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# **Synthetic Rubber from Alcohol**



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# **SYNTHETIC RUBBER FROM ALCOHOL**

**A SURVEY BASED ON THE  
RUSSIAN LITERATURE**

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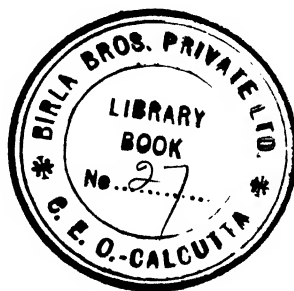
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February, 1945  
New Haven, Connecticut  
London, England\*

A. T.  
M. M.

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# I. THE LEBEDEV PROCESS

## A. CHEMISTRY OF THE PROCESS

Butadiene has been synthesized from alcohol by a number of processes and through a variety of intermediate stages. Most prominent among these is the aldol method, involving conversion of acetaldol to butylene glycol-2,3. In its original form the process consisted of four steps: (1) oxidation of ethanol to acetaldehyde; (2) condensation of aldehyde to aldol; (3) reduction of aldol to butylene glycol-2,3; and (4) dehydration of the glycol to butadiene-1,3.

Butylene glycol has more recently been produced directly from carbohydrate material by controlled fermentation,<sup>1</sup> with a resulting considerable reduction in the number of process steps.

A direct conversion of ethanol to a diene was first reported by Ipatieff<sup>2</sup> (1903) in the course of his classical study on the pyrolysis of alcohols. By passing ethanol vapors over finely divided aluminum at 580° to 680° C., he obtained fractional percentages of butadiene.

In 1915 Ostromislensky<sup>2a</sup> suggested a method of making butadiene by the catalytic action of aluminum oxide on a mixture of acetaldehyde and ethanol, in effect creating a two-stage process of converting ethanol to butadiene-1,3, considering that acetaldehyde is a simple oxidation product of ethanol. Ostromislensky's method proved, in itself, industrially unsuccessful. It became, however, the forerunner of the Carbide and Carbon process upon which the tremendous "butadiene-from-alcohol" program has largely been based in the United States.

The only direct method of converting ethanol to butadiene with a com-

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<sup>1</sup> See G. L. Stahly and C. H. Werkman, *Biochem. J.*, **36**, 575 (1942). L. M. Christensen, *India Rubber World*, **105**, 477 (1942). See also J. R. Callahan, *Chem. & Met. Eng.*, **51**, No. 11, 94 (1944).

<sup>2</sup> V. N. Ipatieff, *J. prakt. Chem.*, **2**, 67 (1903).

<sup>2a</sup> I. I. Ostromislensky, *Zhur. Russ. Fiz.-Khim. Obshchestva*, **47**, 1498 (1915).

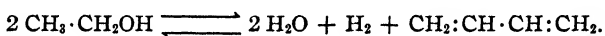
mercially satisfactory yield is the Lebedev process. It was first made known in a British patent<sup>3</sup> which claims:

"1. A process for producing diolefins, consisting in heating methyl, ethyl or propyl alcohols, or mixtures thereof, with a mixture, containing a catalyst capable of catalysing the removal of hydrogen, and a catalyst capable of catalysing the removal of water.

"2. A process for producing diolefins as claimed in claim 1 characterised by the use of reduced pressure and of rapid cooling of the reaction products.

"3. A process as claimed in claim 1 or 2 for producing butadiene, consisting in heating ethyl alcohol with a mixture of aluminium oxide and zinc oxide."

This information was later extended in a Russian patent<sup>4</sup> which claims a method of obtaining diolefins from alcohols, characterized by heating hydrous or anhydrous methyl, ethyl, propyl, or isopropyl alcohol or mixtures thereof, in the presence of a catalyst (such as uranium oxide) capable of simultaneously splitting off from the alcohols water and hydrogen, or of mixtures of catalysts splitting off water and splitting off hydrogen (*e. g.*, mixtures of hydrosilicates, or oxides of aluminum with oxides or salts of manganese, etc.). The process is based on the over-all reaction:



The theoretical yield of the reaction for every 100 parts of alcohol is: 58.7 parts butadiene, 2.2 parts hydrogen, and 39.1 parts water. The practical yield, however, falls short of the theoretical because of the formation of numerous by-products.

In evaluating the relative merits of the direct Lebedev process as against the stepwise formation of butadiene, *e. g.*, via butylene glycol, it must be realized that the one-step method has the advantage of simpler plant equipment, but does not at present yield as complete a conversion as can be obtained by the method in which a series of controlled intermediate steps can be applied. Consequently, the end product of the direct conversion is less pure<sup>4a</sup> and its yield may be lower; but the basic process is simpler technologically and requires less plant outlay. This was an important consideration at the time Russia's synthetic rubber industry was created, and is an equally important factor in wartime industrial planning.

<sup>3</sup> S. V. Lebedev, Brit. Pat. 331,482, issued June 30, 1930 (application, Jan. 30, 1929); French Pat. 665,917.

<sup>4</sup> S. V. Lebedev, Russian Pat. 24,393, issued Nov. 24, 1931.

<sup>4a</sup> The maximum purity of butadiene obtainable under the Lebedev process is about 35%, while a purity of 97% has been claimed for butadiene made by the Carbide and Carbon method.

Many of the problems encountered in converting alcohol to butadiene and in its subsequent purification are common to all the processes.

### 1. General Character of the Lebedev Process

The variety of by-products formed by the catalytic reaction is an indication of the complex nature of the process taking place at the binary catalyst. A study of the compounds formed, both in large and small quantities, may, therefore, lead to an understanding of the mechanism of the butadiene formation, for there can be little doubt that a common basic mechanism is responsible for all these substances. In support of this contention is the fact that most of the products can be arranged into groups of analogous structure, with 2, 4, 6, or 8 carbon atoms in the molecule.

The  $C_4$  group may serve as an example. It is represented by the compounds given in table I-1:

TABLE I-1  
COMPOUNDS WITH FOUR CARBON ATOMS FOUND IN THE PRODUCTS  
OF THE LEBEDEV CATALYSIS

Structure	Compound
$CH_3 \cdot CH : CH \cdot CH_3$ .....	Butene-2
$CH_2 : CH \cdot CH : CH_2$ .....	Butadiene-1,3
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$ .....	<i>n</i> -Butanol
$CH_3 \cdot CH : CH \cdot CH_2OH$ .....	Crotonyl alcohol
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CHO$ .....	<i>n</i> -Butyraldehyde
$CH_3 \cdot CH : CH \cdot CHO$ .....	Crotonaldehyde
$CH_3 \cdot CO \cdot CH_2 \cdot CH_3$ .....	Methyl ethyl ketone

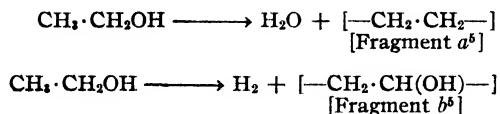
Formation of groups with an even number of carbon atoms is readily envisaged by a doubling, trebling, or quadrupling of the two-carbon chain of ethanol. Formation of groups with an odd number of carbon atoms would involve a more complex mechanism. Consequently, compounds with 3 and 5 carbon atoms occur less frequently.

The catalyst used is, as already mentioned, made up of two components: a dehydrating part which, if it were to act independently on the ethanol, would produce (at the temperature selected) mainly ethylene and water; and a dehydrogenating part which would yield of itself hydrogen and aldehyde.

Ethylene and acetaldehyde should thus be the main reaction products of the independent action of the catalyst components. On the other hand, experiments show that mixtures of ethylene and acetaldehyde passed over the compound catalyst result in only negligible butadiene yields. The

stable molecules of olefin and aldehyde apparently do not interact under the conditions of the Lebedev catalysis; interaction must have taken place in their active stage, *i. e.*, prior to their reconstitution to stable molecules.

The following explanation, advanced by Lebedev, appears very plausible: As a result of the two catalytic processes, two types of "free radicals" (we shall call them "fragments") are formed at the active surfaces of the catalyst:



Analogous fragments can be formed from *n*-butanol and *n*-hexanol.

The subsequent behavior of the fragments of type [a] and type [b], adsorbed on the surface of the catalyst, will largely depend upon such factors as: the composition of the catalyst (distribution of active areas) and the condition of its surface; the individual nature of the fragments; the duration of their sojourn on the surface or in the surrounding gas phase; the concentration of such fragments and of the nascent hydrogen present; and the temperature conditions on the surface of the catalyst, in the gas phase, etc.

Fragments, upon losing their adherence to the catalytic surface, may either reconstitute themselves to stable molecules or react with one another. Reconstitution results in the formation of ethylene and acetaldehyde from fragments [a] and [b], respectively, the latter having passed through an enolic stage (see page 8).

Alternatively, the free valencies at the end of fragments or complexes of fragments may add the nascent hydrogen copresent, thus arresting further reaction, for it must be remembered that heterogeneous catalysis is, at least partly, a reversible phenomenon. The addition of nascent hydrogen is favored by the presence of conjugated double bonds.

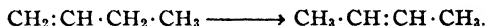
Further insight into the mechanism can be gained by considering the general behavior of substances likely to arise under the operating conditions of the Lebedev catalysis: *i. e.*, 400° to 450° C., 2 to 10 seconds sojourn in the catalytic zone, and atmospheric pressure. The temperature is

<sup>6</sup> Formation of fragments of the type  $[\text{CH}_3 \cdot \text{CH} < ]$  and  $[\text{CH}_2 \cdot \text{CH} < \overset{\ominus}{\text{O}} \text{---}]$  could not be easily tied in generically with the formation of the resulting by-products. As for the dehydration fragment, Lebedev's assumption is in conformity with the views of A. A. Balandin, *Z. physik. Chem.*, **B2**, 289 (1929), and A. Bork, *Acta Physicochim. U.R.S.S.*, **12**, 899 (1940). A variance of view apparently exists, though, between Lebedev on the one hand and Balandin and Bork on the other regarding the dehydrogenation fragment.

too high to favor formation of high-molecular compounds. Doubling (and trebling) will predominate. In fact, at such temperatures, the thermal stability of a number of substances formed is very low. As a result, thermal decomposition takes place, with appreciable quantities of carbon depositing, during the process on the dehydrating component of the catalyst.

The major products which can be expected to be formed comprise: (1) unsaturated hydrocarbons, (2) alcohols, and (3) carbonyl compounds. Their characteristic behavior at conditions prevailing during the reaction is general chemical knowledge and is briefly outlined:

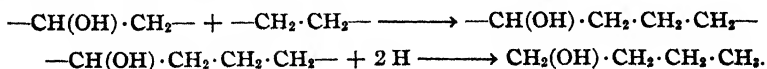
(1) *Unsaturated hydrocarbons.* Various investigators have shown that dehydrating catalysts act as powerful isomerizing agents, transforming less stable forms into more stable ones. Thus, Ipatieff reported that, under the action of aluminum oxide, isopropyl ethylene is isomerized to trimethyl-ethylene. An even more powerful isomerizing effect is produced<sup>6</sup> by activated hydrosilicates (Florida earth, kaolin, etc.). The manufacture of high-octane gasoline with the aid of the Houdry catalyst also belongs to this group of phenomena. King has shown that, by dehydrating *n*-butanol with phosphoric acid (on a pumice carrier), at temperatures below 400° C., a mixture of butene-1 and butene-2 is obtained, indicating that partial isomerization takes place:



Above 400°, the butene-2 conversion is almost complete. Similar isomerizations take place in the Lebedev process, whereby  $\text{CH}_2:\text{CH}\cdot\text{CH}_2-$  is isomerized to  $\text{CH}_3\cdot\text{CH}:\text{CH}-$ .

(2) *Alcohols.* Part of the ethanol escapes further decomposition and appears among the reaction products. The same holds true for other primary alcohols formed. Secondary alcohols, being less stable, are completely dehydrated.

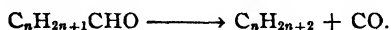
Unsaturated alcohols may react with nascent hydrogen at the double bonds forming saturated alcohols. Formation of saturated alcohols under the conditions of the process is, however, more likely through the addition of hydrogen directly to the free end-valencies of doubled, trebled, etc., complexes of fragments. An example is the formation of *n*-butanol by hydrogenation of end valencies of the complex  $[b] + [a]$ :



<sup>6</sup> S. V. Lebedev and E. P. Filonenko, *Ber.*, 58, 163 (1925).

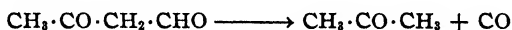
(3) *Carbonyl compounds.* Such compounds arise in the form of both saturated and unsaturated aldehydes and ketones. Under the conditions of the process, unsaturated carbonyl compounds seem to add hydrogen at the double bonds, especially if the double bonds are conjugated with the carbonyl group.

Of particular interest, for the proper understanding of the Lebedev process, is the decomposition of aldehydes into hydrocarbons and carbon monoxide at temperatures prevailing during the reaction:

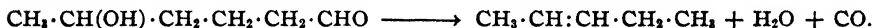


Such a reaction accounts, on the one hand, for the presence of appreciable amounts of carbon monoxide in the contact gases; on the other hand, it may well explain the occurrence in the by-products of substances with odd numbers of carbon atoms such as 1, 3, and particularly 5. Examples are:

- (1) The pyrolytic decomposition of acetaldehyde to CO and CH<sub>4</sub>.
- (2) The formation of acetone:

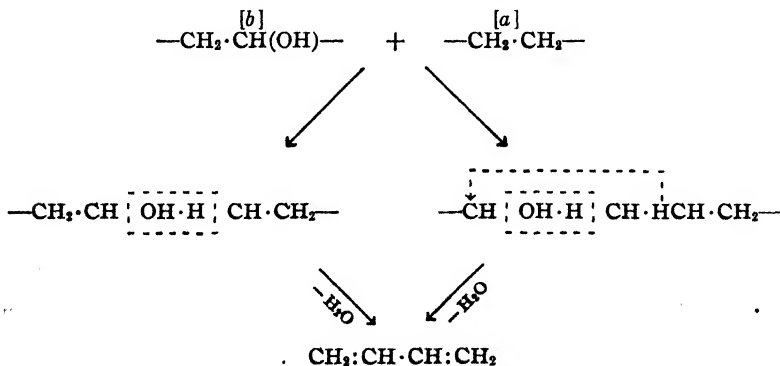


- (3) The formation of pentene-2:



## 2. Mechanisms of Butadiene Formation

On the basis of the above considerations, the following two mechanisms of butadiene formation are suggested by Lebedev:



In the first and simplest instance a fragment [b] combines with a fragment [a]; the elements of water are removed and the molecule stabilizes itself.

In the second instance on different orientation of the fragments and removal of water one hydrogen atom migrates from the third to the first carbon. Either of the two paths indicated is possible.

Further light on the mechanism of the Lebedev catalysis may be shed by a study of the relative yields of the various by-products. A material balance is presented in table I-4 on page 22. The yields are as of the date of original publication in 1934, and have considerably changed since. In particular, the butadiene yield has been nearly doubled. The general characteristics of the catalyst have been maintained. The catalyst still contains the basic components, *A* and *B* (see page 24), to which have been added later quantities of promoters, (*c*) and (*d*). It may, therefore, be assumed that the original generic ideas about the formation of products stand substantially unchanged.

The high butadiene yield suggests that the combination of different fragments, *i. e.*, [*a*] + [*b*], seems to take precedence over the recombination of identical fragments. This is further confirmed in that combination [*a*] + [*a*] can be made accountable only for the formation of butene-2; however, butene-2 could just as simply have been formed by the hydrogenation of butadiene.<sup>7</sup>

According to Rubinshtein and Gracheva,<sup>8</sup> the "active" areas of a binary catalyst (more specifically the Zelinskiĭ-Komarevskii<sup>9</sup> catalyst consisting of one mole nickel plus one mole alumina are located along the borderline regions between the two components of the catalytic surface. If this assumption is correct, the two types of fragment, [*a*] and [*b*], would be formed in close proximity and their combination would therefore be facilitated.

The difficulty of polymerizing gaseous ethylene (at atmospheric pressures),<sup>10</sup> may well serve as an indication of the reluctance of fragments [*a*] + [*a*] to intercombine.

Fragments of the [*b*] type should have a much greater tendency to interlink, judging from the ease with which aldehydes condense to aldols. Nevertheless, the number of compounds whose occurrence can be definitely

<sup>7</sup> Volzhinskiĭ and Rotkevich showed that nascent hydrogen generated by metallic sodium in an ethanol solution of butadiene could hydrogenate up to 40% of the butadiene to butene-2. Unpublished work.

<sup>8</sup> A. M. Rubinshtein and E. P. Gracheva. See *Zhur. Fiz. Khim.*, **8**, 725 (1936); **14**, 1209 (1940). The theory is based on a constant ratio of heat of activation of the two reactions.

<sup>9</sup> N. D. Zelinskiĭ and V. Komarevskii, *Ber.*, **57B**, 667 (1924). The catalyst is not suitable for butadiene formation.

<sup>10</sup> R. Burk, *Polymerization*. Reinhold, New York, 1937, p. 126.



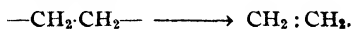
attributed to the  $[b] + [b]$  combination is not great; these are crotonaldehyde and possibly crotonyl alcohol.

### 3. Mechanism of Formation of Other Products

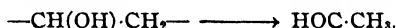
The probable mechanisms of formation of the major products of the Lebedev catalysis are summarized in the following section from the original work (about 1933) of Lebedev *et al.*<sup>11</sup> It is reasonable to assume that at least some of the individual products of the catalytic reaction are the result of more than one mechanism. Butadiene, for instance, may have been formed in at least three or four different ways.

#### GROUP C<sub>2</sub>

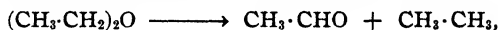
- (1) *Ethylene*. Forms by stabilization of one  $[a]$  that failed to intercombine with other fragments:



- (2) *Acetaldehyde*. Forms in the same way from one fragment  $[b]$ :



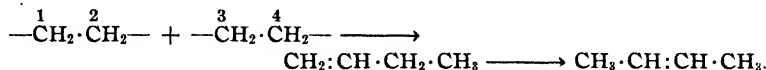
- (3) *Ethane*. Forms by decomposition of ether (see below):



or possibly by hydrogenation of fragment  $[a]$ .

#### GROUP C<sub>4</sub>

- (4) *Butene-2*. From fragments  $[a] + [a]$ :



By the migration of one hydrogen atom from 2 to 4, butene-1 is formed, which in turn, under the action of the water-removing component of the catalyst, isomerizes almost completely to butene-2.

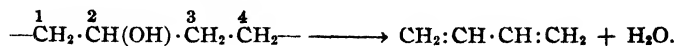
- (5) *Butadiene-1,3*. (a) From fragments  $[b] + [a]$ :



The elements of water are removed and one hydrogen atom migrates from 3 to 1.

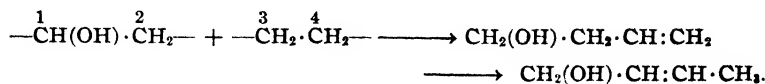
<sup>11</sup> S. V. Lebedev, *Zhur. obshchei Khim.*, **3**, 698 (1933); reprinted in *Zhizn' i Trudy, Onti, Leningrad*, 1938, p. 491.

(b) From the complex [b] + [a], on different orientation of the fragments:



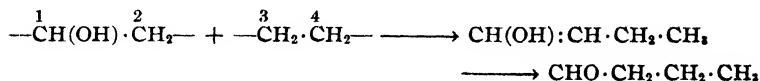
By removal of water and subsequent stabilization of the molecule.

(6) *Crotonyl alcohol*. From [b] + [a]:



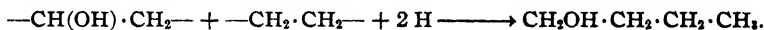
Migration of one hydrogen from 3 to 1 forms allyl carbinol, which isomerizes to crotonyl alcohol.

(7) *n-Butyraldehyde*. From [b] + [a]:



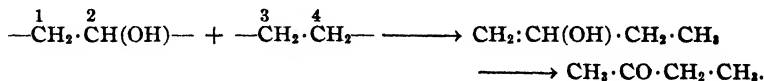
Migration of hydrogen from 2 to 4 forms butyraldehyde, via an enolic stage.

(8) *n-Butanol*. From [b] + [a]:



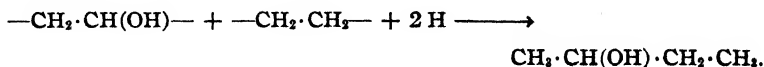
Addition of hydrogen to the free end valencies of the complex forms butyl alcohol. The latter, on dehydration and isomerization, may give butene-2.

(9) *Methyl ethyl ketone*. From [b] + [a] on different orientation of fragments:



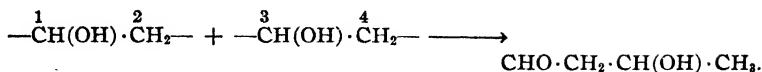
By migration of a hydrogen from 2 to 4, methyl ethyl ketone is formed, via an enolic stage.

(10) *sec-Butanol*. From [b] + [a]:



Addition of hydrogen to the free end valencies of the complex in the configuration above should lead to secondary butyl alcohol, which apparently is subsequently completely dehydrated to butene-2.

(11) *Aldol*. From  $[b] + [b]$ :<sup>12</sup>



Aldol forms via an enolic stage by the migration of one hydrogen atom from 2 to 4.

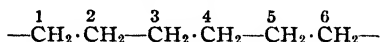
(12) *Crotonaldehyde*. Aldol splits off water, forming crotonaldehyde:



### GROUP C<sub>6</sub>

This group, formed by trebling fragments  $[a]$  or  $[b]$ , constituted a total of 2 to 3% on the alcohol decomposed at the time of Lebedev's basic work. It is represented mainly by hexene-2, hexadiene-2,4, and *n*-hexanol. Their most likely mechanism of formation is given below. It is in part based upon the fact that hexene-2 and hexadiene-2,4 are considered the most stable members of their respective groups of isomers.

(13) *Hexene-2*. (a) From the complex  $[a] + [a] + [a]$ :



by migration of one hydrogen from 2 to 6 with the subsequent isomerization of hexene-1 to hexene-2.

(b) From the complex  $[b] + [a] + [a]$ :



by addition of hydrogen to the end valencies, removal of water from the hexanol formed, and subsequent isomerization of hexene-1 to hexene-2.

(c) From the complex  $[a] + [b] + [a]$ :



by hydrogen addition to the end valencies and removal of one molecule of water.

(14) *n-Hexanol*. See (13b) above.

(15) *Hexadiene-2,4*. (a) From the complex  $[b] + [a] + [a]$  by migration of hydrogen from 5 to 1, dehydration, and subsequent isomerization.

(b) From the complex  $[b] + [a] + [b]$  by hydrogen addition to the end valencies and subsequent removal of two molecules of water.

<sup>12</sup> The polar arrangement of fragments  $[b] + [b]$  was accepted by Lebedev as the most likely one.

## PRODUCTS WITH ODD NUMBERS OF CARBON ATOMS

It is more difficult to present a plausible scheme for the formation of compounds with odd numbers of carbon atoms than for those with even numbers. There is evidence that compounds with odd numbers of carbon atoms are formed by dissociation of substances with even numbers of carbon atoms, mainly carbonyl compounds. Acetaldehyde, which readily dissociates into carbon monoxide and methane, may serve as an example. Carbon monoxide may also interact with nascent hydrogen, yielding formaldehyde, which, in turn, due to its high activity, will react with even-numbered compounds to form odd-numbered ones. Thus, two ways are open for the formation of products with an odd number of carbon atoms:

- (a) The splitting off of carbon monoxide from aldehydes.
- (b) The association of formaldehyde with fragments of carbonyl compounds.

GROUP C<sub>1</sub>

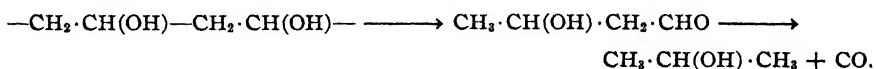
(16) *Carbon monoxide.*  $\text{CH}_3\cdot\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$ .

(17) *Carbon dioxide.*  $2 \text{CO} \rightarrow \text{CO}_2 + \text{C}$ . Such a reaction is generally favored by dehydrogenating catalysts. Carbon dioxide may have been formed also by the interaction of carbon monoxide and water vapor.

GROUP C<sub>2</sub>

To this group belong acetone and propene. They may occur concurrently, apparently as the result of either of two reactions for which the following schemes are possible:

(a) By splitting off carbon monoxide from substances forming the C<sub>4</sub> group. The reaction may proceed via condensation of aldehyde fragments [b] to acetaldol, followed by a splitting off of carbon monoxide.



The isopropyl alcohol formed is converted into acetone or into propene, depending upon whether the dehydrating or the dehydrogenating part of the catalyst acts upon it, that is:

(18) *Acetone.*  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_3 \xrightarrow{\text{dehydrogenation}} \text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 + \text{H}_2$

or

(19) *Propene.*  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_3 \xrightarrow{\text{dehydration}} \text{CH}_3\cdot\text{CH}:\text{CH}_2 + \text{H}_2\text{O}$ .

(b) By addition of formaldehyde to fragment [b] and hydrogenation, with either propylene glycol or acetol (1-hydroxy-2-propanone) as an intermediate product.

### GROUP C<sub>5</sub>

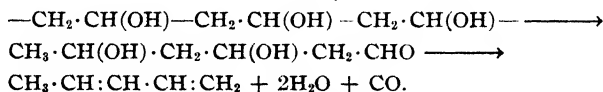
This group comprises pentene-2 and pentadiene-1,3, as well as amyl alcohol. The hydrocarbons are formed in small, and the alcohol in negligible, amounts, by splitting off carbon monoxide from carbonyl compounds of the C<sub>6</sub> group or else by association of fragments of ethyl and isopropyl alcohols.

