the peroxides can be concentrated during a single distillation.

SUMMARY

1. The most prominent polymerization of pure butadiene in the absence of peroxides is dimerization. This reaction is thermally activated and does not appear to be catalyzed by peroxides or by steel surfaces.

2. Butadiene is also capable of independent polymerization to high-molecular-weight polymer, but in the absence of peroxides this reaction is insignificant compared to dimerization. The effect of temperature on the rates of each of these reactions has been determined.

3. In the presence of appreciable amounts of peroxides, polymerization to high-molecular-weight polymer becomes prominent and is superimposed additively on the thermal dimerization reaction.

4. The addition of suitable antioxidant inhibits the formation of high-molecular-weight polymer but has no appreciable effect on the rate of dimer formation.

5. The rate of high-molecular-weight polymerization is directly proportional to the square root of the concentration of peroxides (active oxygen).

6. Butadiene is readily peroxidized by air, but this peroxidation may be inhibited for a time by the presence of antioxidants.

7. The peroxides are not readily volatile and tend to accumulate in the residue if the diene is evaporated or distilled away. Concentration beyond a certain point yields an unstable residue which may decompose with violence when heated. Precautions for distillation of such peroxidized material are given.

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Conductivity of Tread Stocks

NATURAL AND SYNTHETIC RUBBERS

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IN THE last few years many applications have been found for semiconducting rubber. In automobile and trolley bus tires, airplane landing gear tires, shoe soles for munition workers, etc., where it is desirable to dissipate annoying and hazardous accumulations of static electricity, semiconducting rubber has been found useful. Electrically conducting rubber stocks can be prepared by incorporating powdered graphite or other carbon pigments in the rubber formula. To obtain conductivity without sacrificing other desirable physical properties, black pigments prepared from either acetylene or natural gas have generally been used.

Recent investigations (*4*) in this laboratory have been directed toward discovering what fundamental properties of carbon blacks determine the electrical conductivity of rubber stocks. The results show that in a typical tread stock, conductivity depends primarily on crystal structure, particle size, and surface structure of the carbon black. Crystal structure and particle size are the more important properties; surface structure is less important.

Since crystal structure is probably similar for channel carbon blacks (*2*, *5*), the principal factor in determining conductivity in a series of channel blacks is particle size. Results included here show that this is true for natural rubber, reclaim, Buna S, Thiokol N, Neoprene GN, and Butyl (GR-I).

TEST METHODS

Resistance measurements were made on cured tensile sheets (approximately 6 × 6 × 0.075 inch) placed between circular brass electrodes (*4*). An apparatus (*3*) using the voltmeter-ammeter method of measuring resistance was employed (Figure 1). The upper electrode, *E*, is connected through ammeter *A* and battery *B* to the lower electrode, *C*. Rubber test sheet *T* is placed between the electrodes. To obtain good contact between the electrodes and test sheet, circles slightly larger in diameter than the upper electrode were painted on both sides of the test