(20) *Pentene-2*. CH<sub>3</sub>·CH:CH·CH<sub>2</sub>·CH<sub>3</sub>.

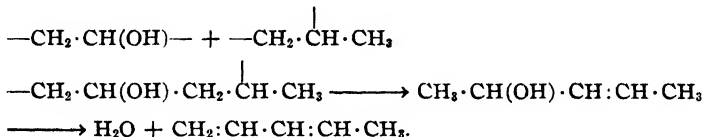
(21) *Pentadiene-1,3*. CH<sub>2</sub>:CH·CH:CH·CH<sub>3</sub>.

In the case of pentadiene-1,3 the two reaction paths may be visualized as follows:

(a) from fragments [b] + [b] + [b], on migration of one hydrogen atom a complex carbonyl compound is formed which decomposes into pentadiene-1,3, water, and carbon monoxide:



(b) combination of a fragment [b] with a fragment of isopropyl alcohol, *viz.*:



### CYCLIC HYDROCARBONS

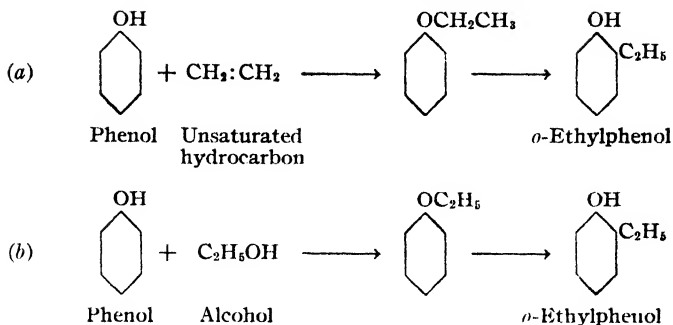
Aside from the dimer of butadiene (4-vinylcyclohexene-1) this group contains *p*-xylene and toluene, for the formation of which no satisfactory explanation was advanced by Lebedev.

Likhosherstov *et al.*<sup>13</sup> discovered in the hydrocarbon layer of the "condensate" (see page 52) also, homologs of phenol and isolated in pure form *o*-ethylphenol and *o*-cresol. Phenols occur not infrequently in pyrolytic processes, where they are formed from fragments of more complex molecules. Phenol as such is not detected because, in the presence of dehydrating catalysts, it readily reacts with alcohols<sup>14</sup> and with unsaturated hydrocarbons<sup>15</sup> to form, for example, ethylphenol.

<sup>13</sup> M. Likhosherstov, A. Petrov and S. Alekseev, *Zhur. Obshcheĭ Khim.*, **4**, 1274 (1934).

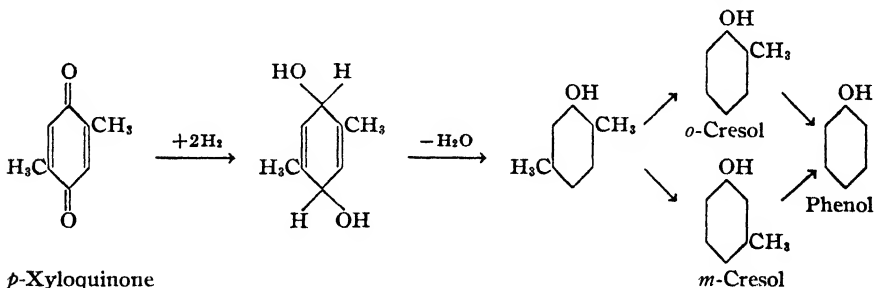
<sup>14</sup> G. Errera, *Gaz. chim. ital.*, **14**, 484; H. Auer, *Ber.*, **17**, 669 (1884); T. Zincke, *Ann.*, **322**, 187.

<sup>15</sup> V. N. Ipatieff, N. A. Orlov and A. G. Razuvaev, *Ber.*, **60**, 130 (1927).

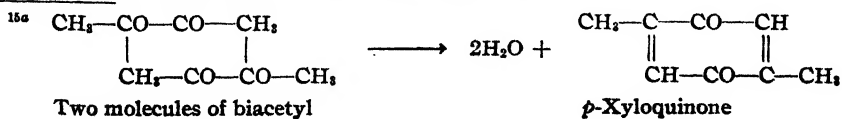


Lebedev considered *p*-xyloquinone (phlorone) as the starting substance for toluene and xylene, phlorone having been formed by condensation of two molecules of butanedione-2,3 (biacetyl).<sup>15a</sup> The formation proceeds for xylene, via hydrogenation and the splitting off of water, and for toluene, of an additional methyl group.

Likhosherstov<sup>13</sup> showed that cresols can be formed from the same starting substance (phlorone) and via a similar mechanism of hydrogenation and partial dehydration, followed by isomerization and splitting off of a methyl group:



Slobodin (see page 122) contributed further to the clarification of the genesis of cyclic compounds in the Lebedev catalysis by showing that, in the presence of a dehydrogenating catalyst at 400° to 425° C., butadiene—in addition to forming the dimer (see page 96)—also polymerizes, forming *p*-xylene as an end product. Intermediate products formed are probably 1,4-dimethylcyclohexadiene-2,5 and 1-methyl-4-methylenecyclohexene-2. Slobodin contends that the ratio of *p*-xylene to [dimer + ethylbenzene + toluene] is 1:2. Ethylbenzene is the dehydrogenation product of the Lebedev dimer. This work is discussed in greater detail in the chapter on thermopolymerization (see page 122).



## ETHERS

The formation of simple ethers from alcohols by partial dehydration (*i. e.*, withdrawal of *one* molecule of water from *two* molecules of alcohol) proceeds favorably in the temperature range of 200° to 250° C. Above 300°, the ethylenic dehydration prevails (*i. e.*, the removal of *one* molecule of water from *one* molecule of alcohol). On the other hand, catalysts possessing dehydrogenating properties only, at temperatures of below 400° may, at a temperature of 400° C., also acquire some dehydrating faculties.

It may be assumed that this partial dehydrating power of the dehydrogenating catalyst (component *B*) is responsible for the formation of ether, possibly activated by the presence of component *A* (see maximum in the ether yield in figure I-3). It may also be assumed that the amount of ethyl ether originally formed exceeds that found in the by-products, since ether, like alcohol, is capable of forming butadiene on the compound catalyst (see Fig. I-2).

#### 4. Effect of Admixtures to the Alcohol Feed Stock

The discussion so far has been concerned with the primary decomposition of ethyl alcohol, *i. e.*, with the process of passing it once over the Lebedev catalyst and analyzing the mixture of products formed. Only the ethyl alcohol escaping conversion was recovered from the reaction products and rectified and recycled.

Quantitatively, aldehyde, ether, ethylene, and water are most prominent among the by-products of the Lebedev catalysis. Experimental evidence points to the fact that, with the exception of ether, none of these compounds, used by itself, will yield butadiene in contact with the binary catalyst. To be more precise, acetaldehyde will form traces of butadiene under conditions identical with those for the Lebedev catalysis, but ethylene or water yield, of course, no diene whatever. This is not, however, conclusive evidence that the admixture of aldehyde, ether, ethylene, or water to the alcohol feed stock (in a practical case, by their partial or complete recirculation) will have no effect on the ultimate butadiene yield. It is, for example, fairly obvious from the preceding discussion that the concentration of aldehyde and ethylene in the catalytic zone, or rather the number of their active fragments [*a*] and [*b*] present, may well have a bearing on the course of the process. If such is the case, the recirculation of some of the by-products of the primary decomposition of ethanol may have an economic advantage.

A study of the effect of admixtures to the alcohol stock would be ex-

pected to shed further light on the mechanism of the Lebedev process. The action of admixtures to the alcohol feed stock, especially of by-products of its primary decomposition, was therefore investigated by Gorin *et al.*<sup>16</sup>

The literature devoted to the question of the displacement of equilibria by admixtures in catalytic reactions similar to the Lebedev catalysis is not very extensive. Engelder,<sup>17</sup> Armstrong and Hilditch,<sup>18</sup> Hoover and Rideal,<sup>19</sup> Constable,<sup>20</sup> and others<sup>21</sup> established that the addition of water to ethyl alcohol enhances the dehydrogenation reaction and impedes the dehydration of the alcohol molecule, in the presence of a dehydrogenating or a dehydrating catalyst, or of a catalyst with mixed function. Hoover and Rideal<sup>19</sup> attribute the effect to a selective adsorption, with water predominantly adsorbed by the dehydrating centers, which thus become blanketed, so that only the dehydrogenating centers remain active. Ostromislensky<sup>22</sup> studied the catalytic conversion of mixtures of ethyl alcohol and acetaldehyde to butadiene in the presence of a dehydrating catalyst.

#### A. ADMIXTURE OF ACETALDEHYDE

The experiments of Gorin *et al.*<sup>16</sup> showed that, when increasing quantities of acetaldehyde are admixed with ethanol, and the mixture passed over the Lebedev catalyst, certain significant changes take place in the yields.

The quantity of gaseous products generated is drastically reduced. Thus for a mixture containing 50 parts by weight of alcohol and 50 parts aldehyde, the amount of gas generated per unit of feed stock is 2.5 times smaller than for pure alcohol. The butadiene content in the gas rises gradually, reaches a maximum at an alcohol-aldehyde ratio of 70:30 (or 50:50), and then falls off abruptly. The butadiene output, calculated on the total mixed feed stock, rises somewhat, reaching a maximum at a mixture of 80 parts alcohol plus 20 parts aldehyde, and then too falls off sharply. The butadiene yield, *i. e.*, butadiene calculated on the mixed feed stock decomposed, remains practically constant up to 20% aldehyde, and falls off for mixtures containing more than 20% acetaldehyde.

Butadiene output and yield, when calculated on the alcohol component

<sup>16</sup> S. V. Lebedev, И. А. Gorin and S. N. Khutoretskaia, *Sintet. Kauchuk*, **4**, No. 1, 8 (1935). Reprinted in *Zhizn' i Trudy*, Leningrad, Onti, 1938, p. 602.

<sup>17</sup> C. J. Engelder, *J. Phys. Chem.*, **21**, 676 (1917).

<sup>18</sup> E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc. London*, **A97**, 262 (1929).

<sup>19</sup> G. I. Hoover and E. K. Rideal, *J. Am. Chem. Soc.*, **49**, 104 (1927).

<sup>20</sup> F. H. Constable, *Proc. Roy. Soc. London*, **A108**, 355 (1925).

<sup>21</sup> Zhur. *Priklad. Khim.*, **5**, 581 (1932).

<sup>22</sup> I. I. Ostromislensky, *Zhur. Russ. Fiz.-Khim. Obshchestva*, **47**, 1498 (1915).



of the feed stock (that is, disregarding the expended aldehyde), rise at first, reach a maximum in mixtures containing 20 to 30 parts (by weight) of aldehyde, and then fall off severely. Pure acetaldehyde, although completely decomposed to a mixture of liquid and gaseous products, when passed over the Lebedev catalyst yields but negligible quantities of butadiene.

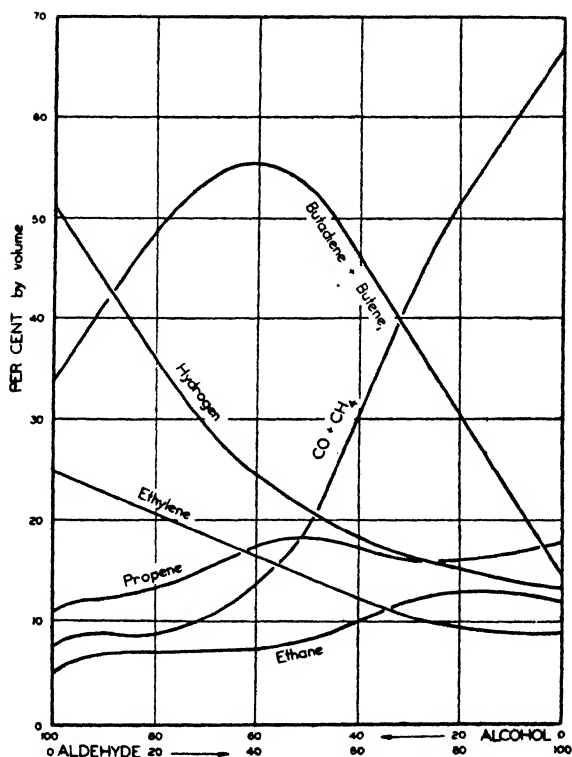


Fig. I-1.—Composition of gaseous reaction products as a function of ethanol-acetaldehyde ratio in feed stock.<sup>16</sup>

The changes taking place in the composition of the gaseous products are illustrated in figure I-1. The hydrogen content decreases markedly; the total of carbon monoxide + methane just as rapidly increases; the ethylene content declines; and ethane and propene increase in quantity. The content of butadiene plus butene-2 first rises, reaches a maximum at an aldehyde content of 30 to 50%, and then falls off.

## B. AN ALDEHYDE BALANCE

Making certain theoretical assumptions, which appear justified, Gorin *et al.*<sup>16</sup> calculated from the amount of hydrogen the hypothetical quantity of all aldehyde formed in the process. Assuming further, in conformity with Lebedev's theory of active fragments, that each molecule of butadiene was formed in the process from one aldehyde fragment [b] and one ethylenic fragment [a], they calculated the amount of aldehyde consumed in the synthesis of butadiene. From the sum of carbon monoxide and methane found in the gaseous products, the quantity of aldehyde pyrolytically

TABLE I-2  
AN ALDEHYDE BALANCE

Line No.	Constituent	Experiment <sup>a</sup> No.					
		3 + 4	7 + 8	9 + 10	13 + 14	18 + 19	21 + 22
	Feed stock composition						
1	Alcohol, % by wt.	100	95	90	80	70	50
2	Aldehyde, % by wt.	0	5	10	20	30	50
3	Aldehyde in feed stock, g.	0	3.45	7.87	16.17	24.82	42.72
4	Aldehyde formed (calcd. from hydrogen), g.	16.68	14.93	12.72	10.70	7.24	2.33
5	Total aldehyde (sum of 3 and 4), g.	16.68	18.38	20.68	26.87	32.06	45.03
6	Aldehyde decomposed to CO + CH <sub>4</sub> , g.	0.89	1.19	1.25	0.86	1.37	1.94
7	Aldehyde expended for butadiene formation, g.	9.18	9.81	10.71	13.41	12.15	6.76
8	Aldehyde used for propene formation, g.	3.67	4.28	4.20	4.83	5.98	4.54
9	Aldehyde returned, g.	2.00	2.07	2.52	1.66	1.71	3.86
10	Aldehyde accounted for, g.	15.72	17.35	18.67	20.75	21.25	17.10
11	Aldehyde not accounted for, g.	0.955	1.03	2.01	6.12	10.81	27.94
12	Water-insoluble substances, g.	1.03	1.78	2.56	5.26	9.92	18.77

<sup>a</sup> Average of two experiments each.

destroyed in the reaction could be estimated. Assuming further that two parts of aldehyde may condense to aldol, which on splitting off carbon monoxide and water forms propene, Gorin calculated from the amount of propene found in the gas the equivalent amount of aldehyde expended in the formation of propene.

His calculations are summarized in table I-2. The aldehyde added to the feed stock (line 3) and the aldehyde formed in the reaction by the dehydrogenation of alcohol (4), add up to the total aldehyde (5). On the other side of the balance are: the aldehyde pyrolytically destroyed (6), used in the formation of butadiene (7), in the formation of propene (8), and found intact in the by-products of the reaction (9). Lines 6 through 9

are added in line 10 and termed "aldehyde accounted for." The difference between lines 5 and 10, *i. e.*, the aldehyde not accounted for, is given in line 11. It was evidently expended in the formation of other by-products. For purposes of comparison, the increasing amount of hydrocarbons (water-insoluble substances) found in the by-products is recorded in the last line (12) of the table. The table reveals the following trends:

(1) As the admixture of aldehyde to the feed stock is increased, the amount of aldehyde generated by the dehydrogenation of alcohol gradually decreases.

(2) Simultaneously, especially at aldehyde additions to the feed stock in excess of 20%, the amounts of aldehyde consumed in butadiene formation (line 7) are increased beyond the quantity of aldehyde formed from the alcohol (as calculated in line 4).

We must therefore conclude that the aldehyde produced by dehydrogenation and the aldehyde added to the feed stock are at least partly interchangeable, and that a part of the aldehyde in the feed stock contributes directly to the formation of butadiene.

A part of the hydrogen formed initially may have been consumed for the hydrogenation of intermediary products (see page 8). The balance of aldehyde as presented in the table I-3 is therefore probably not complete. The formation schemes of butanol or of butene-2 may well require a hydrogenation step (page 9). The hydrogen so consumed may in turn be related to an additional amount of aldehyde initially formed, thus obtaining for "aldehyde formed in the reaction" figures in excess of those recorded in line 4. This consideration may, however, be omitted, since for each hydrogen used in the hydrogenation one aldehyde fragment [b] was consumed in the formation of one butanol or one butene-2 molecule, respectively. Thus the hydrogen and the aldehyde not accounted for in the table cancel out one another, and the balance given remains unaffected.

Any attempt to explain the situation meets with considerable difficulties in view of the numerous side reactions taking place. It appears plausible (Gorin *et al.*) that the acetaldehyde, introduced simultaneously with the alcohol vapors into the catalytic zone, is partially activated. The active aldehyde radicals thus formed may be assumed to be equivalent to the fragments [b] formed by the dehydrogenation of alcohol molecules, and as such can take part in all reactions discussed in conjunction with the [b] fragment (pages 8 to 12). Through the influx of available fragments [b], the equilibrium in the catalytic zone is displaced. For one, a better utilization of the dehydration fragments [a], *i. e.*,  $-\text{CH}_2\text{CH}_2-$ , may now take place, and, in turn, the number of [a] · [b] combinations formed is enhanced. One evident consequence would be a reduction in ethylene in the escaping

gas, which, as will be remembered, was formed by reconstitution of fragments [a] which failed to interlink with other fragments.

The reduction in the quantity of ethylene formed can also be conditioned by a decline in the activity of the dehydrating centers of the catalyst, as a result of their poisoning by adsorbed aldehyde. The same cause may be responsible for a marked decline in butadiene formation from feed stocks with a high aldehyde and a low alcohol content. On the other hand, the great reduction in the quantity of hydrogen formed with progressive increase of the aldehyde component in the mixed feed stock may well suggest that the acetaldehyde is preferentially adsorbed at the dehydrogenating regions. Several other explanations can be advanced, though, for the reduced generation of hydrogen. It is possible to assume a reversibility of the dehydrogenation reaction ( $C_2H_5OH \rightleftharpoons -CH_2CHOH- + 2 H$ ) whereby an enrichment in active aldehyde fragments [b] in the catalytic zone could well displace the equilibrium in the direction of subdued hydrogen generation. Part of the hydrogen may also have been used up in hydrogenating carbon monoxide to methane and water or to formaldehyde.

The increase in water-insoluble compounds (hydrocarbons) recorded in the last line of table I-3 may be explained by the increased chance of intercollision of active [b] fragments and also their collision with active radicals with more than two carbon atoms.

At high aldehyde concentrations a number of artifacts enter the reaction picture. One of them is the formation of excessive amounts of carbon on the catalyst.

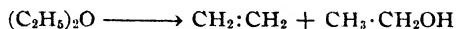
Gorin's work has proved to be of considerable practical consequence. The recognition that acetaldehyde, added in moderate quantities to the alcohol feed stock, takes an active part in the formation of butadiene led to the practice (beginning around 1938) of recirculating the aldehyde with the rectified alcohol, and was in no small measure responsible for boosting the butadiene yield.

#### C. ADMIXTURE OF ETHYL ETHER, ETHYLENE, WATER, AND *n*-BUTANOL

The effect of admixing ether, ethylene, water, and *n*-butanol to the feed stock is summarized in figure I-2 (Gorin *et al.*). In the same graph are recorded the previously discussed results with acetaldehyde. The amount of butadiene formed is presented as percentage of alcohol decomposed. The data of figure I-2 may be supplemented by the following observations.

(a) *Ether* takes part in the formation of butadiene. As distinct from the other admixtures discussed here, it is also capable of forming independently some butadiene on the Lebedev catalyst (approximately 7% on ethyl ether passed or 9 to 10% on the ether converted). An explanation may

be found in the fact that ethyl ether will form, on catalytic decomposition a certain amount of ethyl alcohol, *viz.*:



which may, in turn, be subject to the normal Lebedev catalysis.

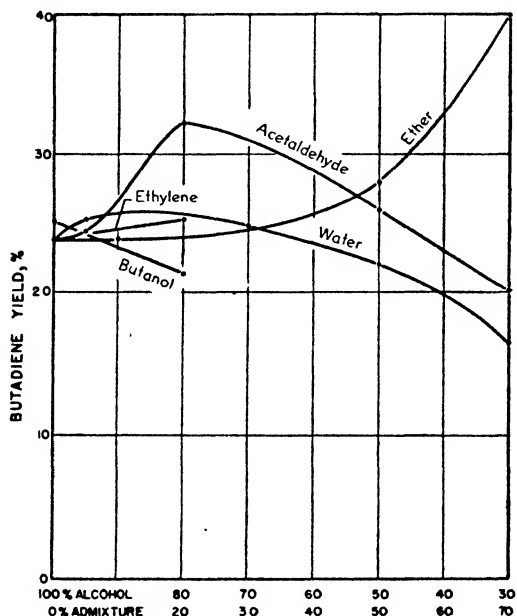


Fig. I-2.—Effect of admixtures to ethanol feed stock on butadiene yield.<sup>16</sup>

(b) Contingent upon the increase in the *ether* component of the mixed ether-alcohol feed stock, the following changes are noted:

- (1) The concentration of butadiene in the gas phase declines.
- (2) The ethylene yield increases.
- (3) The butadiene yield on the mixed feed stock falls off.
- (4) The butadiene yield on the alcohol converted, however, increases steadily (Fig. I-2).
- (5) The volume ratio of butadiene to butene-2 remains virtually unchanged.

(c) Because of its considerable thermal stability, *ethylene* suffers practically no change when passed over the Lebedev catalyst at tempera-

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tures below 500° C. In effect, addition of (up to 20%) ethylene to the alcohol feed stock has therefore virtually no bearing upon the butadiene yield.

(d) A slight to moderate dilution with water (6 to 25%) has practically no effect on the yield of butadiene. With an increasing dilution, however, the yield falls off rapidly. Simultaneously, drastic changes can be observed in the character of the process. The yields of ethylene, butadiene, and butene-2 decline while the contents of carbonyl compounds increase.

In the actual manufacture of butadiene, crude alcohol (84.6% absolute alcohol by weight) is used. The butadiene yield is equal to that of rectified alcohol (92.5% absolute alcohol by weight). According to Sabatier, water is detrimental to the dehydrogenating process. This was confirmed by Lebedev's collaborators, who obtained the yields given in table I-3, when the dilution was varied and all other conditions were kept constant. A slight improvement in yield may be observed when the more dilute alcohol is contacted at higher temperatures.

TABLE I-3  
EFFECT OF DILUTION WITH WATER ON BUTADIENE YIELD

Absolute alcohol in the alcohol used, % by vol.	Temp. °C.	Butadiene yield, %, calcd. on absolute alcohol converted
94.5	440	23.2
76	440	16.5
54	440	15.0
94.5	500	17.7
76	500	19.3
54	500	18.8

(e) *Butyl alcohol* takes no part in the formation of butadiene; and its presence seriously impairs the yield of butadiene.

The above data are of more than mere academic interest. They shed a light on the behavior of by-products returned to the catalytic zone with the rectified alcohol or with the alcohol used as absorbent.

## 5. Yields

The yields given in table I-4 belong to an early period (1932-1933). Improved catalysts, better control and mastery of the manufacturing process, etc., have since changed the balance of products much in favor of higher butadiene yields. Although no comprehensive analysis has been published since Lebedev's days, the following changes are indicated:

(1) The butadiene yield has gradually been increased. It was 20-22% on the alcohol converted through 1934, rose to 28% in 1935 and to 32.5% through 1938, and reached 40-41% (or 70% of theoretical) in December,

1939. This was achieved only in part because of improved technology; it was partly due to the recycling of aldehydes.

TABLE I-4  
MATERIAL BALANCE OF LEBEDEV CATALYSIS (1933)  
(IN PER CENT ON ALCOHOL CONVERTED)

Substance	Mol. wt.	B. p., °C.	Quantity, %
Hydrogen.....	...	...	1.3-1.6
Carbon oxides.....	...	...	0.2-0.5
HYDROCARBONS			
Methane, ethane and other saturated hydrocarbons.....	...	...	0.4-0.6
Ethylene.....	...	...	5-8
Butene-2.....	56.10	<i>cis</i> : +1° <i>trans</i> : +2.5°	3-4
Butadiene-1,3.....	54.09	-3°	20-25
Pentene-2.....	70.13	36.4	0.5-0.7
Pentadiene-1,3.....	68.11	43	0.5-0.7
Hexene-2.....	84.16	67.9-68.1	0.4-0.5
Hexadiene-2,4.....	82.14	82	0.6-0.8
Toluene.....	92.13	110.8	0.1-0.2
<i>p</i> -Xylene.....	106.16	138.5	0.5-0.7
Dimer of butadiene (4-vinylcyclohexene-1).....	108.18	...	0.05 (approx.)
SIMPLE ETHERS			
Ethyl ether.....	74.12	34.6	2-5
Ethyl butyl ether.....	102.17	91.4	0.05-0.1
ALCOHOLS			
<i>n</i> -Butyl alcohol.....	74.12	117.71	2-4
Crotonyl alcohol.....	72.10	118	0.5-1
Amyl alcohol.....	88.15	138	0.1 (approx.)
<i>n</i> -Hexyl alcohol.....	102.17	157.2	0.5-0.8
Unsaturated <i>n</i> -hexyl alcohol.....	102.17	153.7-154	0.05-0.1
<i>n</i> -Octyl alcohol.....	130.23	195	0.3 (approx.)
CARBONYL COMPOUNDS <sup>a</sup>			
Acetaldehyde.....	44.05	21	2.5-5
Butyraldehyde.....	72.10	75.7	0.1-0.2
Crotonaldehyde.....	70.09	104-105	0.05 (approx.)
Acetone.....	58.08	56.5	0.3-0.5
Methyl ethyl ketone.....	72.10	79.6	0.1-0.2

<sup>a</sup> Closer investigation of the carbonyl compounds in the by-products also revealed the presence of *n*-valeric, *n*-capronic, and *n*-caprylic aldehydes.

S. V. Lebedev, G. Kobliānskiĭ, N. Z. Andreev, I. A. Volzhinskiĭ, Ū. A. Gorin, I. K. Gorn, G. N. Sibirĭakova and Ī. A. M. Slobodin, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 3, 44 (1934).

(2) As a result of such changes in technique, aldehyde can no longer be considered a major by-product of the Lebedev catalysis. It is completely

reprocessed with the alcohol slip through, except for small mechanical losses amounting to a few tenths of one per cent.

(3) Because ethylene is a primary product of the catalytic action of the dehydrating catalyst component, its concentration has undergone no drastic changes. Instead of the 5–8% shown in table I-4, it may be assumed today to be in the region of 4–6%. With the introduction of improved analytical methods for fractions boiling below  $-4^{\circ}\text{C}$ . (Podbielniak distillation), it was discovered that about 30% of the fraction designated as "ethylene" in table I-4 is actually propene.

(4) The percentage of butene-2 has dropped off somewhat and is now probably in the region of 2–3%. Along with the concurrent increase in the butadiene yield, this factor has contributed to greater purity of the "rectified butadiene" going to the polymerization.

(5) Ether, from all indications, has remained at a level of 2–5%. This is perhaps understandable in view of the reduced temperature at which the catalysis is now carried out with the more advanced catalysts (below  $400^{\circ}\text{C}$ .).

(6) Higher alcohols (with more than 4 carbon atoms) are less stable in the presence of modern, more powerful, compound catalysts, and are less fully and less extensively represented in the material balance.

## B. FACTORS INFLUENCING THE LEBEDEV CATALYSIS

The simultaneous dehydration and dehydrogenation of ethyl alcohol is a reaction accompanied by an increase in volume. In the ideal case, the volume (in gas phase) is doubled. The process is endothermic. Under factory conditions, 220 kcal. is required to convert catalytically one kilogram of ethanol.<sup>23</sup>

It is evident from thermodynamic considerations that high temperature and low pressure (atmospheric or subatmospheric) will favor a catalytic reaction of this type. Beyond this, the selection of optimal processing conditions becomes, in the main, an empirical task.

In speaking of optimal processing conditions, several criteria can be applied.

(a) It may be desirable to obtain the highest possible butadiene yield. "Yield" will be used to designate the percentage of butadiene obtained from the catalytic conversion of a given amount of absolute alcohol. The figure of 58.7% will represent a theoretical maximum (see page 2).

<sup>23</sup> A. I. Gelikh and V. P. Komarov, *Sintet. Kauchuk*, 1, No. 1, 16 (1932). Figure relates to an early catalyst.



(b) The aim may be a maximum butadiene "output" for a given apparatus, *e. g.*, expressed in kilogram butadiene per apparatus-hour.

Butadiene "yield" and "output" are only partly interrelated. The correlation is provided by:

(c) The amount of alcohol feed stock that escapes catalytic conversion and appears in the products of the reaction. This will be designated as "alcohol slip through" and expressed in per cent of feed stock, or, alternatively, in tons of alcohol escaping conversion for each ton of butadiene produced.

In practice, the economy of operation will depend on all three parameters, (a), (b), and (c). Unfortunately, as will be shown in the following discussion, their optima do not coincide. The parameters of efficiency are complex functions of a great number of extraneous conditions, of which the most obvious are:

(1) Activity of the catalyst, which in turn will depend upon its chemical and physical nature, the degree of subdivision, method of activation, poisoning of the catalyst, mode of reclaiming, and other factors common to problems of heterogeneous catalysis.

(2) Temperature conditions.

(3) Pressure.

(4) Time of contact (rate of delivery of feed stock).

(5) Admixtures to the feed stock.

The integral picture is highly involved. Nevertheless, an attempt will be made to trace the influence of the individual conditions upon the efficiency of the process, on the basis of disclosures of Lebedev and co-workers. As in the preceding section, the data will refer to an earlier catalyst which was not so highly efficient. The trend outlined is, however, of general significance.

## 1. Activity of the Catalyst

### A. COMPOSITION

To recapitulate, the catalyst is a mechanical mixture of its two components, *A* and *B*. Component *A* is the dehydrogenating part, promoting the "hydrogen-aldehyde" decomposition. *B* is the dehydrating component, causing the "water-ethylene" split. More recently, improved catalysts contain added promoters, (*c*) and (*d*).

When the relative proportions of *A* and *B* are varied and the products analyzed, results of the type shown in table I-5 and plotted, in the more pertinent part, in figure I-3 are obtained. As will be observed, the reaction

catalyzed by component *B* is more complete in nature (more efficient) than the reaction promoted by component *A*.

A catalyst consisting of component *B* only, converted all the alcohol processed, and the catalytic efficiency of the water-ethylene split reached 92%.

TABLE I-5  
COMPOSITION OF THE CATALYSTS<sup>a</sup>

Constituent	Catalyst composition						
	100A	90A:10B	75A:25B	50A:50B	25A:75B	10A:90B	100B
Alcohol feed stock (87°), g.	2800	2850	2800	2750	2900	2950	2800
Alcohol returned (87°), %	68.4	70.5	59.3	25.6	6.9	6.8	0.0
Alcohol converted (87°), %	31.6	29.5	40.7	74.4	93.1	93.2	100.0
Obtained:							
Liquor condensate, g.	2650	2600	2450	1900	1500	1550	1400
Gas, l.	252	230	342	731	1021	1060	1193
Composition of gas:							
C <sub>n</sub> H <sub>2n</sub> , % by vol.	20.0	35.5	43.5	84.5	95.5	99.2	98.0
H <sub>2</sub> , % by vol.	66.0	60.3	52.6	12.8	3.9	0.45	1.75
CO, % by vol.	4.1	0.28	0.64	0.41	0.0	0.0	0.0
CO <sub>2</sub> , % by vol.	6.35	3.35	1.92	0.61	0.91	0.0	0.0
CH <sub>4</sub> , % by vol.	1.58	0.0	0.42	0.40	0.0	0.0	0.0
Butadiene content per liter gas, g.	0.18	0.32	0.50	0.20	0.05	0.023	0.00
Yield of products expressed as % (by wt.) of absolute alcohol converted:							
Ethylene	2.25	3.08	5.85	31.0	45.3	45.5	55.7
Ether	4.4	7.13	7.25	3.52	0.69	0.52	0.00
Aldehyde	9.65	10.02	4.36	1.95	1.15	0.89	0.7
Hydrogen	1.72	1.57	1.59	0.45	0.14	0.018	0.07
Butadiene	5.8	10.1	16.6	8.2	2.26	0.99	0.00

<sup>a</sup> Pilot installation: "one-meter retort" (page 41), 435-445° C.

In contrast is component *A*, which, when used by itself, catalyzed under the same physical conditions the conversion of only 30% of all the alcohol processed, allowing almost 70% of alcohol to pass through unchanged. That the reaction is much less unilateral is indicated by the variety of by-products formed, especially of small amounts of ethylene, ether, and butadiene. In fact, component *A* is a dehydrogenating catalyst in a limited sense only.

In the light of Lebedev's theory, we should expect a maximum butadiene yield when the joint catalytic action of *A* and *B* results in the formation of equal amounts of olefin and carbonyl fragments [*a*] and [*b*] (see page 6). It is therefore not surprising that an optimal composition of catalyst corre-

sponds to a mixture of approximately 75% component A and 25% component B. Figure I-3 stresses the close relationship between maximum butadiene yield and balanced yields of acetaldehyde and ethylene.

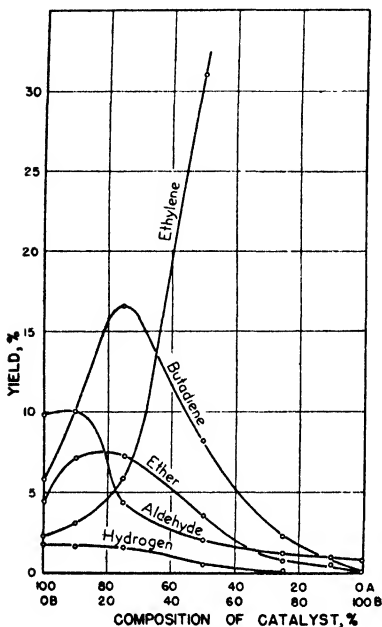


Fig. I-3.—Effect of catalyst composition on yield of major dehydration and dehydrogenation products.<sup>25</sup>

to 80° C. in a moderate current of air. In the drying, agglomerations are formed which are easily broken apart into individual cylinders. The dust is sieved off. Such a catalyst is activated at elevated temperature, whereby further quantities of water (part of which is chemically combined water<sup>24</sup>)

<sup>24</sup> An example is floridin (Florida earth), a hydrosilicate. A typical floridin may contain: 55.3% SiO<sub>2</sub>; 21% (Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>); 4.3% (MgO + CaO); 1.9% (K<sub>2</sub>O + Na<sub>2</sub>O); and 17.9% H<sub>2</sub>O. When heated for 2 hours at 275–325° C., it loses 12–12.5% water and then exhibits maximum dehydrating activity. S. V. Lebedev and Ū. Borgman, *Zhur. Obshchei Khim.*, 5, 1595 (1935).

<sup>25</sup> S. V. Lebedev, I. A. Volzhinskiĭ, Ū. A. Gorin, A. I. Gulfaeva, G. M. Kogan, S. G. Kibirskhtis, G. G. Koblĭanskiĭ, V. P. Krauze, M. A. Krupyshev, I. A. Livshits, S. M. Orlov, Ī. A. M. Slobodin, S. A. Subbotin, M. A. Khokhlovkin, A. N. Reshetov, and A. M. Tatarnikov, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 3, 16 (1934).

## B. SHAPE AND PREPARATION

In view of the fact that the two catalytic functions must proceed simultaneously and in close proximity, an intimate mixture of the catalyst components must be provided. This is achieved by grinding the components individually in porcelain ball mills to a particle size of less than 0.3 millimeter, mixing them and homogenizing the mixture in rotating drums for 4 to 6 hours. To the dry mixture of powders, an equal weight of water is added, and the powder worked into a heavy paste. After about 30 minutes, a certain amount of "seizing" takes place, accompanied by a slight increase in temperature. The paste is pressed through copper sieves having perforations about 3 millimeters in diameter, whereby it assumes the shape of small curved

are removed. Earlier catalysts were activated for 10 hours at 500° to 550° C. in a slight current of air. (A more recently used catalyst requires a longer time at lower temperature. See page 50.) The density of the reground activated catalyst was 2.77 to 2.96 grams per cc.

Since heterogeneous catalysis is a surface phenomenon, the dispersity of the catalyst will play an important part. The shape and size of the particles were investigated by Lebedev and his coworkers,<sup>25</sup> who found that the loose form of catalyst in the shape of free-baked, curved cylinders is superior to catalyst pellets formed by compression. Figure I-4 gives a typical result, and confirms that the surface area for any given mass of catalyst has a profound effect upon the butadiene yield. The area recorded in the figure is only the outward geometrical surface. The cylinders are no doubt porous, and the true surface of the catalyst is not exactly known. Attempts were made to incorporate combustible substance with the catalyst mixture to increase its porosity, but no final results were reported. Summing up their work on the state of subdivision of the catalyst, the investigators

concluded that the most advantageous form of compound catalyst is a loosely packed mass of small curved cylinders, one to three millimeters in diameter. A limiting factor to the reduction in the grain size of the catalyst is the contingency that too fine a catalyst may be carried away by the rapid flow of the gas in the retorts (see page 50).

The macroscopic grain size must not, however, be confused with the size of crystallites, the smallest crystalline regions with a regular space lattice. Rubinshtein<sup>26</sup> reported an optimal size of crystallites (as revealed by x-ray methods) to be found in the range of 70 to 90 Å. for the binary catalyst of the Zelinskiĭ-Komarevskiĭ type (see page 7).

### C. CONSTRUCTION OF RETORTS AND QUANTITY OF CATALYST

It was found that the composition of the retort has some bearing upon the catalytic process. Iron is inferior to copper. However, glass-lined or aluminum-lined iron gives results equal to those for copper. Retorts used

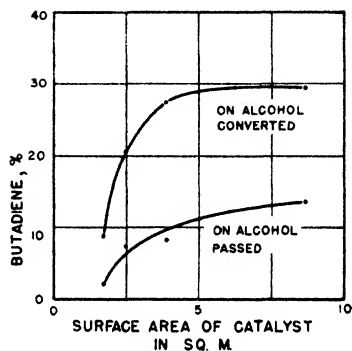


Fig. I-4.—Butadiene yield vs. catalytic surface.<sup>25</sup>

<sup>26</sup> A. Rubinshtein, *Zhur. Fiz. Khim.*, **14**, 1209 (1940).

in production are often glass-lined with fire-resistant enamel. The shape of the catalytic retort seems to be of no consequence, provided a uniform temperature distribution is assured. Smirnov<sup>27</sup> found that, independently of the construction of the catalytic chamber, the optimum output of butadiene obtainable from a retort in a given time, all other factors being equal, is proportional to the quantity of catalyst employed.

#### D. POISONING AND RECLAIMING OF THE CATALYST

Lebedev and coworkers observed from the onset a progressive decline in the efficiency of their catalysts with age. This is in keeping with general

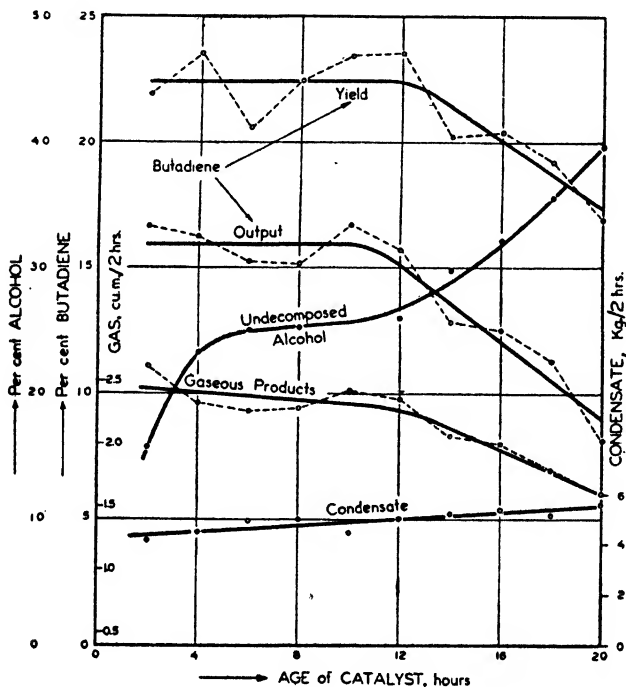


Fig. I-5.—Effect of progressive "tiring" of catalyst on balance of Lebedev catalysis.<sup>25</sup>

experience. Both the absolute amount of gas generated from a given amount of alcohol and the amount of butadiene in the gas decline with time. The butadiene concentration of any one liter of gas, however, remains fairly constant. Figure I-5 typifies the progressive deterioration.

<sup>27</sup> N. I. Smirnov, *Sintet. Kauchuk*, 3, No. 1, 13 (1934).

In a pilot-plant experiment with a constant rate of alcohol feed, the liquid and gaseous reaction products were metered every two hours. The former were analyzed for unconverted alcohol and the latter for butadiene. From such analytical data, the yield and output of butadiene, as shown in figure I-5, were arrived at.

It appears that, after about 14 hours' operation, the efficiency of the catalyst begins to decline; and at the end of 19 hours the yield of butadiene, calculated in per cent of the alcohol converted, has fallen from the initial 23% to about 17%.

The main reason for the "fatigue" of the catalyst is to be found in the fact that carbon becomes deposited on its surface, clogging its pores and reducing the active areas available. Furthermore, the carbon itself acts as a catalyst, influencing the process in an undesirable direction. Carbon is formed on the catalytic surface, evidently as a result of a thermodecomposition of organic molecules whose limits of thermal stability are below the temperature of the catalytic reaction. Observations of Lebedev<sup>28</sup> and other authors<sup>29</sup> suggest that carbon is deposited irregularly over the surface of the catalyst. It is mainly associated with the dehydrating component, *B*. Usually 1 to 2% of carbon, on the weight of the catalyst, is formed during a run of 12 to 16 hours (*i. e.*, 0.16 to 0.23% on the alcohol delivered). Carbon deposits more readily on a fresh than on a regenerated catalyst.

The contention that a carbon screen is deposited, in the main, on the dehydrating centers of activity finds support in the changes taking place in the material balance. In the gaseous products, an increase in hydrogen and a reduction in unsaturated hydrocarbons (ethylene) are observed. Simultaneously, the condensate becomes richer in carbonyl compounds (aldehyde). The total amount of alcohol decomposed decreases. The reduction in the number of available ethylenic fragments, [*a*], is unfavorably reflected in a diminished butadiene yield, while butene-2 and water insoluble hydrocarbons, whose formation is visualized via the aldehyde-type fragment [*b*], increase in quantity.

The theory of the reactive fragments, [*a*] and [*b*], finds further support in the fact that, while the ratio of butene-2 to butadiene rises with increasing "fatigue" of the catalyst, the sum of the two remains constant.

The catalyst is reactivated by burning the carbon deposited on it in a current of air. For this purpose, the delivery of alcohol is interrupted; the chamber is "blown out" with steam (to forestall an explosion); the temperature is brought to 450° C.; and air is fed into the chamber. Since

<sup>28</sup> S. V. Lebedev *et al.* See also footnote 25.

<sup>29</sup> Ū. A. Gorin, O. M. Nelmark, and F. Kogan, *Sintet. Kauchuk*, **4**, No. 5, 6 (1935).

the catalyst, or rather its component *B*, is rendered inactive at temperatures above 600°, air must be introduced carefully in order that the combustion of carbon does not cause overheating of the catalyst. Normally, the temperature is maintained at 520° to 550° C. The combustion of carbon does not occur throughout the entire mass of the catalyst at one time, but begins instead in the zone which first comes into contact with air, and extends gradually from this area throughout the mass.

The uneven deposition of carbon makes inevitable occasional local overheating, which can be effectively combated only by throttling the air stream. In factory operation, reactivation is often accomplished with a mixture of air and steam. The progress of the reactivation is watched by analyzing the amount of carbon dioxide in the escaping air. The time required to regenerate the original catalyst in the "one-meter chamber" was 8 to 10 hours (after 12 hours' contacting time). Tests have shown that regeneration can be materially speeded up, by delivering air simultaneously to different regions of the chamber. See page 50. Regeneration is discontinued as soon as the carbon dioxide content of the escaping gas falls below 1%. Further (absolute) regeneration fails to improve the butadiene yield.

The working qualities of the reclaimed catalyst have been ascertained by a series of pilot-plant experiments, each consisting of a 12-hour contacting cycle, followed by a regeneration at 500° to 550° C. which was continued until no carbon dioxide was detected in the escaping gas. Up to and including the tenth consecutive cycle, the butadiene yield was in the region of 20% (on absolute alcohol converted); then it fell to 16%, and, beginning with the twenty-first consecutive regeneration cycle, to 14%. The useful life of more recent catalysts is in the neighborhood of 1000 hours. See page 50.

Changes taking place in the material balance of catalysis strongly suggest that the decline in activity of the catalyst after repeated regeneration is due to the same underlying mechanism as the decline caused by carbon deposition, *i. e.*, a deactivation of the dehydrating component *B*. In the case of deactivation through repeated regeneration, the decline in catalytic activity is probably due to changes in the crystalline structure of component *B* under the influence of heat.

## 2. Temperature

### A. HEAT OF REACTION

As already mentioned, the process of catalytic conversion of ethanol to butadiene is endothermic, to the extent of some 220 kcal. per kilogram

*absolute* alcohol converted. The reaction does not proceed uniformly throughout the mass of the catalyst. It is more intense in the catalytic layers first to encounter the alcohol vapors. Consequently, heat consumption also is greatest in the regions closest to the alcohol intake.

It was shown,<sup>26</sup> by dividing a layer of catalyst (total height, 3 meters) into four individually heated areas of 0.75 meter each, that almost three times as much heat was required to maintain the first region at 425° to 450° C. as was required for each of the subsequent regions. The alcohol was preheated to 425° to 450° before entering the catalytic zone.

The greater intensity of reaction in the bottom layers of the catalyst causes these layers to lose their efficiency more rapidly.

#### B. PREHEATING OF ALCOHOL

The foregoing discussion indicates that the preheating of alcohol is important. It was shown that, for a given height of catalytic layer, the butadiene yield dropped from 19.4 to 12.0% when the temperature at which alcohol entered the retort was lowered from 450° to 300° C. It appears that, in the latter case, a part of the catalyst acted purely as a preheater. On examination, the layer of catalyst first encountered by the alcohol was found to be noncarbonized and white in color, even after a prolonged run.

#### C. TEMPERATURE OF REACTION

A number of factors must be borne in mind in considering the effect of temperature on the yield of the catalytic reaction:

(a) Butadiene becomes less stable at high temperatures. Increased temperatures, therefore, while generally activating the catalyst in an endothermic reaction, at the same time tend to promote the decomposition of the butadiene formed, provided it remains long enough in the high-temperature zone (at the catalyst).

(b) Increased temperatures may activate the two individual components of the compound catalyst to a different degree, throwing their action "out of balance," and thus creating an adverse effect.

(c) Temperature also affects the active life of the catalyst.

The stability of butadiene at elevated temperatures will be discussed at some length in the chapter on thermopolymerization (page 110).

#### D. TEMPERATURE AND CATALYTIC ACTION

Other implications of increased or decreased temperature, as pertaining to the original Lebedev catalyst, are illustrated by the following series of



experiments. Extreme upper and lower temperature limits for the reaction scheme are suggested by the nature of the dehydrating component *B*. Below 300° C., the ethylene-water split loses precedence over the ether-water dehydration. Above 600° C., component *B* becomes inactive. Excluding for the time being any decline of catalytic activity with time, and keeping the rate of alcohol delivery, as all other factors, constant, experiments for the purpose of studying temperature effect within the limits of 360° to 475° C. produce the typical results shown in figure I-6.

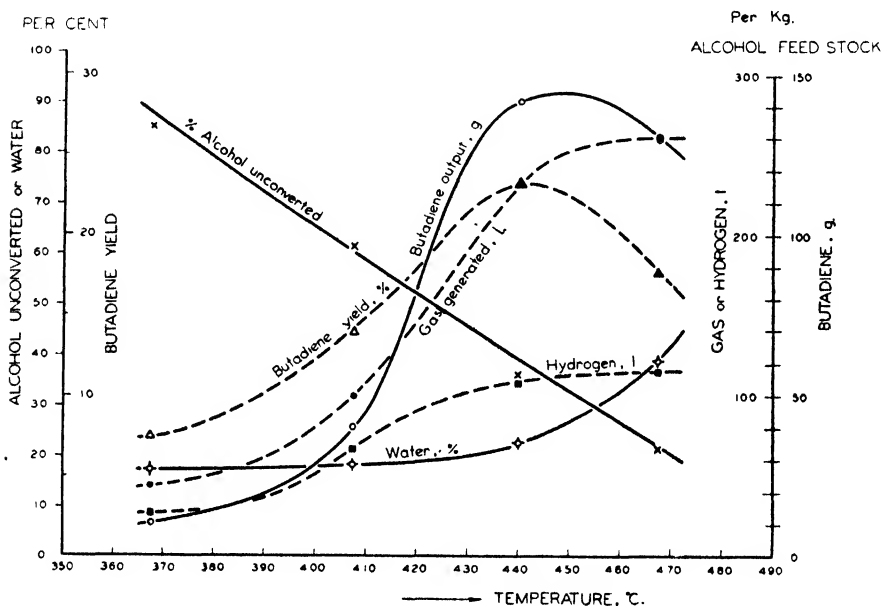


Fig. I-6.—Effect of temperature on Lebedev catalysis.

The experiment extended in each case over a period of 24 hours. The "one-meter retort" was used, the rate of alcohol flow being 10.3 to 10.4 ml. per hr. per sq. cm. It may be observed that an increase in temperature activates both the dehydrogenating and the dehydrating components of the catalyst, as is borne out summarily by the sharp and almost rectilinear decrease in the percentage of alcohol escaping conversion. It is also reflected in the increase in the amounts of hydrogen and water among the products of the reaction over the broad temperature range. These increases are, however, not linear. The curve for water rises very slowly in the range of 360° and 420° C.; at higher temperatures, the increase be-

comes steeper. The dehydrogenation (hydrogen curve) is activated particularly in the temperature range up to 430°, above which the curve seems to flatten out.

Temperatures below 420° C. cannot be considered an economical range, if the alcohol "slip through," the butadiene "yield," and the "output" are taken into account. At temperatures above 450°, the activity of the two catalyst components seems to get "out of step," so that, despite the greater percentage of alcohol decomposed and the larger amount of gas generated, both the butadiene yield and the butadiene output drop off.

TABLE I-6  
EFFECT OF TEMPERATURE ON CATALYTIC ACTIVITY

Factor	Temperature of catalytic reaction, °C.				
	420	440	450	460	470
Butadiene yield, % absolute alcohol converted	26.0	24.5	25.3	22.4	22.5
Butadiene output, % absolute alcohol feed stock	9.5	11.1	12.7	12.9	13.7
Output per retort, kg. butadiene per hour	6.1	7.5	7.7	7.8	8.2
Alcohol returned undecomposed, %	67.2	59.2	54.8	48.2	45.2

TABLE I-7  
EFFECT OF TEMPERATURE OF CATALYSIS ON RECLAIMING TIME

Temperature of catalytic reaction, °C.	Average time of reclaiming, % of time of contacting, <i>i. e.</i> , 11.5 hours
420.....	47.8
440.....	67.2
450.....	78.2
460.....	98.0
470.....	104.3

Smirnov,<sup>30</sup> working under actual factory conditions, confirmed that no real practical gains can be attained by varying the temperature beyond the limits of 420° to 450° C. His data are summarized in table I-6. Smirnov showed that, within these temperature limits, the butadiene yield, expressed as a percentage of the alcohol decomposed, changes very little. Above 450°, it falls off rapidly, offsetting any possible advantage derived from a smaller return of undecomposed alcohol and a fractionally higher output of butadiene per hour and apparatus.

<sup>30</sup> N. I. Smirnov, *Sintet. Kauchuk*, 3, No. 1, 13 (1934). See also A. and L. Talalay, *Rubber Chem. Tech.*, 15, 421 (1942).

A further economic consideration is the fact that increased temperature materially prolongs the time required to reactivate the catalyst<sup>30</sup> (see page 29). This is convincingly shown in table I-7. Increased temperature also shortens the "active life" of the catalyst. Although there is only scanty evidence of the fact in the literature, it appears that, with more recent catalysts, the Russians were successful in reducing the temperature of catalysis to below 400° C.

### 3. Rate of Alcohol Delivery

On the whole, the rate of delivery of alcohol (time of contact with the catalytic layer) affects the yield of butadiene far less than does the temperature. The alcohol "slip through," however, is affected. Figure I-7

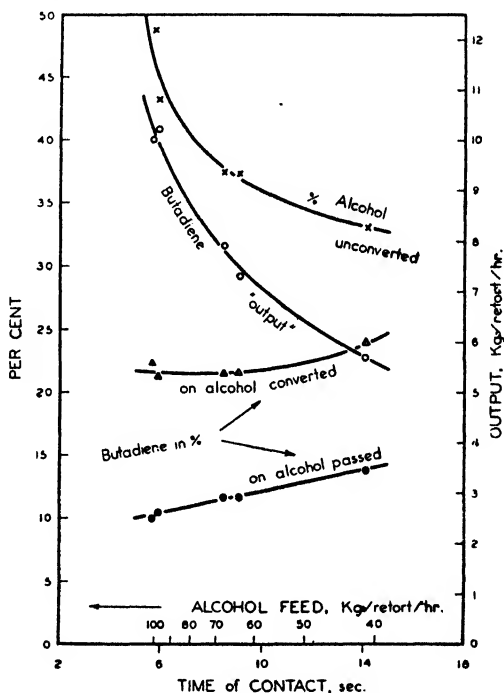


Fig. I-7.—Effect of rate of flow on the Lebedev catalysis.<sup>30</sup>

illustrates the effect of the contact time under actual factory conditions and at the standard temperature of 435° C., as reported by Smirnov.<sup>30</sup> The curve marked "output" clearly shows that distinct advantages can be

gained from a shorter contact time, *i. e.*, a higher delivery rate of alcohol feed stock to the retorts.

#### 4. Combined Effect of Increased Temperature and Increased Rate of Delivery

At increased temperatures, the reaction is enhanced. A similar effect, though less pronounced, attends a decrease in the rate at which alcohol is delivered to the reaction chamber. Furthermore, at a rapid rate of delivery, the temperature effect is lessened because the alcohol vapors remain in contact with the catalyst for a shorter time. Therefore, at a higher temperature and a faster rate of delivery, a normal yield of butadiene should be obtained; by this means it might be possible to increase sub-

TABLE I-8  
JOINT EFFECT OF TEMPERATURE AND RATE OF FLOW

Factor	Temperature of experiment, °C.		
	410-415°	435-445°	460-475°
Alcohol delivery, cc. per sq. cm. per hr.	9.9	10.3	24.4
Gas, l. per kg. alcohol delivered	151	232	308
Water in condensate, % by wt. of alcohol delivered	12.9	22.6	24.7
Alcohol returned, %	57.9	36.0	24.7
Aldehyde, % by wt. of alcohol delivered	0.9	1.35	2.7
Butadiene, g. per liter gas	0.62	0.61	0.52
Unsaturated compounds in gas, %	45.0	50.0	45.5
Hydrogen in gas, %	53.0	46.5	48.2
Butadiene yield, % of alcohol converted	23.1	23.2	22.3

stantially the productivity of a given contact chamber. This is illustrated by the experimental series in table I-8 in which both the temperature and rate of delivery were varied simultaneously in the pilot installation. It may be seen that a simultaneous increase in both temperature and rate of alcohol delivery can produce a normal butadiene yield for the type of catalyst used. (It is well to recall, though, that higher temperatures adversely affect the life of the catalyst.)

#### 5. Pressure

A reduction in pressure in the retort, up to about 130 mm. Hg, improves the butadiene yield, although a further reduction, beyond 240 mm. Hg, then decreases the yield. In the same fashion, increased pressures (above atmospheric) are unfavorable, leading to a reduced yield of gas and a lower butadiene content of the gas, which jointly lower the yield of butadiene.



## II. TECHNOLOGY OF THE S.K. PROCESS

A flowsheet of the Lebedev synthetic rubber process is presented in figure II-1. The diagram also indicates the major by-products of the process and the stage at which each is separated.

Alcohol vapors superheated to the required temperature pass through catalytic reactors in which they undergo simultaneous dehydration and dehydrogenation. The products of this catalytic decomposition constitute a mixture of vapors and gases. They are led through a two-stage condensing system. Gases and vapors of more volatile liquids pass on, while two fractions of condensate are collected.

The condensates contain considerable quantities of by-products, which are separated by fractional rectification and washing. At this stage, unconverted ethyl alcohol is also recovered, rectified, and returned via the evaporator to the catalytic reactors.

Butadiene remains uncondensed. It is extracted from the gas phase in absorption towers irrigated with alcohol, in which it is soluble. Along with vapors of butadiene, butene-2 and a number of other volatile liquids are absorbed.

The "inert" gas not absorbed in the towers is collected. It consists mainly of hydrogen and ethylene, and has a high calorific value.

The vapors retained by the absorbent are desorbed by heating, washed with water to extract further quantities of aldehyde, and finally subjected to rectification.

Wash water and rectification bottoms are each redistilled to separate further by-products.

The resultant butadiene rectificate (now containing butene-2 as the only major impurity) is mass polymerized with metallic sodium. The crude polymer is kneaded under vacuum to remove the butene-2 which did not polymerize. Simultaneously, antioxidants are added. The final step is mill refining of the synthetic elastomer.

The following discussion of the technology of the S.K. process is divided into three main parts:

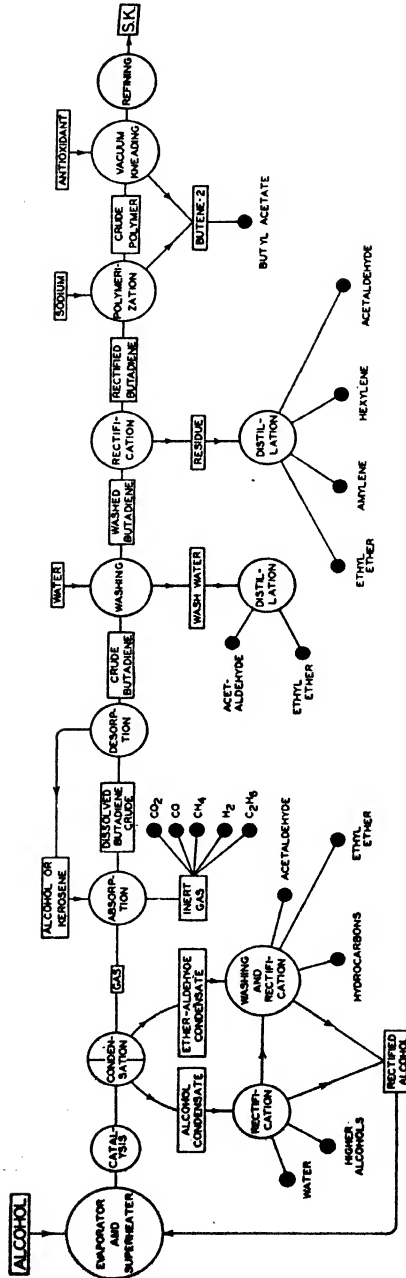


Fig. II-1.—Flowsheet of Lebedev process.

- (1) a brief description of a laboratory apparatus,
- (2) a brief description of a pilot plant, and
- (3) the salient details of commercial installations.

Even at the risk of becoming somewhat repetitious, this presentation has been chosen as having the advantage of better continuity. It is also in line with the historic sequence of development.

### A. LABORATORY INSTALLATION

Aside from a microinstallation used to process samples of alcohol as small as 5 ml. in 50 to 60 min., some of the preliminary work was carried out with

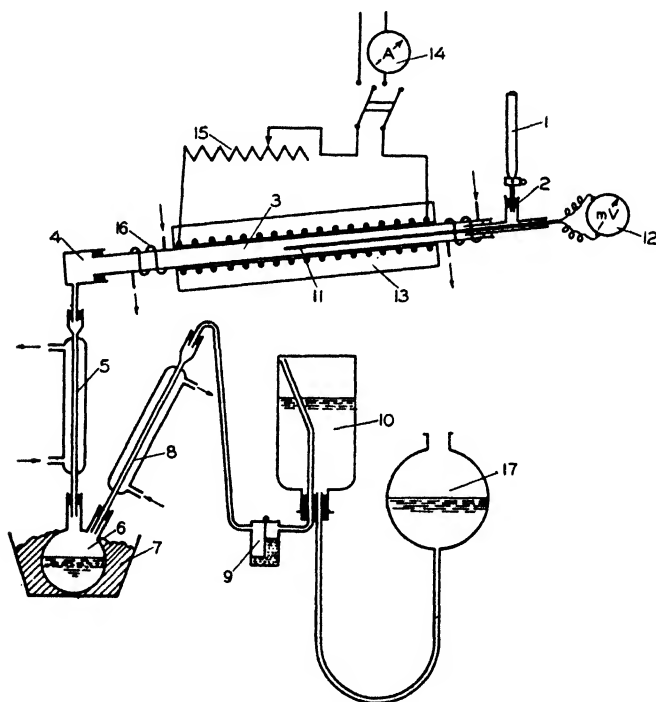


Fig. II-2.—Laboratory installation.<sup>31</sup>

a so-called "laboratory set-up,"<sup>31</sup> which was later employed as standard equipment by the control laboratories of the S.K. factories.

<sup>31</sup> S. V. Lebedev, I. A. Volzhinskii, S. G. Kibirskhtsi, G. G. Kobl'anskii, V. P. Krauze, M. Krupyshev, and A. M. Slobodin, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 3, 7 (1934).



The installation is shown (but not to scale) in figure II-2. The reactor, 3, containing the catalyst is a copper tube 90 cm. long, and with an internal diameter of 28 to 30 mm. It is placed in a tubular electric combustion furnace, 13, provided with rheostat 15 and ammeter 14. The protruding ends of 3 are cooled with lead pipe coils, 16, through which water is circulated. One end of tube 3 is provided with T-shaped adaptor, 2, receiving a burette for alcohol, 1, and a porcelain well for thermocouple, 11, leading to mV-meter 12. The thermocouple well extends halfway into tube 3. The opposite end of tube 3 is joined through a copper elbow, 4, to a condenser, 5, which is 45 cm. long and is mounted atop a two-neck flask, 6, of 250-ml. capacity. The flask is placed in a bath of ice water, 7.

When alcohol is fed, at a rate metered by burette 1, over the heated bed of catalyst at 400° to 450° C., partial decomposition takes place, resulting in a mixture of gases and vapors. The vapors condense in a flask, 6. The gaseous products, after passing through condenser 8, which is identical in size with 5, and check valve 9 (of 250-ml. capacity and filled with 50% NaOH for removal of acetaldehyde), are collected in the 15-l. gas flask, 10 (graduated in units of 250 ml.). A 50-mm. Hg vacuum can be created in the system by lowering leveling bottle 17.

Normally, 50 ml. of alcohol is processed in each experiment (of one-hour duration), and the tube is filled with 65 g. of catalyst. The amounts of liquid and gaseous products of the reaction are measured.

The number of problems that can be investigated with such an installation is necessarily limited.

## B. PILOT INSTALLATION

A more complete pilot installation, capable of processing 3 to 6 liters of alcohol per hour, has been described by Lebedev, Volzhinskiĭ *et al.*<sup>31</sup> With this unit (shown in figure II-5, page 42), most of the data necessary for the design and construction of large-scale plants were obtained.

### 1. Catalytic Conversion

Alcohol is delivered from pressure tower 1, through a distributing manifold to six glass measuring devices, 2. From here it is dispensed through drip valves to evaporators and superheaters 3. After having reached a temperature of 400° to 425° C., alcohol enters the contact chambers, 4, which are filled with the catalyst.

The installation comprises six parallel catalytic converters, 4. One such unit is shown in greater detail in figure II-3. The retort is 1 m. long and 10

cm. in diameter, and has two end flanges. The top flange is removable, and is connected to an individual alcohol evaporator and superheater, 3. The bottom flange is welded on, and contains a well for a thermocouple and a perforated tube through which products of the catalytic reaction are withdrawn.

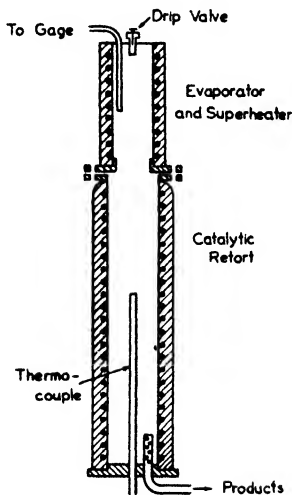


Fig. II-3.—Catalytic reactor (pilot installation).<sup>31</sup>

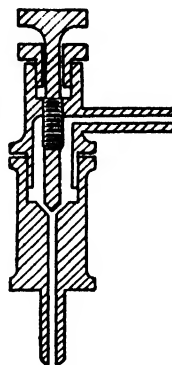


Fig. II-4.—Drip valve for metering alcohol.<sup>31</sup>

The evaporator consists of a copper tube filled with copper rings. The alcohol is introduced through a drip valve (Fig. II-4) at the top of the tube, which also has a connection for a pressure gage.

Each superheater and reactor is electrically heated by a single winding of chrome-nickel wire and is individually controlled. The chamber is heat-insulated with asbestos, containing air spaces.

## 2. Condensation and Absorption

The gaseous and liquid products of the reaction pass (Fig. II-5) through cooler 5, a coiled copper tube, into the receivers, 6, which can be interconnected. Condenser 5 and receivers 6 are placed in a common bath of ice water.

Some of the gaseous products remain dissolved in the condensate. The bulk, however, is removed through the rotary exhaustor, 7, which operates at a vacuum of 30 to 50 mm. of mercury. The gases are pumped through

II. TECHNOLOGY OF THE S.K. PROCESS

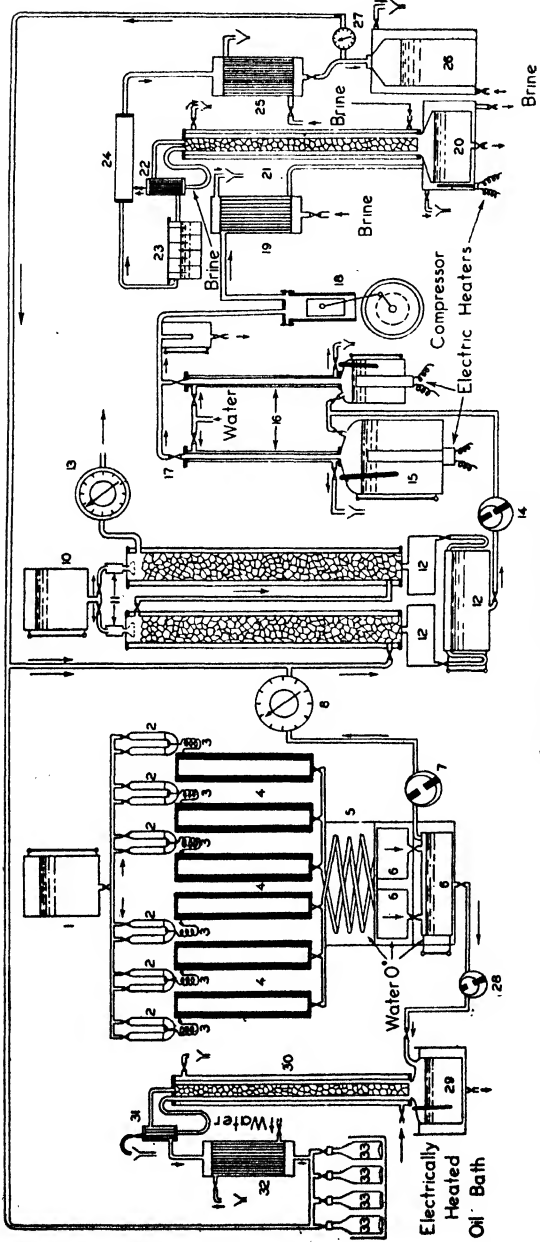


Fig. II-5.—Pilot installation.<sup>31</sup>

the clock 8 to two absorption towers arranged in series. The towers, which are made of iron pipe, are packed with coke and are sprayed, 11, from a pressure feed tank, 10, with alcohol, turpentine, or some other suitable absorbent. The saturated absorbent is collected in three receivers, 12. The gases escaping from the top of the second tower go through gas clock 13 to a storage tank.

### 3. Desorption

The absorbent, saturated with butadiene, is pumped into two copper stills, 15, provided with electric heating elements, and its temperature is raised. When, for instance, turpentine is used as the absorbent, butadiene and the accompanying butene-2 begin to boil over at 30° to 35° C., the major portion is liberated between 100° and 130°, and the final amounts of gas escape at 140° to 150°. The latter temperature is maintained for at least 15 to 30 minutes before the desorption process can be considered complete. To prevent turpentine vapors from passing over into receiver 20, the desorbed gases are led through water-cooled reflux condensers, 16.

At times, the reciprocating pump, 18, was used, reducing the pressure to 400 mm. Hg, in which case the maximum temperature at which the last traces of butadiene are liberated is reduced to 110° to 130° C.

The mixture of gases is now liquefied by brine cooling to -20° C. in condenser 19, and stored in receiver 20, which is designed to withstand a pressure of 10 atmospheres.

By using compressor 18 and increasing the pressure in receiver 20 to 3 or 4 atmospheres, it becomes possible to cool with cold water (eliminating the brine).

### 4. Rectification

The crude butadiene mixture contains 82% of fractions boiling below 4° C. and about 18% of fractions boiling above 4°. The former contain butadiene, butene-2, etc.

To isolate the low-boiling fraction, the crude butadiene is now rectified by using receiver 20 as a still. The coke-packed and jacketed tower, 21, and dephlegmator 22 comprise the remainder of the rectification unit. In carrying out the rectification, water is now substituted for the brine solution in the jacket of 20, and a heating element is immersed. When working at atmospheric pressure, the water in the jacket is heated to 25° or 30° C.

### 5. Washing and Drying

To remove final traces of acetaldehyde, the gas issuing from the partial condenser, 22, is bubbled through a row of three to four washers, 23, filled with a 50% alkali solution. The gas is then dried by passing it through iron tube 24 packed with calcium chloride. It is recondensed in cooler 25, of the same construction and type as cooler 19, and finally collected in receiver 26, which is provided with a reducing valve, 27.

When the rectification is carried out at atmospheric pressure, 21, 22, and 25 are cooled with brine solution in such a way that the temperature in dephlegmator 22 at the end of the rectification does not exceed 2° C., while cooler 25 and receiver 26 are cooled to -20°. If the rectification is carried out at an increased pressure, the dephlegmator can be water-cooled. In such a case, condenser 25 and receiver 26 are refrigerated with ice water.

The crude butadiene normally contains small quantities of dissolved permanent gases, which are the first to escape during the process of rectification and carry with them a certain amount of butadiene. They are, therefore, released through reducing valve 27 and returned to the gas line just ahead of the absorption towers.

The rectified butadiene stored in receiver 26 is transferred to polymerization vats, and there polymerized to the crude synthetic elastomer.

### 6. Recovery of Alcohol and of By-Products

The liquid reaction products of the catalytic decomposition, which have been collected in receivers 6, are pumped into another receiver, 29, located in an electrically heated oil bath. They are rectified in the system consisting of tower 30, dephlegmator 31 and a water-cooled total condenser, 32. As already stated, some of the butadiene is retained in a dissolved state in the liquid reaction products. When the latter are subjected to rectification, the dissolved gases (mostly butadiene) come off first. These are led by means of a special line to a junction point ahead of the absorption towers. The liquid products are gathered in water-cooled receivers, 33, and stored there for further fractional distillation.

### 7. Dimensions of the Pilot Installation

The capacity of pressure tower 1 is 10 l. Each of the two small receivers, 6, also has a capacity of 10 l. The capacity of the large receiver, 6, is 48 l. The absorption towers are 180 cm. high and 15 cm. in diameter and the volume of their feed tank, 10, is 42 l. The volume of each of the small re-

ceivers, 12, is 20 l., and that of the large one, 100 l. The stills, 15, have capacities of 100 and 25 l., respectively. The coolers, 16, are each 1 m. high and 18 mm. in diameter. The cooling surface of condenser 19 is 600 sq. cm. The capacity of receiver 20 is 25 l. and was designed to be slightly in excess of the capacity needed for a 24-hour production of crude butadiene. Each of the dephlegmators, 22 and 31, has a cooling surface of 150 sq. cm.

### C. INDUSTRIAL INSTALLATIONS

In factory operation, considerable deviation from the described pilot-plant technique was found necessary. The remainder of the chapter will be devoted to a discussion, under the following headings, of the changes made necessary when shifting from the pilot-plant stage to actual production:

- (1) Storage, evaporation, and superheating of alcohol.
- (2) Catalytic conversion.
- (3) Cooling, condensation, and rectification of unconverted alcohol.
- (4) Absorption-desorption and recondensation of crude butadiene.
- (5) Refining of crude butadiene.
- (6) Heat and refrigeration consumption.
- (7) By-products and their isolation.
- (8) Analytical and control methods.
- (9) Industrial hazards connected with the S.K. process.

#### 1. Storage, Evaporation, and Superheating of Alcohol

The *storage* of alcohol presents no special difficulties. The tanks can be located outdoors. While alcohol is generally stored in tanks made of iron, concrete cisterns have been successfully used. The storage installation of the S.K. factory No. 4, for example, comprises six alcohol tanks of 1270-cu. m. capacity each, supplemented by two tanks of smaller capacity (635 cu. m. each) for the storage of by-products (one for "higher alcohols" and another for "rectification bottoms"). All metering devices and pumps are located in a nearby machine house.

The importance of *preheating* the alcohol vapors close to the temperature at which catalytic conversion is to take place (420° to 450° C.) has already been emphasized (page 31). From the technological point of view, it is of course desirable to achieve preheating with a maximum utilization of secondary and waste heat of the subsequent catalytic process.

As will be shown in the following chapter (page 48), the catalytic re-torts are installed in oil-fired brickwork furnaces. The sources of secondary

heat are, therefore, the heat of the hot products of catalytic conversion (contact gases), the flue gases of the oil-fired kilns, and the heat of their brick body.

In 1933, a plan to utilize the heat of the contact gases for the purpose of *evaporating* the alcohol was developed which called for the installation of two tubular boilers of 100-sq. m. heating surface each. The contact gases were to travel inside the tubes, and alcohol, through the intratubular space. The installation was not satisfactory because the catalyst dust was carried into the tubes and quickly clogged them. Also, the returned alcohol rectificate initially carried considerable quantities of aldehyde which resinified on the tubes, impairing the heat transfer. The installation was therefore dismantled; but with the elimination of both causes in later years the project was again revived.

This statement contradicts the fact that, in very recent years, aldehyde was again added to the feed stock (page 19). No satisfactory explanation for the discrepancy is found in the published literature.

Originally,<sup>32</sup> smaller steam-heated evaporators of about 30-sq. m. heating surface were used. Each evaporator had a capacity of about 2000 liters of absolute alcohol per hour (1900 kg. per hr. of 85% absolute alcohol). The steam pressure was maintained at about 0.8 atmosphere (116.3° C.) and the alcohol pressure at about 1.5 to 1.6 atmospheres (at 87°). Alcohol was delivered to the evaporators at 30° to 40°. Superheating was achieved in two stages.<sup>33</sup> First, in a central, tubular iron superheater (tube of 46-mm. internal diameter and 3-mm. wall thickness) heated by flue gases escaping from the contact furnaces, the temperature of the alcohol vapors was raised to a maximum of 170° to 180° C. And second, it was planned to heat the vapors to a temperature of about 400° to 450° in individual copper or iron coils (one to each retort), placed in brickwork compartments inside the body of the contact furnaces proper (see page 48). This was not a practical plan, however. The temperature of the alcohol vapors reaching the bottom of the catalytic bed was around 300° (maximum, 350°), and the lower layers of the catalyst were therefore forced to serve as additional superheaters. The volume of the catalytically active zone was cut down, and the yield of butadiene markedly impaired.

Larger and improved "evaporator-superheater" units were first installed in 1938.<sup>34</sup> By including a steam-heated superheater, the problem of the

<sup>32</sup> N. A. Gol'dberg, *Sintet. Kauchuk*, 1, No. 1, 29 (1932).

<sup>33</sup> A. I. Gelikh and V. P. Komarov, *Sintet. Kauchuk*, 1, No. 1, 16 (1932).

<sup>34</sup> P. Balykov, *Kauchuk i Rezina*, 2, No. 8/9, 60 (1938).

inadequate temperature of the alcohol vapor was successfully solved. The unit (Fig. II-6) consists of a vertical tubular evaporator, *E*, with tubes 3 m. long, and of a superheater, *S*, both operated with superheated steam. A buffer *B*, packed with Raschig rings, whose function it is to decrease the moisture content of the alcohol vapors from about 13.0% to about 3.7%, is placed between *E* and *S*. Alcohol is delivered at a rate of about 11,000 kg. per hr. (at 50° C.). Evaporation thus takes place around 100° (pressure of alcohol, 2.0 to 2.5 kg. per sq. cm.). The superheater raises the temperature of the alcohol vapors to about 200° to 210°. At the same time, their moisture content is reduced to approximately 1.8%. The heat efficiency of the evaporator has been given as 80%, with optimum working conditions observed when the water condensate level is kept low (5 to 10 cm.) and the alcohol liquid level is about one-third the height of the evaporator tubes. The steam consumption is 4000 kg. per hr. for the evaporator and 1150 kg. per hr. for the superheater, corresponding to about 328 kcal. per kg. alcohol.

The secondary utilization of heat in the catalytic process is of utmost importance. By utilizing escaping flue gases and the internal heat of the furnaces for superheating, approximately 1,000,000 kcal. per ton S.K. (at 35% butadiene yield and 3.5 tons alcohol slip through per ton butadiene) is saved.

Komarov *et al.*<sup>35</sup> have proposed returning the alcohol slip through (alcohol not decomposed during the catalytic process) from the rectification columns to the superheater in *vapor form*, *i. e.*, without first condensing the vapors.

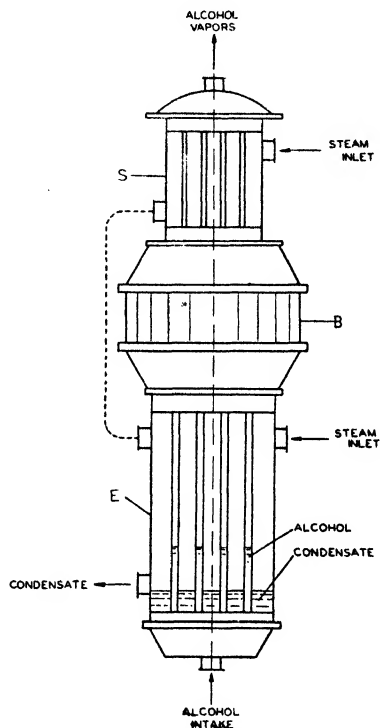


Fig. II-6.—Alcohol evaporator and superheater.<sup>34</sup>

<sup>35</sup> V. P. Komarov, F. Krûchenko, and B. S. Korotkevich, *Sintet. Kauchuk*, 5, No. 1, 34 (1936). Such a suggestion involves rectification at an elevated pressure (minimum, 2 atm.).



## 2. Catalytic Conversion

A number of principal considerations enter into the design of the catalytic converter.

The output of a continuous converter depends greatly upon a uniform supply of heat to the various regions of the catalyst bed and maintaining the temperature within a specific narrow range. Since the solid catalyst grains are in contact with a continuously flowing stream of gaseous material, problems of conduction, convection, and heat consumption are involved. The thermal phenomena in catalytic converters have been treated mathematically, most recently by Wilhelm, Johnson, and Acton.<sup>36</sup>

In addition, the conversion-regeneration cycle calls for a periodic change in temperature from the (lower) temperature of catalysis to the (higher) temperature of regeneration of catalyst.

And, finally, it is desirable to carry out the conversion with the minimum outlay of calorific energy.

The catalytic conversion is effected industrially in retort furnaces designed by Grum-Grzhimałło. These are oil-fired, vertical circular brickwork kilns. In each are arranged in circular fashion 16 vertical oval retorts made of iron plate 4 to 5 mm. thick. An S.K. factory rated at 10,000 to 15,000 tons annual capacity has twelve to eighteen such furnaces. This capacity has been gradually increased until, in present-day operation, it is understood to be 25,000 to 30,000 tons *per annum*.

The oval retorts (shown schematically in cross section in figure II-7)<sup>37</sup> have a longitudinal welded seam and are braced with  $1\frac{1}{2} \times 3 \times \frac{1}{4}$ -inch angle iron hoops, to avoid distortion. Each retort carries a charge of approximately 90 kg. of catalyst, which may present a bed several meters in height. A layer packed with Raschig rings is provided below and above the catalyst bed. The alcohol vapors are introduced at the bottom, and the gas mixture escapes at the top through a manifold into a common gas line.

The oil-burning jets are arranged tangentially (Fig. II-7). The temperature of the fireproof muffling in the vicinity of the jets may reach 1200° C. The temperature of the gases inside the furnace is maintained at about 600°, which results—with skillful manipulation—in a catalyst temperature of  $435^\circ \pm 5^\circ$ .

<sup>36</sup> R. H. Wilhelm, W. C. Johnson, and F. S. Acton, *Ind. Eng. Chem., Ind. Ed.*, **35**, 562 (1943).

<sup>37</sup> It is reasonable to assume that the retorts are more elongated (flatter) than appears in the figure.

The literature implies, though not too specifically, that in more recent years the operating temperature has been lowered to about 400° C. or just below, apparently through the use of a more efficient catalyst.

With one temperature bath surrounding all sixteen retorts of a furnace, the fine adjustment of temperature is effected by regulating the rate of delivery of alcohol to the individual retorts. In this respect, the retort furnace of the type used in S.K. plants does not appear to be a foolproof unit. It relies too largely upon the skill of the operator, whose task is made even more difficult by variations in the efficiency of superheaters (carbon deposition), in the resistance to flow of the catalytic layer, etc.

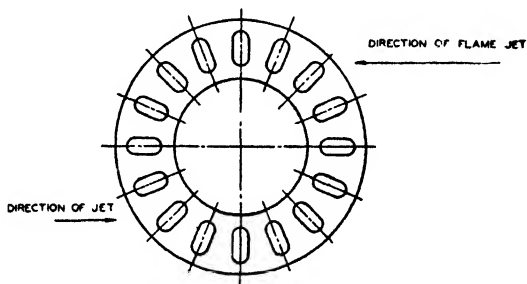


Fig. II-7.—Furnace with 16 catalytic converters.<sup>37</sup>

It is important that the brickwork of the furnace be substantially airtight to avoid excessive admixture (sucking in) of air. The retorts are equipped with draft gages, as well as with automatic carbon dioxide analyzers, and carry a number of thermocouples.

The capacity of a furnace was given, in 1936, as 2000 kg. alcohol per hour. The output per retort (at 31.3% butadiene yield) was 8.8 kg. butadiene per hour active working time (butadiene content of 0.76 to 0.81 g. per l. gas). The butadiene yields, amounts of alcohol undecomposed, and other data are presented in another chapter (see page 21). The figures given here are purely illustrative and do not represent recent operational data.

The percentage of alcohol slip through (return stock) has a major bearing on the output, and has been consistently decreased by better mastery of the process and by improvements in the catalyst.

The slip through (for all S.K. factories operating in 1934) was 8.6 tons alcohol per ton butadiene. Some factories had reduced it, by 1936, to as low as 3.5 tons per ton butadiene (at a butadiene yield of 35%).<sup>38</sup> Still further progress has since been made, concurrent with an improvement of yield to 40 to 42%.

<sup>38</sup> B. S. Korotkevich and N. A. Kozlov, *Sintet. Kauchuk*, 5, No. 4, 34 (1936).

The catalyst must be reclaimed every 12 to 24 hours (figures for early 1936). This is accomplished with a mixture of air and steam. An injector is provided for the purpose at the bottom of each retort. In 1936, reclaiming required 3 to 6 hours, but could be decreased to 2 hours by the use of a second steam injector, by admitting the air-steam mixture simultaneously to various regions of the catalyst bed, and by other suitable means. The same carbon dioxide analyzer used during the catalytic cycle for the control of the furnace operation is employed also to determine the progress of the reclaiming. After about 1000 hours, the catalyst has lost its usefulness and is replaced. Activation of fresh catalyst takes 16 to 22 hours.<sup>39</sup>

Furnaces and retorts have been operated for as long as 6 months before requiring overhauling. Burned out retorts are replaced without allowing the furnace walls to cool off.

In the early days of operation (1932-1933), some S.K. plants were regenerating the catalyst in special reclaiming furnaces, for which purpose the catalyst was shifted from contact retorts to reclaiming apparatus every 12 hours or so. This had serious drawbacks. The catalyst became very brittle, especially after repeated reclaiming. The high rate of gas travel (1 m. per sec. in retorts and 16 m. per sec. in the overhead pipe line) caused a great deal of catalyst dust and of small particles of catalyst to be carried away. Because they were only incompletely caught by cyclone collectors provided atop the furnaces, other apparatus was clogged. Also as much as 10% of the catalyst was often lost for each cycle. These early difficulties were eliminated by installing more efficient ("shock") cyclones, including fine mesh screens in the collecting manifolds, and mainly by reducing crumbling of the catalyst by carrying out reclaiming in the same retorts as the conversion.<sup>40</sup>

The circular, oil-fired furnaces proved to be quite economical in operation. In early 1936, for each ton of synthetic rubber, about 0.5 ton of crude oil was consumed in the flame heating of reactors. Optimal oil consumption figures are likely to be even some 25% lower.

### 3. Cooling, Condensation, and the Rectification of Alcohol

#### A. COOLING OF CONTACT GASES

The contact gases issue from the retorts at a temperature of about 450° C. Their heat content between 450° and 150° is utilized for preheating alcohol feed stock (going to the evaporators) or for the generation of steam. From 150° to 80°, cooling is effected by spraying the gas lines with water.

<sup>39</sup> M. Klimenko, *Sintet. Kauchuk*, 5, No. 3, 45 (1936).

<sup>40</sup> Retorts for continuous replacement and regeneration of catalyst have been suggested, but it is doubtful that they were ever used for actual operations in the S.K. industry.

## B. CONDENSATION

In the most commonly used scheme, the gases are first condensed with water. At 20° C., an initial condensate (the so-called "alcohol condensate") is obtained. In the subsequent process of brine cooling to 0° C., another liquid fraction is received (ether-aldehyde condensate). The alcohol condensate is a mixture of the ethyl alcohol which has not decomposed in the catalytic process with hydrocarbons, aldehydes, ethers, and higher alcohols.

## C. RECTIFICATION

The alcohol condensate, which is then subjected to rectification, may, for practical purposes, be considered as composed of four major fractions: a low-boiling ether-aldehyde fraction; unconverted ethyl alcohol; a mixture of higher alcohols (and water).

It has been demonstrated, in theory as in practice, that at least two towers are required to separate fairly completely a ternary mixture. The use of at least two rectification columns is therefore indicated:

(a) A low-temperature purification column (to be designated as an *epuration* column) operating at a stock temperature of approximately 90° C. and employed to drive off the low-boiling admixtures (ether, aldehyde, hydrocarbons). It is inevitable that some ethyl alcohol distills over at the same time.

(b) A *rectification* column proper, used to obtain an ethyl alcohol of sufficient strength and with a minimum content of higher alcohols and other higher-boiling admixtures (from traces to 0.5%).

When working substantially at atmospheric pressure, the following rectification conditions are suitable.

(a) Epuration column: temperature at the bottom, 91° to 92° C., and at the top, 72° to 73°; pressure at the bottom, 0.24 atm.

(b) Rectification column: temperature at the bottom, 106° C., at the fifth plate (strip-plate for higher alcohols), 98° to 99°, at the middle of the column, 88° to 88.5°, and at the top, 78°; pressure at the bottom of the column, 0.24 atm., and at the middle, 0.15 atm.

The ether-aldehyde fraction issuing from the epuration column is pooled with the ether-aldehyde condensate from the brine coolers. This pooled condensate may contain 20% and more of hydrocarbons. It is then washed (see page 67) with water, whereby an (upper) hydrocarbon layer separates, which contains: hydrocarbons up to 85%, ethyl alcohol up to 10%, ether-aldehyde 3 to 10%, small amounts of water and higher alcohols, and a

lower, aqueous washed condensate layer. The washed condensate contains the bulk of the ether and aldehyde and appreciable amounts of ethyl alcohol. The washed condensate is rectified once again, in order to obtain an ether-aldehyde fraction containing hydrocarbons not in excess of 1% and a rectified alcohol which also contains but negligible amounts of hydrocarbons.

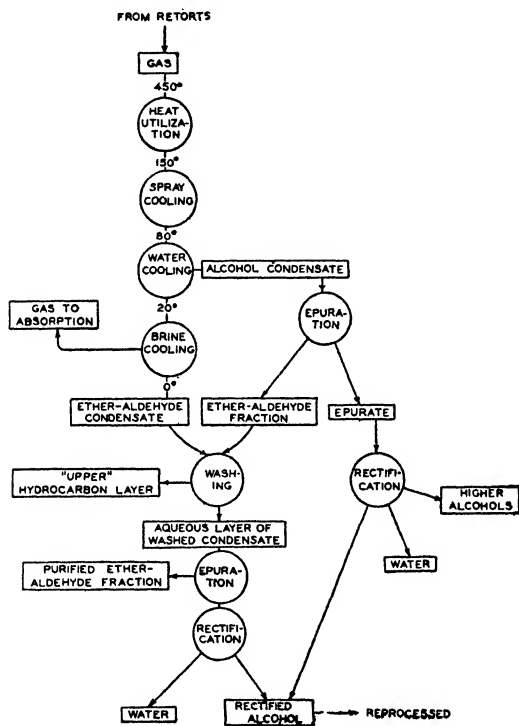


Fig. II-8.—Flowsheet: condensation and rectification of unconverted alcohol.

A flowsheet of the process is presented in figure II-8 above.

The respective compositions of the (unwashed) alcohol condensate, of the ether-aldehyde fraction, and of the liquid stock issuing from the alcohol epuration columns are given in table II-1.<sup>41</sup> The table is given only by way of an example. In more recent years, the amount of higher alcohols formed has been drastically reduced (see page 21).

<sup>41</sup> A. P. Kriúchkov, *Sintet. Kauchuk*, 5, No. 3, 17 (1936) (figures for 1936).

At first sight, the method outlined appears very cumbersome. Its justification, however, lies in the following factors:

(1) For 1 ton of butadiene obtained, at least 3.0 to 3.5 tons of unconverted alcohol pass the catalytic zone. A fairly complete recovery of such an alcohol slip through is dictated by economic considerations.

(2) It is true that ether and aldehyde would, if returned to the catalytic retorts, contribute to the formation of butadiene. They were, in earlier years, however, more valuable as by-products of the S.K. synthesis when obtained in reasonable concentration and purity. In later years, the ether was still separated as a by-product, while the aldehyde, although separated, was added to the feed stock.

TABLE II-1  
MATERIAL BALANCE OF EPURATION COLUMNS

Substance	Alcohol condensate, % by wt.	Ether-aldehyde fraction, % by wt.	"Epurate," % by wt.
Ethyl alcohol	53.58	34.0	54.44
Water	42.66	5.7	43.55
Butadiene	0.09	3.0	0.01
Aldehydes and ketones	1.16	25.0	0.38
Ether	0.66	18.0	0.13
Hydrocarbons	0.66	14.1	0.25
Higher alcohols	1.19	...	1.24
TOTAL KG. PER HR.	10270	300.8	9961.0

(3) Excessively diluted alcohol (about 50% by weight) is not suitable as catalytic feed stock (see page 21).

(4) Hydrocarbons in the catalytic feed stock have an adverse effect upon the catalyst.

The operation of alcohol rectification occupies first place in the S.K. factory with respect to steam and water consumption. In fact, one-half of all the steam expended in the S.K. process is used in this step. Various suggestions have therefore been advanced over a period of time to effect steam and water economies, and a number have been adopted in one or the other of the S.K. plants.<sup>41a</sup>

A plan to utilize the heat content of the fusel water<sup>42</sup> between the temperature limits of 105° and 45° to 55° C. to preheat feed stock going to the epuration column

<sup>41a</sup> On the subject of alcohol distillation see, *e. g.*, C. S. Robinson and E. R. Gilliland, *Elements of Fractional Distillation*, McGraw-Hill, New York, 1939; also *Chem. & Met. Eng.*, **36**, 716 (1929).

<sup>42</sup> A term designating the alcohol rectificate residues consisting mostly of water and containing not in excess of 2% organic components, often called "slop."

found quite universal acceptance. Such a procedure results in a saving of 290,000 kcal. of heat per ton S.K. rubber.

Another method<sup>43</sup> advocates a two-stage differential pressure rectification. This is a system wherein the dephlegmator of the first rectification column serves simultaneously as an evaporator for a second rectification column, which works at a lower pressure than the first one. The pressures suggested are 5 kg. per sq. cm. and less than 2 kg. per sq. cm., respectively. The method is represented diagrammatically in figure II-9.

Feed stock (the alcohol condensate) is delivered by a centrifugal pump to a heat exchanger, 2, where its temperature is raised to 70° C. at the expense of the heat content of the fusel water. From exchanger, 2, part of the stock is fed directly to the low-pressure purification column, 7. Another part, after passing through a second heat exchanger, 3, is fed at a temperature of 85° to 90° to eparation column 4 of the high-pressure system.

The still of rectification column 5—part of the high-pressure unit—is heated with live steam (6.0 kg. per sq. cm.). Subsequently, the same steam, now at a lower pressure, heats the still of eparation column 4.

Vapors from column 5 pass the intratubular space of combined condenser-evaporator 6. The residue from the still of column 5—at a temperature of about 150°—is discharged, under the force of the prevailing internal pressure of 5 kg. per sq. cm., through a trap to the tubular space of condenser-evaporator 6.

One part of the residue vaporizes because of the pressure decrease (105° C.); and another part vaporizes at the expense of the latent heat of the reflux and of the condensate. Both the liquid and the vapor phase of the eparate are fed from evaporator 6 to the still of column 8 (of the low-pressure unit).

Fusel water "slop" from the bottom of column 8 passes heat exchangers 3 and 2 consecutively, and is collected.

The distillate (rectified alcohol), *D*, issues from the top plates of both columns 5 and 8. The ether-aldehyde fraction comes off at the top plate of eparation columns 4 and 7.

The uncondensed vapor issuing from condensers 9, 11, and 13 is returned for condensation (marked "to C").

Cooling water (not shown in the figure) passes consecutively through dephlegmators 9, 10, 11, and 12, thus effecting considerable water economy. Appreciable steam economy likewise results.

Krûchenko<sup>44</sup> fails to see the necessity for one eparation unit for each rectification column. In a factory having four parallel units, each consisting of one eparation and one rectification column, he suggests having two eparation columns do the work previously done by four, and arranging the remaining two eparation columns plus four rectification columns for work in series. Rectified alcohol (of azeotropic com-

<sup>43</sup> V. P. Komarov, F. Krûchenko, and B. S. Korotkevich, *Sintet. Kauchuk*, 5, No. 1, 34 (1936).

<sup>44</sup> F. Krûchenko, *Sintet. Kauchuk*, 5, No. 3, 17 (1936).

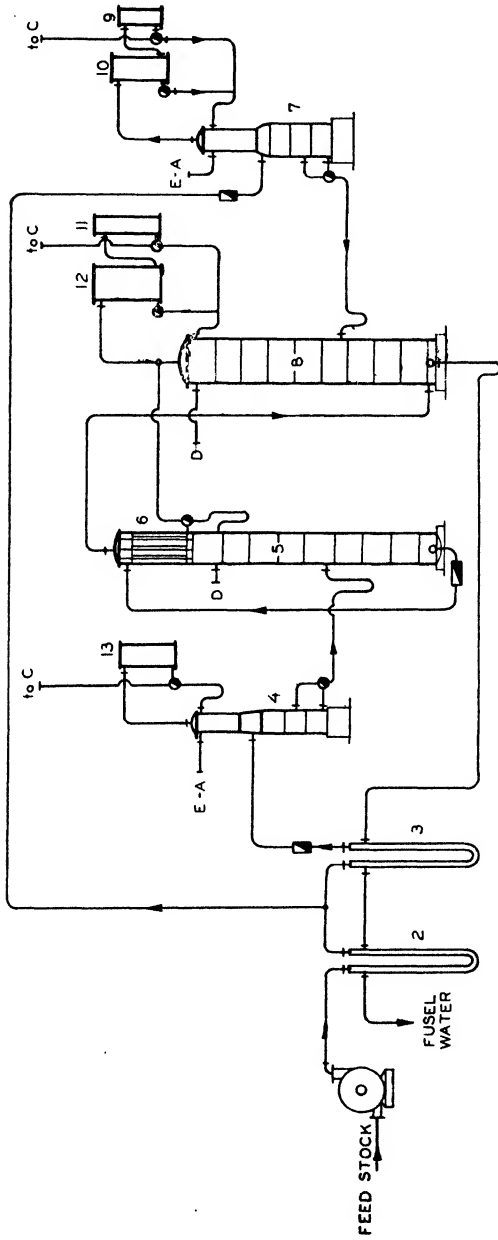


Fig. II-9.—Two-stage differential pressure rectification of alcohol.<sup>43</sup>



position) is withdrawn at the top plates of each rectification column, while the residue is carried consecutively from one rectifier to the next. Fusel water and higher alcohols are withdrawn only from the still or the lower plates, respectively, of the last column.

In still another suggested method,<sup>45</sup> it is advocated not to segregate the ether-aldehyde fraction but to let it pass on to the absorption towers by refraining from cooling the contact gas below 60° C.

#### 4. Absorption, Desorption, and Recondensation

##### A. ABSORPTION-DESORPTION

The unit process of selective absorption is widely used in the chemical industry. It is the transfer of one or more components of a gas mixture from the gas phase into a liquid in which they are soluble. The process has been given elaborate mathematical treatment, based upon a very helpful approach, the so-called "two-film" theory.<sup>46</sup> For the present, it may suffice to recall that, if an area of contact and a sufficient length of time are provided, an equilibrium will be reached at which the partial pressure of the gas in the liquid phase and the partial pressure of the gas in the gas phase will be equal. The liquid phase is then "saturated" with gas. For a given "pair" of gas and liquid (and excluding secondary chemical reactions), such an equilibrium, obeying simple thermodynamic laws, will depend upon the prevailing temperature and pressure. Lower temperatures and higher pressures will favor absorption.

In industry, the process is accomplished in absorption towers (packed with suitable materials or provided with plates), and both phases are kept in continuous counterflow motion. The distribution equilibrium, being too time-consuming, is not reached at any one point. Efficiency and rate of absorption then become contingent, in addition to pressure and temperature, upon: (a) the "active" interfacial area; (b) the rates of movement of the two phases; (c) the driving force of absorption (defined as the extent to which the actual distribution of gas between the two phases is removed at any one time from the distribution equilibrium, and generally expressed in mole per cent); and (d) an "over-all absorption coefficient,"  $K$ .  $K$  is a characteristic of the particular two-phase system present, but is also dependent upon other parameters.  $K$  is expressed in units of weight absorbed per unit of active interfacial area in a unit of time. If all physical conditions are fixed, and the nature of the liquid absorbent is the only variable,

<sup>45</sup> A. I. Gelikh and V. P. Komarov, *Sintet. Kauchuk*, 1, No. 1, 16 (1932).

<sup>46</sup> See, for example, E. M. Baker and C. R. Harte, in J. H. Perry, *Chemical Engineers' Handbook*, McGraw-Hill, New York, 1940, pp. 1138 *et seq.*

the amount of soluble gas component absorbed in a time unit will be proportional to the product of the coefficient of absorption and the driving force.

**Absorbents for Butadiene.**—A liquid is not known which will absorb butadiene exclusively. There are, however, a number of common substances in which butadiene is very highly soluble, although not selectively. Of these, kerosene and ethyl alcohol have been used industrially in the U.S.S.R. Along with butadiene, these substances dissolve butene-2, aldehydes, ethers, and a number of other products found among the reaction products of the Lebedev catalysis.

TABLE II-2  
SOLUBILITY OF PURE BUTADIENE

Temp., °C.	Distilled water		Ethyl alcohol		Tetralin		Kerosene		Turpentine	
	Mm. Hg	C <sub>4</sub> H <sub>6</sub> , g.	Mm. Hg	C <sub>4</sub> H <sub>6</sub> , g.	Mm. Hg	C <sub>4</sub> H <sub>6</sub> , g.	Mm. Hg	C <sub>4</sub> H <sub>6</sub> , g.	Mm. Hg	C <sub>4</sub> H <sub>6</sub> , g.
0	800	0.22	798	47.5	797	68.22	796	82.34	799	39.7
0	790	0.23	804	47.1	806	68.65	790	82.01	799	40.5
15	793	0.13	807	15.0	818	28.6	800	23.08	788	24.1
15	789	0.13		15.5	801	28.4	799	22.66	798	23.8
30	...	...	804	7.76	820	13.46	800	13.66	809	13.1
30	...	...		7.84	815	13.20	794	13.61	...	...

The solubilities (equilibrical) of pure butadiene<sup>47</sup> in the following liquids: (a) distilled water; (b) ethyl alcohol,  $d_4^{15} = 0.8140$  (b. p. = 78° at 758 mm.); (c) tetralin  $d_0^{15} = 0.9751$  (b. p. = 204° to 207°); (d) kerosene,  $d_4^{15} = 0.8124$  (boiling range = 148° to 255°); and (e) turpentine,  $d_4^{15} = 0.8660$  (boiling range = 150° to 200°) are given in table II-2 for 0°, 15°, and 30° C. (in grams butadiene dissolved in 100 grams solvent at the pressure indicated).

From these and other data, the isotherms of absorption for technical crude butadiene have been empirically expressed<sup>48</sup> as:

$$y = [102 + 2.55 (T - 273)] x^{0.98}$$

for kerosene, and:

$$y = [200 + 7 (T - 273)] x^{0.74}$$

<sup>47</sup> S. V. Lebedev, G. G. Kobljanskii and A. I. Guljaeva, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 1, 94 (1933).

<sup>48</sup> N. I. Smirnov, A. A. Třitina and N. F. Izyl'meteva, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 177 (1935).

for ethyl alcohol;  $y$  is the concentration of "butadiene" in the gas (in g. per cu. m.),  $x$ —the concentration of "butadiene" in the absorbent (in weight %), and  $T$ —the absolute temperature. Thus the solubility of butadiene in alcohol is, at all practical temperatures, lower than that in kerosene; and so, at a given concentration of butadiene in the gas phase, all other physical conditions being equal, the driving force will also be less. On the other hand, measurements show the absorption coefficient  $K$  to be higher for ethyl alcohol than for kerosene; and the two parameters tend to compensate one another.

Smirnov, Trútina, and Izyl'meteva<sup>48</sup> studied the absorption of butadiene and its accompanying impurities from a mixture of contact gases in the ring-packed tower of experimental S.K. factory B. Under their particular working conditions (2° to 5° C., at atmospheric pressure) the absorption coefficient,  $K$ , was found to be: for alcohol, 0.000374, and for kerosene, 0.000167 kg.-moles per hr. per sq. m. However, with a mean concentration of 14.0 mole per cent absorbable vapors in the gas phase, the equilibrium concentrations would have been: for kerosene, 4.75 mole per cent, and for alcohol, 10.00 mole per cent. Consequently, the driving forces are: kerosene, 9.25 mole per cent; and alcohol, 4.00 mole per cent. A calculation of the tower height required for the same absorption efficiency results in: kerosene—8.08 meters, alcohol—8.36 meters, *i. e.*, in practically identical figures.

The same experimental series<sup>48</sup> reveals that, with a rising rate of flow of gas through the scrubber tower, the absorption coefficient increases much more rapidly for ethyl alcohol than for kerosene.

The empirical expressions are:

$$K_{\text{kerosene}} = 1815 \cdot W^{1.77}$$

$$K_{\text{alcohol}} = 67900 \cdot W^{2.71}$$

where  $K$  is the absorption coefficient in g. per sq. m. per hr., and  $W$ , the rate of gas movement in the full cross section of the tower, in m. per sec.

Alcohol is therefore a more economical absorbent at higher rates of gas flow. A point in favor of alcohol is the fact that, when "worked out" or "fatigued" (*i. e.*, diluted with water and contaminated with substances of higher boiling point than the crude butadiene) it need not be reclaimed. It is, instead, sent to the catalytic converters, carrying with it any residual butadiene it may contain.

Because of their size, towers must be located outdoors. An added advantage of the use of alcohol here, then, is its antifreeze quality, even when it is somewhat diluted with water.

It is therefore not surprising that, after starting with kerosene as an absorbing medium, the industrial S.K. plants changed over (1934–1935) to alcohol.

**Closed Systems.**—The discussion of absorption has so far been confined to "fresh" absorbent, *i. e.*, to one delivered to the towers practically

free of absorbed butadiene. In a closed system (absorption-desorption-absorption), conditions may be different. The absorbent will contain more or less appreciable quantities of absorbed gas when it returns to the towers. This tends to reduce the driving force. The effect is of necessity more pronounced with alcohol than with kerosene, because of the lower boiling point of alcohol, necessitating desorption at a lower temperature as compared with kerosene, and because of the lower solubility of butadiene in alcohol.

Thus, the "residual butadiene concentration" after desorption becomes a major issue. If desorption is carried out at a temperature too close to the boiling point of alcohol, appreciable amounts of the latter will be carried

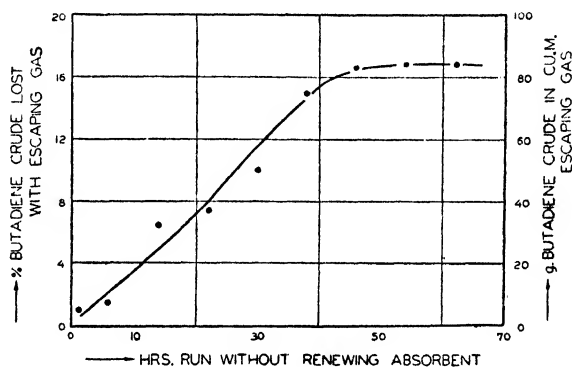


Fig. II-10.—Decline in efficiency of absorbent.<sup>49</sup>

away with the crude butadiene. If desorption is too incomplete, the alcohol will not be an efficient absorbent and butadiene will be lost with the gas escaping from the top of the towers. The efficient operation of the absorption bay will thus depend upon the judicious selection of the optimal temperature of desorption and of the rate of replacement of the absorbent with fresh alcohol.

Factory experiments reported by Smirnov<sup>49</sup> may serve to illustrate the problem. The absorption-desorption system of S.K. factory No. 3 was filled with 120 tons of alcohol (concentration of 90% by volume) and the system continuously operated for 66 hours without renewing the absorbent. The percentage of total synthesized butadiene escaping with the gas is plotted in figure II-10. Only in the first 20 to 25 hours could the work of the towers be termed satisfactory (less than 5% of the butadiene was lost with the escaping gas). After about 45 hours, the losses reached 17-18%.

<sup>49</sup> N. I. Smirnov, *Sintet. Kauchuk*, 2, No. 6, 5 (1933).

In an attempt to preserve the working efficiency of the first few hours, Smirnov tried without success to lower the temperature of alcohol delivered to the top of the towers from  $-7^{\circ}$  to  $-15^{\circ}$  C., to double or even treble the rate of alcohol delivery, and to increase the pressure in the towers from atmospheric to 4 kg. per sq. cm. None of these procedures was successful in reducing the butadiene loss to less than 10%. An analysis of the alcohol returning from desorption revealed that 15 to 30% of the absorbed butadiene remained dissolved in the alcohol. It was not until the temperature of desorption was raised to above  $90^{\circ}$  C. (made possible in part by increasing the reflux ratio in the desorption apparatus) and a part of the alcohol in the absorption system was continuously replaced and dispatched to the catalytic reactors that the losses of butadiene with the escaping gas were reduced to a reasonable figure (less than 5%).

Zhigalin,<sup>50</sup> employing the analysis of Kremser,<sup>51</sup> comes to the following conclusions:

(1) A pressure of 5 kg. per sq. cm. in the towers is most economical for the absorption of butadiene with alcohol.

(2) At the operating pressure of 5 atmospheres, absorption with alcohol can be conducted at room temperature.

(3) About 6.6% of the alcohol contained in the absorption-desorption system must be replaced every 24 hours with fresh alcohol.

At the time the basic butadiene absorption installations were designed, the composition of the gas going to the towers was roughly as given in table

TABLE II-3  
COMPOSITION AND QUANTITIES OF GAS GOING TO ABSORPTION TOWERS

Gas	Per cent by wt.	Mole per cent	Gas	Per cent by wt.	Mole per cent
Ethyl alcohol	2.16	1.38	Ethylene	11.49	12.02
Butadiene	40.77	22.12	Hydrogen	2.50	36.65
Butene-2	8.32	4.36	Methane	0.83	1.53
Aldehydes	6.18	4.11	Carbon monoxide	1.67	1.79
Ethers	3.11	1.23	Carbon dioxide	3.67	2.44
Hydrocarbons	11.53	4.55	Air	7.77	7.87

II-3.<sup>50</sup> Although the ratio of products has changed in more recent years, through improved catalytic action, the total load on the absorpton installation has not increased too drastically. The original installations have thus been able to cope with the increased butadiene yield (which occurs partly at the expense of other absorbable vapors).

An industrial installation is shown schematically in figure II-11. In a

<sup>50</sup> A. L. Zhigalin, *Sintet. Kauchuk*, 4, No. 5, 22 (1935).

<sup>51</sup> A. Kremser, *Natl. Petroleum News*, 22, No. 21, 43 (1930).

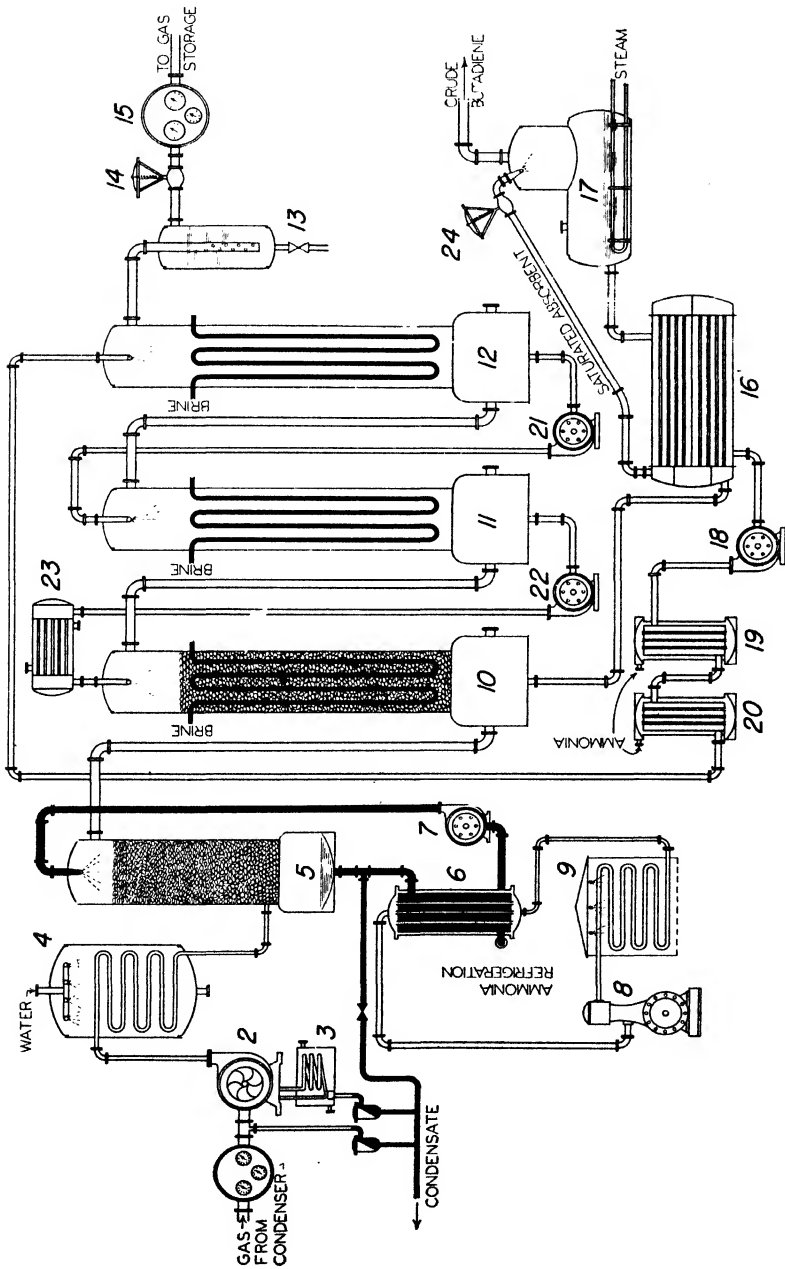


Fig. II-11.—Butadiene absorption bay.

plant rated at 10,000 to 15,000 tons of butadiene annually, two such complete parallel installations are provided. The gas is received and metered, 1, at a temperature of 0° C. (or, alternatively, at 30°) and atmospheric pressure. With the aid of rotary two-stage compressors, 2 (three to each installation), with intermediate water cooling, 3, it is compressed to 5 kg. per sq. cm. Concurrently, the temperature rises, often reaching 150°. In tubular, water-sprayed coolers, 4, the temperature of the gas mixture is reduced to 30°.

In mixing tower 5, packed with one-inch Raschig rings and sprayed with its own condensate, the gas mixture is further cooled to 0° C., whereby the heat transmitted to the recirculated condensate is withdrawn by means of boiling ammonia in a shell and tube evaporator, 6. Surplus condensate from this operation is pooled with liquid condensing in the compressor (between the stages) and in the pipe line and may be added to the crude butadiene (see page 65), or used as a reflux in the preceding operations of condensation and rectification. The evaporated ammonia is recompressed (8) and recondensed in spray coolers, 9, arranged on the roof of the building.

Petrenko<sup>52</sup> reported that, in 1939, an installation was completed at one of the plants to intensify partial condensation of butadiene prior to absorption.

S.K. factory No. 4 has two sets of absorption towers, each set consisting of three packed towers, 2.3 m. in diameter and 25 m. high.

Factories built earlier were provided with three sets of scrubbers, of which the first was of the bubble-plate type (50 plates), 1.9 m. in diameter and 17 m. high, while the two succeeding packed towers were 2.3 m. in diameter and 32 m. high, and were packed to a height of 29 m. with wooden slugs (their use dictated by the desire to conserve less available materials). The saving in tower size, the reduction of their number, and the economies effected in construction were made possible by increasing the operating pressure to 5 atm.

The gases, after passing all three towers (10, 11, 12), are released through regulating valve 14, metered at 15, and collected in a gas storage tank.

It has been claimed that, for each mole of absorbed substance, 8500 cal. (heat of absorption) is generated. There is reason, though, to suspect that such a figure is high. This heat of absorption must be removed. Removal is effected partly by circulating brine through cooling devices incorporated in the body of the towers, and partly by precooling the absorbent itself to between 0° and -10° C. with ammonia or brine. The returning absorbent contained, in earlier days, about 3% by weight of crude butadiene. This figure was later raised, for reasons of economy, to about 6%, and finally reached about 12%.

<sup>52</sup> A. V. Petrenko, *Kauchuk i Rezina*, 4, No. 4/5, 1 (1940).

The process of absorption is based on the counterflow principle: The alcohol (kerosene) leaving desorption apparatus 17 at a temperature of 80° to 90° C. (120°)<sup>53</sup> passes heat exchanger 16 where it is cooled by the returning saturated absorbent. It then passes through centrifugal pumps 18 and a two-stage cooling system (19, 20) which employs ammonia-cooled brine as the refrigerant. In the first stage, 19, the temperature of the absorbent is usually reduced from +15° (+10°) to about +5° (0°); in the second stage, 20, -5° (-10°) is reached. The cold absorbent now moves to the top of the (last) tower, 12, and slowly cascades to its bottom. From the bottom of tower 12 it is pumped (21) to the top of tower 11, then again through centrifugal pump 22 and brine cooler 23, to the top of tower 10.

TABLE II-4  
TOTAL VAPOR PRESSURES OF BUTADIENE-KEROSENE

C <sub>4</sub> H <sub>6</sub> , g./100 g. soln.	Total vapor pressures, mm. Hg at temperature (°C.) indicated												
	-20°	-10°	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
0	25	32	40	49	59	72	85	99	116	133	153	174	195
0.5	34	44	55	68	83	100	119	139	164	188	217	245	278
1	45	58	72	90	109	130	155	181	212	244	281	316	360
2	64	83	105	132	162	195	234	277	317	378	437	497	568
3	78	103	134	171	214	265	321	386	462	541	635	733	841
4	91	123	161	209	266	331	404	493	597	708	836	973	1125
5	107	145	191	248	316	394	484	597	718	851	1009	1175	1368
6	121	165	219	287	364	450	569	700	847	1000	1202	1396	1644
7	134	185	246	324	417	525	656	813	989	1183	1419	1660	1950
8	145	200	269	357	462	582	733	908	1107	1334	1611	1906	2223
9	151	209	282	372	484	617	776	962	1170	1413	1698	2014	2360
10	155	218	295	394	513	661	824	1002	1223	1528	1854	2183	2582
11	161	226	309	417	549	700	895	1122	1393	1690	2065	2455	2924

The "saturated" absorbent, having a temperature of approximately 5° C. (0°), is passed through the tubular, intensive multipass heat exchanger, 16, where it is preheated to 100° for kerosene and to 65° for alcohol by the counterflowing absorbent issuing from the desorption apparatus. It is then released through condensate traps into desorption apparatus 17. The desorber is an horizontal tank of about 25-cu. m. capacity (4 m. long) with a reflux dome mounted to one side atop the main body. The preheated absorbent enters the dome through jets and is atomized. The bottom of the desorption apparatus carries a steam coil. When kerosene is the absorbent, a partial vacuum is maintained in the unit.

The economic significance of the heat exchanger is appreciable. In preheating the absorbent (alcohol) from 5° to 75° C., and at a butadiene

<sup>53</sup> The first temperature given here refers to alcohol. The second figure (in parentheses) refers to kerosene.



(crude) content in the absorbent of 6% (by weight), a saving of 600,000 kcal. per ton S.K. was effected,<sup>55</sup> or—expressed in other terms—steam consumption was cut in four and, in addition, cooling water was saved.

In connection with the absorption-desorption problem, it may be of interest to reproduce a table of vapor pressures of butadiene (pure)-kerosene solutions (Table II-4) and of butadiene (pure) ethanol solutions (Table II-5).<sup>54</sup>

TABLE II-5  
TOTAL VAPOR PRESSURES OF BUTADIENE-ETHANOL

Per cent by wt.	Total vapor pressures, mm. Hg at temperature (°C.) indicated										
	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
0.0	12	24	44	78	133	220	350	541	812	1187	1692
2.08	118	174	247	350	481	652	869	1125	1456	1828	2290
3.19	164	230	314	432	593	804	1074	1390	1799	2259	2838
5.04	221	323	452	631	875	1146	1510	1936	2477	3083	3837
6.00	246	359	501	702	953	1277	1683	2158	2761	3436	4276
10.2	337	497	702	991	1327	1837	2443	3140	4055	5082	6354

Butadiene escaping the absorption towers with the "inert" gases can be caught and recovered by adsorption with activated carbon,<sup>55</sup> which can adsorb the following amounts of butadiene from considerable dilutions: at  $-20^{\circ}\text{C.}$ , 13.80% (of its own weight); at  $-10^{\circ}$ , 12.64%; at  $0^{\circ}$ , 11.84%; and at  $14^{\circ}$ , 9.20%. The desorption is quite complete (90 to 99%) and the concentration of butadiene in the desorbed gas is fairly high (50 to 70% by volume). Repeated regeneration does not seem to impair materially the adsorptive power of activated carbon. Naturally, alcohol and aldehyde vapors escaping the towers are adsorbed simultaneously with the butadiene.

## B. RECOVERY OF ESCAPING ALCOHOL

The vapor pressure of ethanol at  $272^{\circ}\text{K.}$  is only 11 mm. Hg; nevertheless, the large amount of gas escaping from the absorption towers always carries away considerable quantities of alcohol.<sup>56</sup> Methods have been advocated, and in some cases adopted, for recovering these escaping alcohol vapors. One method employs bubbling through water the gas containing

<sup>54</sup> I. N. Bushmakin and K. I. Kuchinskaja, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 160 (1935).

<sup>55</sup> G. A. Pankov and A. S. Malinkina, *Sintet. Kauchuk*, 4, No. 1, 37 (1935).

<sup>56</sup> G. G. Barashkov, *Sintet. Kauchuk*, 5, No. 2 (1936).

the alcohol (see 13 in figure II-11).<sup>57</sup> More effective, though, is a packed tower irrigated with calcium chloride solution.<sup>58</sup>

### C. RECONDENSATION OF CRUDE BUTADIENE

The desorbed vapors of crude butadiene are cooled in water-sprayed tubular towers arranged above the desorption apparatus on the roof of the building. They are then recompressed to 5 kg. per sq. cm. with the aid of rotary two-stage compressors (with intermediate water cooling), whereby their temperature may rise to 100° C. Superheating is eliminated by passing the vapors through a packed tower where they are irrigated with their own refrigerated condensate. The saturated crude is cooled and condensed in tubular spray towers (also arranged on the roof), at times assisted by a brine cooler. Gas that fails to condense in these operations is returned to the intake of the first tower in the absorption bay. All the elements of such an installation are similar to those described in the first part of figure II-11.

The crude butadiene is received and stored at 5 kg. per sq. cm. in stationary tanks of 3.1-cu. m. capacity each. It is transported through a system of pipes by compressed butadiene gas (7 kg. per sq. cm. at approximately 60° C.). For this purpose, a small steam-heated butadiene evaporator is provided.

## 5. Refining of Crude Butadiene

Because, as already outlined, no selective absorbent for butadiene (or even for the butadiene-butene-2 fraction) is known, the "crude" stock, as desorbed and recondensed from alcohol or kerosene, contains a number of admixtures. Among them are some highly volatile substances, such as carbon monoxide or propene, which should have come off at an earlier stage in the process but were recondensed with the butadiene because of their high solubility in the crude. The condensate also contains appreciable quantities of aldehydes (predominantly acetaldehyde), of ethers and ketones, and of hydrocarbons, such as butene-2, pentene, pentadiene, and hexene all having a higher boiling point than the butadiene.

Such crude could not be polymerized. In earlier years, it contained butadiene in too great a dilution (in 1932, only 40 to 55%). See page 177. But even with improved catalytic efficiency and a consequent increase in

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<sup>57</sup> A drilled pipe of 8-in. diameter immersed in water in a vessel of 8-cu. m. capacity. It has been claimed that absorption can be carried to a 10% or even 20% concentration of alcohol in water.

<sup>58</sup> *Sintet. Kauchuk*, 4, No. 6, 47 (1935).

the concentration of pure butadiene in the crude, there still remained the problem of detrimental effect on polymerization (with sodium) of a number of the above admixtures. These must be removed before efficient mass polymerization can be attempted. The largest single fraction having an antagonistic effect upon the polyreaction is the acetaldehyde (see page 176). The aldehyde content in the diene must be lowered to below a few hundredths of one per cent.

Initially, it was assumed that the refining of crude butadiene could be accomplished in a single-stage rectification. But Lebedev's laboratory work already foreshadowed the difficulty of separating butadiene and aldehyde by rectifying alone. Therefore, rectification was combined with alkali washing (in the vapor phase). See figure II-5. The vapors of butadiene, coming from the dephlegmator of a packed rectification column, were first led through an alkali absorption tower and then to the total condenser.

At the Leningrad experimental plant, alkali absorption was practiced as a combined "wet" and "dry" process. In the wet tower, the butadiene vapors were bubbled through a 50 Bé. solution of sodium hydroxide (at 60° to 80° C. to forestall condensation in the process). In the following dry tower, packed with solid sodium hydroxide, further quantities of aldehyde, as well as moisture carried over from the wet scrubber, were to be removed. The underlying principle was, of course, to resinify any aldehyde escaping rectification.

The complete inadequacy of such a scheme was established with the very first experiments: The concentration of aldehyde proved too formidable; the wet scrubbers became resin logged; and, besides, several passes were needed to reduce the aldehyde content to the required limits of a few hundredths of one per cent.

The refining operation finally evolved was first divided into two stages: washing the *liquid* crude butadiene with water, and then rectifying it to remove other impurities. Very much later (1936), the scheme was expanded by including as a first and additional step in the process of refining (prior to washing) an epuration (low-temperature rectification) designed to remove quantities of highly volatile components from the crude.

Water was selected for the "washing" step because of the ease of recovering aldehyde from aqueous solutions in comparatively pure form and because of the lesser tendency of the apparatus to corrode, as compared with the use of salt solutions.

#### A. REMOVAL OF HIGHLY VOLATILE COMPONENTS

The presence of small but yet important amounts of highly volatile compounds<sup>59</sup> in the crude is illustrated by the first and second columns in table

<sup>59</sup> A. V. Petrenko, *Sintet. Kauchuk*, 5, No. 11/12, 34 (1936).

II-6, as revealed by fractionation of its volatile overhead fraction in a Podbielniak apparatus.

Aside from their effect on polymerization, the highly volatile components tend to increase the gas pressure in the polymerizers (see page 187) for the temperature range needed and thus create an unnecessary hazard.

TABLE II-6  
PODBIELNIAK FRACTIONATION OF CRUDE BUTADIENE

Substance	Crude butadiene before purification, % of wt. of crude	Crude butadiene after purification, % of wt. of crude
Overhead distillate (boiling below $-4^{\circ}$ C.)		
Butadiene-1,3	4.96	0.624
Propene + butene-2	1.87	0.08
Ethylene	0.965	0.005
Carbon dioxide	0.395	0.00546
Carbon monoxide	0.024	...
Hydrogen	0.011	0.0007
Residue (boiling above $-4^{\circ}$ C.)	91.775	99.28484

In the earlier (two-stage) scheme of refining, an attempt was made to remove the highly volatile components by exhausting them from the top of the total condenser of final rectification (after washing). Concurrently, appreciable quantities of butadiene were carried off. To avoid these losses, the gas had to be piped back to the intake of the towers in the gas absorption bay. Such a procedure imposed an added load on the towers. The returned butadiene vapor often amounted to 300 to 400 kg. per hr.

Figures in the third column of table II-6 show the analysis of fractions below  $-4^{\circ}$  C. after rectification on a special experimental column. The results were obtained under unfavorable conditions (great overload, insufficient reflux ratio, too coarse a packing, etc.) all of which tended to increase the amount of butadiene carried away with the volatile components. Nevertheless, these experiments were encouraging, and an epuration step was generally adopted in the scheme of butadiene refining.

The operating conditions for this rectification were: temperature of tower base (still),  $48^{\circ}$ ; of top of column (tower),  $37^{\circ}$ ; and of escaping overhead vapor (discharged),  $35^{\circ}$ ; pressure in still, 3.7 atm. The tower was packed with one-inch Raschig rings.

## B. WASHING OUT OF ALDEHYDE

The intimate mixing of water with liquid crude butadiene is complicated by the considerable difference in densities of the two liquids (0.62 to 0.65 vs. 1.00). Tests showed that about 15 to 30 minutes were required to reach

distribution equilibrium of aldehyde between the water and the butadiene phase in a batch process employing a large vat and an agitator. Each such washing resulted in an 80% extraction of all aldehyde present at the time.

Industrially, the process is carried out<sup>60</sup> by a system of centrifugal pumps (or injectors) arranged in series with an equal number of separatory vats (Florentine receivers). See figure II-12. The role of the latter is to separate the immiscible phases after they have been brought into intimate contact in the centrifugal pumps. The process is continuous, and employs the principle of counterflow of the extracting and the extracted liquids.

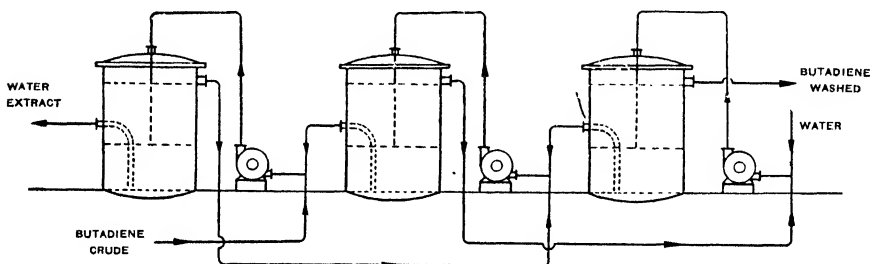


Fig. II-12.—Continuous washing of butadiene.<sup>60</sup>

The centrifugal (four-stage) pumps installed in the S.K. factories are of 3-in. delivery. The Florentine receivers are cylindrical, welded vessels, about 2 m. in diameter and 3 m. high, and are sometimes, though not necessarily, provided with labyrinth baffles. See figure II-13. The capacity of the vessels is calculated for a maximum two hours' "sojourn" of the liquids in the separator. The emulsion of crude butadiene and water created by the pumps is introduced through flange *a* in the lid of the vessel and tube *b* reaching about halfway down the vessel. The bottom end of tube *b* is blind, and its lower third drilled with holes of 5-mm. diameter.

Inside the Florentine receivers originally used is a labyrinth composed of two incomplete cylinders (arranged concentrically about tube *b*) of 750-mm. diameter and 1500-mm. diameter, respectively, and a radially arranged baffle plate (see longitudinal and cross section shown in figure II-13). The water-butadiene emulsion moves slowly outward through the labyrinth and the two liquids separate. Water (containing aldehyde) is displaced by continuously incoming fresh water-butadiene emulsion, and is withdrawn through flange *d*, leveling tube *e*, and regulator *f*. The washed butadiene leaves through the pocket and flange, *c*, at the top.

<sup>60</sup> N. I. Smirnov, *Sintet. Kauchuk*, 2, No. 1, 13 (1933); 2, No. 2, 6 (1933).

Although the bulk of the emulsion separates fairly rapidly, and in spite of the differences in density, some 5% *stable* emulsion<sup>61</sup> is formed which, if pooled with the wash water, would constitute an undue butadiene loss, and, if added to washed crude butadiene, would unduly increase its moisture content. Such an emulsion can be destabilized by small additions of calcium chloride to the fresh water, as well as by slight heating. Some dissolved butadiene can be conveniently removed from the wash water by evacuation, for example, by connecting the intake of the compressors preceding the absorption towers to the wash water storage tanks. The aldehyde remains in solution because of its incomparably greater solubility in water. The preferred ratio of water to crude butadiene is about 1:1 (2 cu. m. of each per hour). A pressure of 3 to 4 atmospheres is maintained in the entire washing system.

Some experimental data on the washing process<sup>60</sup> gathered in the pilot plant of S.K. factory B dispelled the apprehension as to the feasibility of a method in which the mixing cycle ("sojourn" in the pumps or in ejectors) is only a fraction of the time (15 to 30 minutes) that would be required to establish a distribution equilibrium of aldehyde in batch (paddle) mixers. Table II-7 shows one of the results obtained:

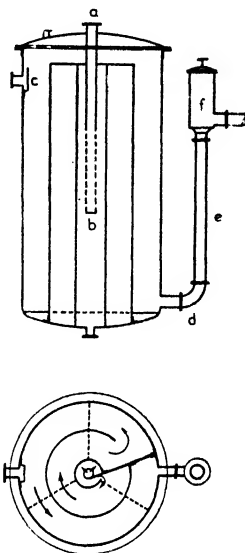


Fig. II-13.—A Florentine separator.<sup>60</sup>

TABLE II-7  
EFFECT OF PUMP WASHING AND RESEPARATION<sup>a</sup>

Sample	"Aldehyde" content, %	
	In butadiene	In water
Before washing	17.13-17.17	0
1 pass through pump	4.48-4.75	5.48-5.61
2 passes	1.28-1.29	1.63-2.18
3 passes	0.30	0.58-0.63
4 passes	Traces to 0.074	0.11-0.113

<sup>a</sup> Ratio of water to crude butadiene, 1:1; fresh water used each time.

The table shows again that each washing operation (with fresh water) removed some 80% of the aldehyde present at the time.

<sup>61</sup> An emulsion is termed stable if its disintegration time exceeds two hours.

The mathematical treatment of the aldehyde washing is not simple,<sup>62</sup> partly because what is here termed "aldehyde" is really a mixture of acet-aldehyde, butyraldehyde, acetone, methyl ethyl ketone, and other carbonyl compounds, acetaldehyde being, however, the principal component.

Washing by counterflow in ring-packed towers has been suggested. It was given mathematical treatment as an alternative to pump washing, in 1936,<sup>63</sup> and was adopted<sup>64</sup> in 1939 in one of the S.K. plants. The method claims greater simplicity: The difference in the densities of the immiscible liquids creates a natural counterflow; the packing assures an intimate mixture; while the principle of an absorption tower as such provides the continuity of process.

TABLE II-8  
VAPOR PRESSURES OF ALDEHYDE (PURE)-WATER SOLUTIONS

Concn., %	Total vapor pressure, mm. Hg at temperature (°C.) indicated										
	2°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
0.23	11	17	31	53	83	130	199	297	433	617	866
2.6	19	31	56	92	147	233	355	530	772	1092	1518
5.8	31	53	88	149	238	377	567	839	1211	1699	2347
9.6	43	71	125	211	340	532	805	1191	1709	2398	3307

In connection with the recovery of aldehyde from its aqueous solution, table II-8<sup>64</sup> is of interest.

### C. ALDEHYDE WASHING IN THE GAS PHASE

Since aldehyde, unlike butadiene, is so highly water-soluble, it is pertinent to ask why the absorption of aldehyde from butadiene crude is not carried out in the gas phase, *e. g.*, in irrigated absorption towers. Such a procedure, for instance, would eliminate the recondensation step following desorption.

A suggestion of this nature was made by Karzev in 1931. Preliminary tests at S.K. plant B revealed, however, that only a fraction of the aldehydes could be absorbed with water from the gas phase, which is rather surprising. An explanation was offered by Smirnov and Tūtina.<sup>65</sup> From the data in table II-8 plus some

<sup>62</sup> N. I. Smirnov, *Sintet. Kauchuk*, 2, No. 4, 14 (1933).

<sup>63</sup> S. V. L'vov, *Sintet. Kauchuk*, 5, No. 2, 38 (1936).

<sup>64</sup> A. Petrenko, *Kauchuk i Rezina*, 4, No. 4/5, 1 (1940).

<sup>65</sup> N. I. Smirnov and A. A. Tūtina, *Sintet. Kauchuk*, 3, No. 4, 12 (1934).

theoretical assumptions that appear justified, they arrived at the following empirical expression for the absorption isotherm of acetaldehyde in water:

$$y = [0.725 + 0.0775 (T - 273)]x^{0.77}$$

where  $y$  is the concentration of aldehyde in the gas phase, in mole per cent,  $x$  is the concentration of aldehyde in the liquid phase in per cent by weight, and  $T$  is the absolute temperature.

When plotted, the character of these isotherms reveals that the system deviates considerably from Raoult's law. The curves are of marked convexity, and thus the driving force of absorption declines many times more rapidly with dwindling aldehyde concentrations in the gas phase than would be the case if Raoult's law were followed. Consequently, the process of absorption is not particularly favored at low aldehyde concentrations in the gas phase and fairly complete absorption of aldehyde from the gas phase is made very difficult.

The theoretical predictions were confirmed by laboratory experiments<sup>66</sup> and by factory tests<sup>66</sup> with an absorption tower of 0.25-m. diameter and 9 m. high, packed to a height of 7.5 m. with one-inch iron Raschig rings. Both experimental series showed that a maximum of 70 to 75% of the aldehyde content could be extracted from the butadiene crude by washing the gas, while 99.5% had to be removed before the material became suitable for polymerization. Also, twice the amount of water had to be expended for gas washing as compared with pump washing in the liquid phase.<sup>67</sup> Nevertheless, it is technically feasible to wash the gas first in order to extract the bulk of aldehyde, then to recondense the gas and carry out the final washing in the liquid phase.

## 6. Heat Consumption and Refrigeration in S.K. Manufacture

Throughout the preceding sections, occasional references were made to the consumption of heat and to conditions of refrigeration as they pertain to the individual steps in the S.K. process. These scattered data are briefly summarized in the following paragraphs.

### A. HEAT CONSUMPTION

For a butadiene yield of 35 parts per 100 parts alcohol converted, an aggregate butadiene loss of 5 to 6% in all operations following the catalysis proper, and a slip through of alcohol equal to 3.5 tons per ton butadiene, the plans call for *18,000,000 kcal. heat per ton S.K.*

A part of the calorific energy is provided by the oil (mazut) used in firing

<sup>66</sup> A. Vasil'ev, *Sintet. Kauchuk*, 2, No. 5, 5 (1933).

<sup>67</sup> By way of illustration, it may be stated that desorbed crude butadiene may contain 400 g. per cu. m. "butadiene-butene-2" and 80 g. per cu. m. (4.3% by volume) of "aldehyde fraction."



the contact furnaces (one ton of mazut supplying approximately 1,000,000 kcal.), and the other part, by the steam (one ton of steam being equivalent to 650,000 kcal.). Roughly, 0.45 ton mazut (equal to 4,500,000 kcal.) and 21 tons steam (corresponding to 13,500,000 kcal.), is required per ton S.K.

Almost one-half of all the steam, *i. e.*, 5,500,000 kcal. per ton S.K., is consumed in the alcohol rectification (recovery of alcohol slip through). Another 2,000,000 kcal. (3 tons of steam) per one ton S.K. is used in the evaporation and superheating of the alcohol.

TABLE II-9  
HEAT CONSUMPTION IN S.K. MANUFACTURE (1934 AND 1935)

Time	Butadiene yield on alcohol converted, %	Subsequent butadiene loss, %	Slip through, tons alcohol/ton S.K.	Steam, tons/ton S.K.	Mazut, tons/ton S.K.	Amount absorbable in absorbent, %
1934 (entire year)	21	26	8.6	70	1.4	4
1935 (entire year)	28	12	6.8	40	0.7	6
1935 (December)	30	..	..	32	0.53	..

The planned figures were reached only gradually in actual operations. The earlier results did not compare favorably at all (see table II-9). On the other hand, the above figures are based on a yield of 35%, which is short of the 40 to 42% butadiene yield reported in later years.

## B. REFRIGERATION

Table II-10 summarizes the calorific balance, per hour and per ton S.K., of the refrigeration<sup>68</sup> department of an S.K. factory. The installed capacity is rated at 2,000,000 kcal. per hr. The 10,000-ton S.K. *per annum* figures provide for absorption (of butadiene) at atmospheric pressure using brine cooling. The 15,000-ton *per annum* data provide for absorption at 5 atmospheres and the absorbent is water-cooled.

The refrigeration systems of S.K. plants were originally operated with 22% sodium chloride or calcium chloride brine. Later, several plants changed to the use of 30% alcohol as the coolant, mainly to prevent corrosion of, and leakages in, the apparatus. Such a changeover met with considerable criticism on the part of a number of the engineers,<sup>69</sup> mainly on

<sup>68</sup> G. K. Denisov, *Sintet. Kauchuk* 4, No. 6, 30 (1935).

<sup>69</sup> See B. S. Korotkevich and N. A. Kozlov, *Sintet. Kauchuk*, 5, No. 2, 34 (1936).

the grounds that, because the kinematic viscosity of alcohol is almost three times that of brine, the cost is increased for circulating the coolant through the rather extensive pipe system of an S.K. plant. Rectification and ab-

TABLE II-10  
GROSS COLD CONSUMPTION (TRANSMITTED TO FACTORY AS REFRIGERATED BRINE)

Manufacturing stage requiring refrigerating	Cold consumption for 10,000 tons <i>p. a.</i> S.K., kcal.	Cold consumption for 15,000 tons <i>p. a.</i> S.K., kcal.
Alcohol rectification	526,000	820,000-1,000,000
Absorption	960,000	75,000-90,000
Desorption and rectification of butadiene	207,000	220,000-250,000
Polymerization	171,000	270,000-330,000
Butene-2 absorption	...	135,000-155,000
Losses	Included in above	320,000
TOTAL	1,864,000	1,800,000-2,125,000

sorption at elevated pressures and changes in the polymerization technique have reduced the refrigeration consumption to a level at which it has become insignificant in the over-all economic picture of an S.K. factory.

## 7. By-Products, Their Separation and Utilization

The economic efficiency of the Lebedev catalysis for making butadiene from ethanol depends in no small measure upon the efficient utilization of the liquid (and gaseous) by-products formed. It has been variously estimated that one ton of useful by-product can be produced for each ton of S.K.

The liquid by-products of the butadiene synthesis were summarized on pages 21 *et seq.* They comprise hydrocarbons,<sup>70</sup> ethers,<sup>71</sup> phenols,<sup>72</sup> alcohols, and carbonyl compounds.<sup>73</sup> These products are formed as part of complex mixtures at various stages of the process (see figure II-1, page 38), in particular:

(1) During condensation and alcohol rectification (see pages 51 *et seq.*):

(a) An ether-aldehyde condensate is recovered from the condenser of the first rectification columns and from the brine coolers. The condensate is split (by washing with water) into an "upper" hydrocarbon layer and a "lower" aqueous layer. The latter is freed from ethanol by rectification.

<sup>70</sup> I. A. M. Slobodin *et al.*, *Zhur. Obshchei Khim.*, **5**, 1414 (1935).

<sup>71</sup> M. V. Likhosherstov, *Trudy Voronezh Gosudarst Univ.*, **8**, No. 4, 81 (1935).

<sup>72</sup> M. V. Likhosherstov, *Zhur. Obshchei Khim.*, **4**, 1274 (1934).

<sup>73</sup> S. V. Lebedev, *Zhur. Obshchei Khim.*, **3**, 698 (1933).

(b) A fraction designated as "higher alcohols" is stripped from the lower plates of the second (alcohol) rectification columns.

(c) From the still of the same columns a residue called "fusel water" or "slop" is withdrawn.

(2) During absorption (see pages 56 *et seq.*):

(d) An "inert" gas of high calorific value escapes from the top of the last tower.

(3) In the process of purifying the crude butadiene:

(e) An "aldehyde" containing wash water falls off and finally

(f) A rectification residue results.

(4) During polymerization, vacuum kneading, and the refining of S.K.:

(g) Considerable quantities of butene-2 are liberated.

The isolation in pure form of the various valuable by-products and/or their conversion into other industrially important materials is no simple task and cannot as yet be regarded as fully solved. The unit processes employed are, in the main, washing with water, salting out of aqueous solutions, and fractional distillation.

Ether and aldehyde, when occurring simultaneously, are separated by mixing the solution with concentrated sodium chloride brine. The choice of temperature will depend upon the ultimate aim, that is, whether an aldehyde with minimum ether content is sought or vice versa. It was found<sup>74</sup> that a lower temperature (0° C.) favors a purer ether component, while a higher temperature (30°) reduces the amount of ether in the aldehyde-brine layer.

The separation of acetaldehyde from ethyl ether by distillation is not successful.<sup>75</sup> The pure substances form an azeotropic mixture at about 74% aldehyde concentration, boiling at about 20.4° C. (at 757 to 767 mm. Hg). The addition of some 5% of a third component, for example, of the hydrocarbon fraction boiling at 38° to 43° (consisting in the main of pentadiene-1,3 and pentene-2, two common by-products of the S.K. synthesis), changes the composition of the azeotropic mixture to 89% aldehyde and depresses its boiling point by approximately 0.3°. About 60% of all by-product aldehyde is obtained from the ether-aldehyde condensates. The remaining 40% originates in the wash water of crude butadiene, from which it is again salted out and rectified.

<sup>74</sup> I. N. Bushmakin and M. M. Gol'dman, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 168 (1935).

<sup>75</sup> I. N. Bushmakin and K. I. Kuchinskaia, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 164 (1935).

Ethyl ether, the second largest fraction of the liquid by-products, is in the ether-aldehyde condensates. It also constitutes about 25 to 30% of the bottoms from the rectification of washed butadiene. The remainder of the bottoms is composed of pentene and pentadiene (25 to 30%), hexadiene-2,4 and hexene-2 (25 to 30%). The acetaldehyde content of this residue is small (1 to 3%). In earlier days, the bottoms comprised about 5 to 6% of all the catalytically converted alcohol.

The fusel water fraction has practically no commercial value. It contains only 2% of organic admixtures.

The higher-alcohol condensate, on the other hand, is, or was for a time (see page 22), important. A typical composition of this condensate has been given<sup>76</sup> as:

Ethyl alcohol.....	27.6%
Water.....	24.8%
Aldehydes and ketones.....	3.7%
Ethers.....	..
Hydrocarbons.....	4.0%
Higher alcohol.....	39.9%

The higher alcohols may (see table I-4, page 22) have constituted up to 1.25% of the total "alcohol condensate" (*i. e.*, up to 10% on the butadiene). About two-thirds of the higher alcohols were of the C<sub>4</sub> group, while one-third was of the C<sub>6</sub> type or higher.

Among these are the following normal primary alcohols (see page 22): Butyl, crotonyl, amyl, and hexyl alcohols. Lebedev<sup>77</sup> also assumed the presence of unsaturated amyl alcohol, unsaturated hexyl alcohol, and octyl alcohol, but these could not be definitely established.

For the purposes of their isolation, these products are diluted with water. As a result, an upper layer separates which consists mainly of hydrocarbons (*i. e.*, the least water-soluble substances), while in the aqueous, lower layer are the unreacted ethyl alcohol and the higher alcohols formed in the S.K. process.

With the exception of butyl alcohol, for the purification of which a number of methods have been suggested, most of these alcohols were not commercially exploited, first, because of the difficulty of effecting their separation and, second, because of the presence of colored impurities which render them worthless for many commercial applications.

<sup>76</sup> Unpublished work quoted from S. M. Rivkin, *Kauchuk i Rezina*, 1, No. 3, 16 (1937).

<sup>77</sup> S. V. Lebedev, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 3, 41 (1934); 4, 3 (1935).

## A. HIGHER ALCOHOLS

Filipov<sup>76</sup> has clarified considerably the nature of the difficulty encountered when attempting to distill off the higher alcohols from the aqueous liquor. His results, presented in figure II-14, show that, while the boiling points of the pure alcohols in question may form a straight line if

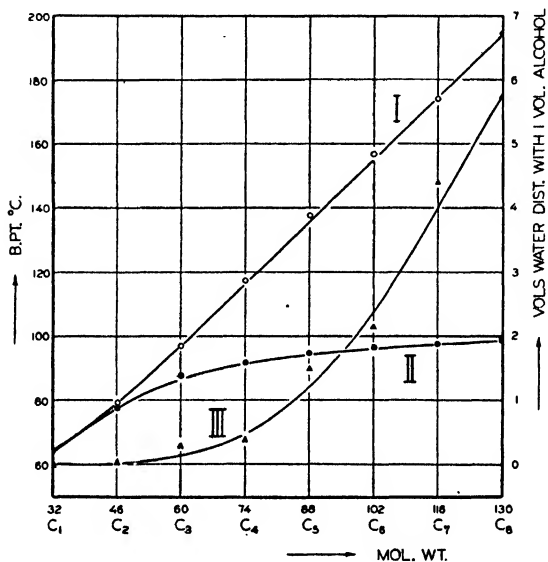


Fig. II-14.—Distillation of higher alcohols from aqueous mixtures.<sup>76</sup>

Curve I—boiling point of pure normal alcohols.  
 Curve II—boiling point of their azeotropic mixtures with water.  
 Curve III—volumes water distilling over with one volume of alcohol.

plotted against their molecular weights (curve I), they distill over in mixture with water at considerably lower temperatures (curve II), asymptotically approaching 100° C., and in so doing carry with them increasing quantities of water (curve III). Thus, a successful fractionation of the residue from the butanol distillation is precluded.

“Drying” by the addition of sodium chloride helps to reduce the “available” water, and aids in some cases in the distillation of the ethyl fraction.

Rivkin<sup>76</sup> claims a good measure of success by esterifying the higher alcohols with boric acid,<sup>78</sup> that is, by forming triborates, which are later hydrolyzed to the alcohols and acid by a stoichiometric quantity of water.<sup>79</sup>

TABLE II-11  
 UTILIZATION OF HIGHER ALCOHOLS

Author and reference	Conversion	Method employed	Yield
Sosnov, Rivkin, and Paul <sup>80</sup>	Butyl alcohol to butyraldehyde	<i>Pilot plant-experiments: catalytic dehydration</i> with ZnO at 450° C. Butanol used was normal S.K. industrial fraction (115–118°), containing 3.3% aldehyde, 2.0% water, 6.4% unsatd. compds. ( $d = 0.81$ )	48–54% on butanol converted, 42–50% on butanol passed, plus 2.6–4.7% butyl butyrate
Andreev and Nazarov <sup>81</sup>	Same conversion with different crude	<i>Catalytic dehydration.</i>  ANALYSIS  Before 90% butyl alcohol 20% crotonaldehyde 0.3–0.5% carboxylic compds. 0.6–2.6% water butyraldehyde butyl butyrate butyric acid	After 42% 4.5% 40% 11% 2.5%
Radchenko and Katorcha <sup>82</sup>	Butyraldehyde to butyric acid	<i>Catalytic oxidation</i> by slow heating at 50° C. with air in presence of 0.5% manganese butyrate as catalyst (with KNO <sub>3</sub> added)	82–93%
Batalin and Sekretareva <sup>83</sup>	<i>sec</i> -Butyl alcohol to methyl ethyl ketone	<i>Catalytic dehydration</i> with commercial ZnO at temp. of 500° C. Speed not critical (0.4–1.4 ml./min.).	85–88%
Batalin, Sekretareva, and Filipovskaiâ <sup>84</sup>	Crotonyl alcohol <sup>a</sup> to methyl-glycerol	<i>Chlorohydration</i> of crotonyl alcohol contained in the butyl fraction (and forming some 20% thereof)	50–60%

<sup>a</sup> Gulâeva and Dauguleva<sup>85</sup> also isolated butadiene-1,2 from the crotonyl alcohol fraction.

<sup>78</sup> For the technique involved, see Brit. Pat. 252,570 (1925); French Pat. 601,939 (1925); German Pats. 444,640 (1927) and 448,419 (1928); and French Pat. 702,154 (1930).

<sup>79</sup> Kh. Vinograd and T. Rabinovich, *Kauchuk i Rezina*, 1, No. 3, 21 (1937), have suggested a method of distillation with azeotropic mixtures, which uses benzene as the third component.

<sup>80</sup> A. Sosnov, S. M. Rivkin, and M. K. Paul', *Kauchuk i Rezina*, 1, No. 4, 34 (1937); *Sintet. Kauchuk*, 5, 7/8, 20 (1936).

<sup>81</sup> N. Z. Andreev and V. Nazarov, *Kauchuk i Rezina*, 1, No. 4, 41 (1937).

<sup>82</sup> I. Radchenko and N. Katorcha, *Kauchuk i Rezina*, 1, No. 4, 29 (1937).

(See page 78 for footnotes 83–85.)

For the subsequent utilization of the higher alcohols, see table II-11.

### B. BUTENE-2

Butene-2 and butadiene-1,3 occur simultaneously throughout the process. In view of the proximity of their boiling points ( $+1^{\circ}$  C. vs.  $-4.5^{\circ}$  C.), and especially of the constancy of the ratio of their vapor pressures (1.2:1) between  $60^{\circ}$  and  $80^{\circ}$  C.,<sup>86</sup> the physical separation of the two hydrocarbons must be considered an impossibility. This constitutes, however, no serious drawback, since butene-2 comes off in the polymerization, and, in moderate concentration, has no adverse effect on the polyreaction (see page 174).

The chemical separation of butadiene and butene-2 has been studied in detail.<sup>87</sup> The most suitable method<sup>88</sup> found for gas mixtures containing more than 5% butadiene is the use of neutral, concentrated aqueous solutions of cuprous chloride (containing 0.2 to 0.25 g.  $\text{Cu}_2\text{Cl}_2$  per ml. water). The absorption of butadiene should be carried out at  $+10^{\circ}$  to  $+15^{\circ}$  C. at normal pressure. The amount, 7.3 kg., of cuprous chloride found necessary to absorb 1 kg. butadiene was about twice the theoretical. Under such conditions, the butadiene concentration in the escaping butene-2 does not exceed 2.5 to 3.5%. A complex compound,  $\text{Cu}_2\text{Cl}_2 \cdot \text{C}_4\text{H}_6$ , is formed.<sup>89</sup> It can be rapidly and completely decomposed at  $80^{\circ}$  C., with a yield of 85 to 98% butadiene. Through the action of the air present in most gases, cuprous chloride undergoes partial oxidation. After about twenty cycles, some 15 to 30% has been oxidized to cupric chloride, which, however, can be easily reduced by hydrochloric acid and copper metal filings at a temperature of  $40^{\circ}$  to  $60^{\circ}$  C.

<sup>82</sup> V. S. Batalin and E. V. Sekretareva, *Sintet. Kauchuk*, **5**, No. 1, 14 (1936). See also P. Ā. Ivannikov, M. G. Tatarskaĭa, and E. Ā. Gavrilova, *Sintet. Kauchuk*, **5**, No. 9, 16 (1936).

<sup>84</sup> V. S. Batalin, E. V. Sekretareva, and N. N. Filipovskaĭa, *Kauchuk i Rezina*, **1**, No. 2, 28 (1937).

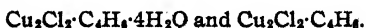
<sup>85</sup> A. Gulĭaeva and T. Dauguleva, *Kauchuk i Rezina*, **1**, No., 53 (1937).

<sup>86</sup> V. Dzivil'skiĭ, *Kauchuk i Rezina*, **1**, No. 9, 8 (1937). I. N. Bushmakin and K. I. Kuchinskakĭa, *Sintet. Kauchuk*, **5**, No. 5, 3 (1936).

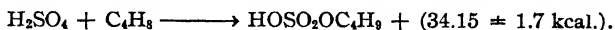
<sup>87</sup> I. L. Fridshteĭn, A. F. Tĭl'neva, and M. K. Safonova, *Sintet. Kauchuk*, **4**, No. 3, 13 (1935).

<sup>88</sup> U. S. Pat. 1,795,549 (1931); Brit. Pat. 359,234.

<sup>89</sup> G. G. Koblĭanskiĭ, A. A. Shul'ĭs and K. B. Piotrovskiĭ, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* **4**, 20 (1935), identified two compounds of butadiene and cuprous chloride:



The utilization of butene-2 was studied by Lebedev and coworkers,<sup>90</sup> who checked the method suggested by King<sup>91</sup> for making butyl sulfuric acid from butene-2, and investigated the conditions for its saponification to *sec*-butanol. A yield of 70 to 72% of the theoretical was established. The thermal effect of the reaction<sup>92</sup> between butene-2 and sulfuric acid is:



It was found necessary to work with butene-2 containing not more than 3 to 4% butadiene. The reaction of butadiene with cuprous chloride can be used to eliminate the diene from butene-2.

Suitable conditions were also found for the formation of *sec*-butyl acetate (with a yield of 60% of the theoretical calculated on butene-2).

Ākubchik<sup>93</sup> studied the possibilities of converting butene-2 to butadiene-1,3. Two theoretical paths are possible:

(1) Converting butene-2 to dichlorobutane and then removing two molecules of hydrogen chloride, as:



(2) Withdrawing from butene-2 at an elevated temperature (with or without the aid of a catalyst) one molecule of hydrogen.

Ākubchik investigated the second possibility, and found that a yield of up to 18 or 20% can be obtained when using as a catalyst carbon deposited on unglazed porcelain and when working at a temperature of 670° to 750° C.

Batalin, Sekretareva, and Filipovskaja,<sup>94</sup> continued the experiments of Ākubchik. The carbon catalyst was made by passing "aviation-grade" gasoline (b. p. 78° to 82° C.) over unglazed porcelain at 700° C. They contend, however, that the catalyst plays only a subordinate role, and that the material of which the retort is constructed is of greater consequence, *e. g.*, iron is not suitable. The maximum output obtained was 18% on a single pass of butene-2 through an empty copper tube at 700° C. and for a contact of 20 to 25 seconds. Recalculated on converted butene-2, this cor-

<sup>90</sup> S. V. Lebedev, V. P. Krauze, I. A. Volzhinskii, Ū. A. Gorin, and O. M. Neĭmark, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 3, 68 (1936).

<sup>91</sup> A. King, *J. Chem. Soc.*, 115, 1406.

<sup>92</sup> M. A. Khokhlovkin, A. V. Kalacheva, and M. A. Smirnova, *Sintet. Kauchuk*, 5, No. 2, 12 (1936).

<sup>93</sup> A. I. Ākubchik, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 60 (1935).

<sup>94</sup> V. S. Batalin, E. V. Sekretareva, and N. N. Filipovskaja, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 67 (1935).



responds to a yield of 25–26%. A “technical” butene-2 fraction was used. It has not been revealed whether the process has been used industrially.

### C. RECTIFICATION BOTTOMS

The residues from the rectification of crude butadiene can be polymerized by heating them with activated clay in autoclaves. The result is a viscous product called “Eskol,” a dark yellow liquid composed of a mixture of different, evidently cyclic, unsaturated hydrocarbons. Its physical characteristics are:  $d_{25}$ , 0.884; iodine number, 233; acid number, 5.4; saponification number, 7.2; viscosity (*vs.* glycerol), 1.38. Fractionation shows: 9% at 78° to 130° C. (colorless); 11.3% at 170° to 200°; 23% at 215° to 230° (yellow); 19.2% at 238° to 250°; and a brown residue, 35.4%. Eskol has found a use as a softener in S.K. compounding. Along with various fractions of “upper hydrocarbon layers” accompanying various by-products it has also been used in reclaiming S.K. scrap.

Products similar to Eskol are the “polydienes” (polymers of pentadiene and hexadiene). “Polydienes” are used as addition agents for rodless polymers to make them suitable for processing. Compounds of rodless S.K. polymers with high-viscosity “polydiene” (polydienes have a viscosity of 6 to 30 centipoise) have become accepted in the U.S.S.R. as integral ingredients in the carcass compounds of passenger tires.

Some of the liquid by-products of the S.K. synthesis played an interesting part in the war effort. At the high-water mark of the German advance into the Caucasus, they were used by Russia as a substitute for the much-needed motor fuel.

## 8. Analytical and Control Methods

The necessity for controlling closely the products resulting from the catalytic conversion of alcohol, as well as all phases of subsequent processing, is dictated, on the one hand, by economic considerations (efficiency of the catalytic process) and, on the other, by the fact that the polymerization step is—as will be shown—very sensitive to small quantities of impurities which might be present in the monomeric mixture of butadiene and butene-2.

These considerations have caused Russian chemists to devote considerable attention to the development and adoption of specialized analytical methods for the control of the many phases of the process and of the products which are formed. In many instances, a great number of known chemicoanalytical methods had to be tested and modified before one could be evolved which was suitable for the special conditions of concentration

and the impurities copresent. Aside from the question of accuracy, the applicability of a method to rapid laboratory control of factory processes played an important role in its selection.

Since a detailed discussion of the methods would go well beyond the scope of this volume, they are summarized in table II-12, with information about the substance to be tested for, the basic chemical reaction involved, the accuracy of the method as claimed by the authors, additional pertinent information, and the reference to the literature source.

#### A. GAS-CONDENSATE RATIO

The most important control task in an S.K. plant is a check on the operation of the catalytic converters. A rough idea of the "metabolism" of the operation can be obtained by drawing off samples of the mixture periodically and determining the ratio of condensable liquid to gas. A further step is the determination of the amount of butadiene present in the gas phase.

A number of apparatus were suggested for the determination of the gas-condensate ratio.<sup>95, 96</sup> A continuously operating unit was described by Skachkov.<sup>97</sup> It has since been generally adopted in the S.K. industry.

The apparatus is shown schematically in figure II-15. It consists of a brine-cooled condenser, *A*, two flowmeters (rotameters), *R*<sub>1</sub> and *R*<sub>2</sub>, and a number of other metering devices. The gas is drawn from the main overhead collector of the catalytic converters through valve *a* and brine-cooled condenser *A*. The uncondensed gaseous component then proceeds consecutively through gas clock *G* and flowmeter

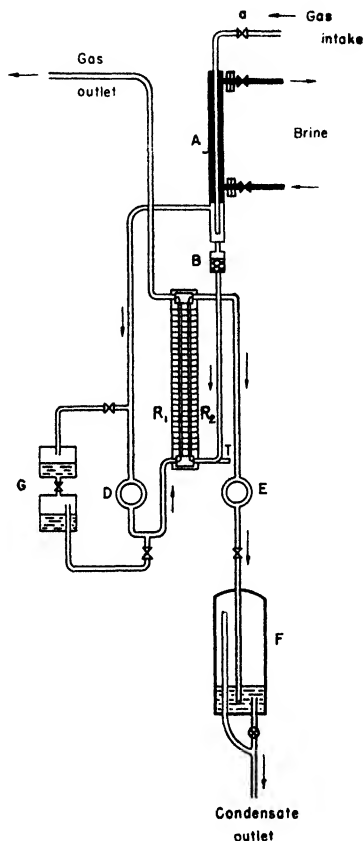


Fig. II-15.—Continuous gas-condensate analyzer.<sup>97</sup>

<sup>95</sup> I. A. Livshits and G. M. Sinaiskii, *Sintet. Kauchuk*, 5, No. 6, 17 (1936).

<sup>96</sup> A. M. Sanovich, *Sintet. Kauchuk*, 3, No. 3, (1934).

<sup>97</sup> A. Skachkov, *Sintet. Kauchuk*, 5, No. 7/8, 39 (1936).

TABLE II—12

## ANALYTICAL METHODS EMPLOYED IN THE LABORATORY CONTROL OF LEBEDVY PROCESS

Compound tested for.	Stage at which it occurs	Disturbing impurities	Concn. encountered, %	Basic method	Original method	Error	Time needed to complete test	Authors
Ethanol (in high aqueous dilutions).	(a) Fusel water of alcohol rectification: 98% water, 2% organic material (see p. 53)	Higher alcohols, ethyl ether, acetaldehyde, unsaturated hydrocarbons	0.5-0.3	Bromination at 0° C. until yellow tint appears (to remove unsatd hydrocarbons). Removal of excess Br with alkali (simultaneously resinifying aldehyde present). Removal of ether by bubbling air <sup>10</sup> at 30-35° C for 1 hr. (no alcohol losses occur). Alcohol detd by oxidation with 0.5 N K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (acid medium) and titrating the excess back with Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> .	Determining alcohols in high aqueous dilution by oxidation with K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> or KMnO <sub>4</sub> .	±1% of the concn. present	2.5-3 hours	Shatalov and Lashinova <sup>10</sup>
	(b) Hydrocarbon layer from washing ether-aldehyde fraction (p. 67)		1-10	Same method applicable for (b) and (c) if preceded by intensive shaking of hydrocarbon containing alcohol with water and analyzing the aqueous extract		±25% (less accurate in presence of butanol) ±10%		Shatalov and Radchuk <sup>10</sup>
	(c) Butadiene rectificate		0.1					Belešič and Mičho <sup>11</sup>
Acetylene (in small concns)	Butadiene rectificate		0.01 0.06	Colorimetric. Formation of colored colloidal dispersions of an acetylenic Cu in Hiosvay reagent <sup>12</sup>	Hiosvay <sup>10</sup> , Also Schulze <sup>13</sup>	4%		Chernikova <sup>14</sup>
Analysis of gas formed during catalytic reaction	Prior to absorption towers			Gas analysis in Orsat type app.—83% H <sub>2</sub> SO <sub>4</sub> suitable for above as sealing liquid instead of Hg	Dobřanskij <sup>15</sup>			Zafkova <sup>16</sup> Belešič and Melnikova <sup>17</sup>
Carbon monoxide	Rectified butadiene	Unsaturated hydrocarbons		Niclour's spectroscopic method based on property of hemoglobin to bind CO to form carbonyl hemoglobin	Niclour <sup>18</sup>	±0.004 mg. Willmex ure as literature as 0.01% CO in butadiene	55 min.	Vtorova <sup>19</sup>

Water <sup>†</sup>	Rectified butadiene	0.02	Ability of calcium carbide to react with water giving equiv. amt. of acetylene, which is detd. colorimetrically by the flow-say method, as above		Max. error 0.014%	3-4 hours	Vtorova <sup>110</sup>
Water	Rectified butadiene		Quantitative reaction: $MnO_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 3NH_3$ , $NH_3$ is then titrated with 0.1 N $H_2SO_4$	Dietrich and Conrad <sup>111</sup>	Max. error, 0.015%	1.5 hours	Shatalov <sup>113</sup>
Crotonaldehyde	Catalytic decomposition of alcohol. Fusel water. Rectified alcohol		Colorimetric detn. of yellow color produced with solns. of benzidine. Condensate dil. with 2X its quantity of water. After shaking, lower aq. layer sepd. from upper hydrocarbon-containing layer. Aq. layer distd. to separate out fraction with b. p. below 75° C. (containing most of the acetaldehyde). In fraction coming off at 75-100°, crotonaldehyde detd. colorimetrically with benzidine hydrochloride soln.		Max. error 5-6%		Alekseev <sup>113</sup>
Butyraldehyde	Catalytic decomposition of alcohol		Mixture oxidized to acids with silver oxide in presence of $MgSO_4$ + 0.01% $NaCl$ (selective oxidizing agent for aldehyde group). Resultant mixture steam distd. in alk. medium with excess silver oxide present. Oxidation with $H_2O_2$ in presence of catalyst (Klink). Detn. of acetone (as by Messinger <sup>115</sup> )	In part on work of Klink, who showed that 1 g. butyric acid yields on oxidation 0.18 g. acetone	Max. error, 5-6% if other aldehydes predominate	Special apparatus has been designed to make the process continuous	Alekseev and Zviragina, <sup>114</sup> Messinger, <sup>115</sup> or Chelintsev <i>et al.</i> <sup>116</sup>

<sup>†</sup> 0.75 g.  $CuCl_2 \cdot 3H_2O$ , 1.5 g.  $NH_4Cl$ , 3 ml. cf.  $NH_3$  (20%), 2.5 g. hydroxylamine hydrochloride.

<sup>‡</sup> Maximum solubility of water in butadiene is at 45° C. and is 0.06%.

(See following page for numbered footnotes)

$R_1$ , and is returned to the main gas line. Gasometer  $D$  (or, alternatively, an automatic gas analyzer) is shunted across gas clock  $G$ . The condensate formed in condenser  $A$  passes consecutively through filter  $B$ , meter  $R_2$ , and condensate clock  $E$ . It is collected in metering tank  $F$ , which has a capacity of 20 liters, and is periodically returned to the condensate line. The installation is designed for an hourly analysis of 300 liters of gas and 2.5 liters of condensate;  $T$  is a thermometer.

## B. BUTADIENE

**Maleic Anhydride Method.**—This method has been generally adopted in S.K. plants for the determination of the butadiene content of the gas mixture. It is based upon the findings of Diels<sup>117</sup> that molten maleic anhydride will react quantitatively with butadiene to form tetrahydrophthalic anhydride.

The reaction is conveniently carried out in an apparatus devised by Korotkov.<sup>118, 119</sup> In the apparatus, shown schematically in figure II-16 (a number of details are omitted), the gas mixture is bubbled 5–6 times through molten maleic anhydride (*i. e.*, until a constant volume is observed). The lower part of the reaction vessel is placed in a bath of boiling water while its

<sup>98</sup> V. P. Shatalov and I. I. Lapshinov, *Sintet. Kauchuk*, **5**, No. 1, 38 (1936).

<sup>99</sup> A. Vansheidt and O. Eremeeva, *Sintet. Kauchuk*, **1**, No. 3, 6 (1932).

<sup>100</sup> V. P. Shatalov and N. P. Āadchuk, *Sintet. Kauchuk*, **5**, No. 1, 40 (1936).

<sup>101</sup> Ī. A. Beleŕskii and E. M. Mil'cho, *Sintet. Kauchuk*, **5**, No. 2, 27 (1936).

<sup>102</sup> L. Īlosvay, de Nagy Īlosva, *Ber.* **32**, 2698 (1899).

<sup>103</sup> A. Schulze, *Z. angew. Chem.*, **29**, 341 (1916).

<sup>104</sup> T. F. Chernĭkovskafā, *Sintet. Kauchuk*, **5**, No. 2, 29 (1936).

<sup>105</sup> A. F. Dobriĭnskii, *Neftĭnoe Khoz.*, No. 9 (1925); No. 10 (1926).

<sup>106</sup> B. Zaĭkova, *Sintet. Kauchuk*, **3**, No. 5, 34 (1934).

<sup>107</sup> Ī. A. Beleŕskii and E. S. Mel'nikova, *Sintet. Kauchuk*, **5**, No. 3, 10 (1936).

<sup>108</sup> *Bull. soc. chim.*, **33**, 818 (1923); **37**, 760 (1925). H. Hartridge, *J. Physiol.*, **44**, 1 (1912); **57**, 47 (1922).

<sup>109</sup> E. I. Vtorova, *Sintet. Kauchuk*, **5**, No. 4, 27 (1936).

<sup>110</sup> E. I. Vtorova, *Sintet. Kauchuk*, **5**, No. 4, 29 (1936).

<sup>111</sup> K. R. Dietrich and C. Conrad, *Z. angew. Chem.*, **44**, 532 (1931).

<sup>112</sup> V. P. Shatalov, *Sintet. Kauchuk*, **5**, No. 4, 31 (1936).

<sup>113</sup> S. V. Alekseev, *Sintet. Kauchuk*, **5**, No. 10, 13 (1936).

<sup>114</sup> S. V. Alekseev and S. I. Zviĭgina, *Sintet. Kauchuk*, **5**, No. 9, 19 (1936).

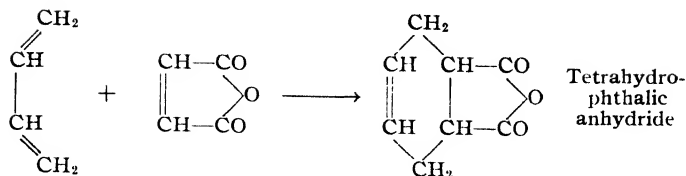
<sup>115</sup> F. Messinger, *Ber.*, **21**, 3366 (1888).

<sup>116</sup> V. V. Chelintsev *et al.*, *Zhur. Obschcheĭ Khim.*, **3**, 319 (1933).

<sup>117</sup> O. Diels, *Ann.*, **460**, 98, 122 (1928).

<sup>118</sup> A. A. Korotkov, *Sintet. Kauchuk*, **2**, No. 4, 23 (1938).

<sup>119</sup> The instrument is similar in principle to the one described a year later by H. Tropsch and W. J. Mattox, *Ind. Eng. Chem., Anal. Ed.*, **6**, 104 (1934).



upper part is maintained in contact with tepid water of constant temperature.

The reactor consists of a U-shaped capillary tube having six bulblike sections arranged symmetrically. The reaction occurs in the lower two bulbs

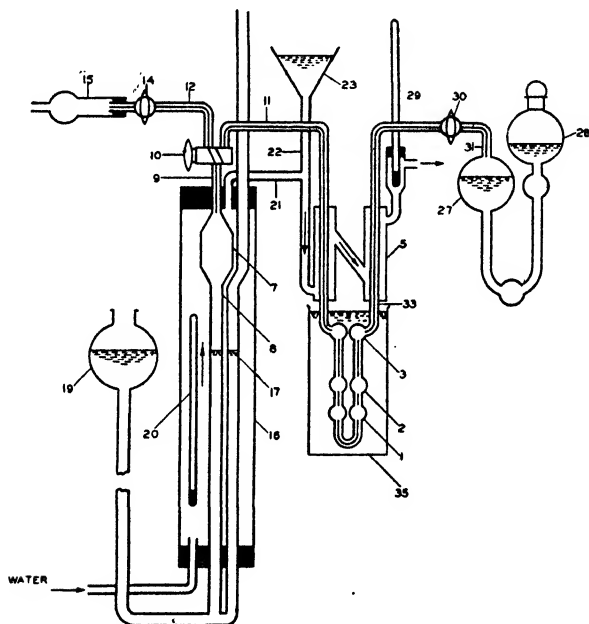


Fig. II-16.—Korotkov apparatus for butadiene determination.<sup>118</sup>

(1), of 1.5 to 2.0-ml. capacity, which are filled with 1 to 1.2 g. anhydride. Two more bulbs, 2, formed 4 to 6 mm. above the first set by a widening of the capillary tube, have a capacity of 1 ml. each. These bulbs prevent the molten anhydride from splashing up into the coolers. A third set of bulbs, 3, approximately 35 mm. above the second set, serves as a reflux area. Each end of the U-shaped reactor is connected with a rubber hose (at 33) to cooler 5, in which the temperature of the gas is restored to a standard value. The gas moves from a burette (on the left) to a pipette (on the right) and vice versa. The sealing liquid used is mercury.

The graduated burette 8, has a wide portion, 7. Through capillary 9 and a two-way glass stopcock, 10, the burette can be connected either with U-tube reactor 1 via capillary 11, or with the gas source by way of capillary 12, stopcock 14, and tube 15 filled with calcium chloride. The mercury level in burette 8 is varied by means of leveling bulb 19 attached by means of a thick-walled rubber tube. For a more accurate reading of the meniscus, a narrow tube, 17, is arranged parallel to the burette. Tubes 8 and 17 are placed in a common water bath, 16, which also contains thermometer 20. Cold water is circulated through sleeve 16, tube 21, and coolers 5.

Since a certain amount of maleic anhydride vapor is condensed in coolers 5 in each experiment, the cold water supply to the cooler is shut off after each determination and warm water is fed into the sleeve of the cooler from funnel 23 through a valve at 22.

The pipette (on the right) consists of two glass bulbs, 27 and 28, of 55-ml. and 75-ml. capacities, respectively. It is connected through stopcock 30 and capillary 29 to U-shaped reactor 1. The capillary leading to the pipette has an etched marker (at 31). The gas is passed from burette to pipette and back five to six times, each passage requiring 1.5 to 2 minutes. If certain precautionary measures are observed, the accuracy obtained is quite high.

**Other Methods.**—Numerous methods have been suggested for the analytical determination of butadiene.

Ivanov<sup>120</sup> and others showed that small concentrations of the diene can be determined with an interferometer.

Mixtures of butadiene and butene can be analyzed in the gas phase by measuring the dielectric constant, since, at frequencies of the order of  $10^8$  sec.<sup>-1</sup>, the constants for butadiene ( $\epsilon = 1.00285$ ) and for isobutylene ( $\epsilon = 1.0034$ ) are sufficiently distinct. As Perumova<sup>121</sup> showed, the dielectric constants of the two gases mixed in different proportion and at various pressures are strictly additive.

Shushin<sup>122</sup> found that, in liquefied mixtures of butadiene and isobutylene, the dielectric constants of the two components show greater divergence than most of their other physical characteristics. This divergence increases with falling temperature, as is illustrated in table II-13.

<sup>120</sup> A. Ivanov, *Sintet. Kauchuk*, 1, No. 1, 10 (1932).

<sup>121</sup> E. D. Perumova, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 199 (1935).

<sup>122</sup> P. P. Shushin, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 213 (1935).

TABLE II-13  
COMPARATIVE PHYSICAL CHARACTERISTICS OF BUTADIENE AND ISOBUTYLENE

	Density at 12° C.	Latent heat of evaporation at 11° C.	Dielectric constant (liquid)	
			at 0° C.	at -70° C.
Isobutylene	0.608 ± 0.006	85.8 ± 2.4	2.208 ± 0.02	2.487 ± 0.02
Butadiene	0.617 ± 0.006	85.4 ± 2.2	2.095 ± 0.02	2.249 ± 0.02

The infrared analysis of rectified butadiene is gaining increasing popularity.<sup>122a</sup>

### 9. Explosion Hazards in S.K. Manufacture

Through the various phases of the Lebedev process for converting alcohol to butadiene and of the butadiene polymerization, gaseous mixtures are encountered which present explosion hazards. Although the literature gives the limits of explosive concentration for a great number of pure substances, it does not provide data for the explosive ranges of the particular mixtures encountered. Such a study was undertaken by Dolgoplosk,<sup>123</sup> who investigated the more important gas mixtures which occur by sparking them in a Hempel burette and analyzing the resulting products of combustion. His major results are summarized in table II-14. The values refer to air mixtures. Partial substitution of air with "inert" gas (nitrogen or carbon dioxide) has little bearing upon the lower explosive limit. The upper limit declines rapidly and ultimately approaches the lower—in other words, the explosive range becomes narrower upon progressive replacement of air with inactive gas. Finally (*e. g.*, at eight volumes of nitrogen to one of oxygen for pure butadiene), a point is reached when explosion no longer can occur.

The pressure at which the gas mix is sparked has considerable bearing on the results. Rising pressure increases the intensity (force) of detonation for

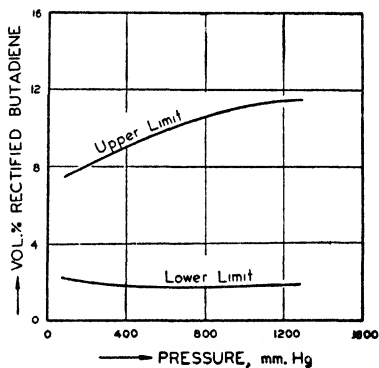


Fig. II-17.—Explosive limits of butadiene-air mixtures at varying total pressures.<sup>123</sup>

declines rapidly and ultimately approaches the lower—in other words, the explosive range becomes narrower upon progressive replacement of air with inactive gas. Finally (*e. g.*, at eight volumes of nitrogen to one of oxygen for pure butadiene), a point is reached when explosion no longer can occur.

The pressure at which the gas mix is sparked has considerable bearing on the results. Rising pressure increases the intensity (force) of detonation for

<sup>122a</sup> See, *e. g.*, L. J. Brady, *Ind. Eng. Chem., Anal. Ed.*, 16, 422 (1944).

<sup>123</sup> B. Dolgoplosk, *Sintet. Kauchuk*, 3, No. 4, 20 (1934).



TABLE II-14  
EXPLOSIVE RANGES OF VARIOUS GAS MIXTURES<sup>a</sup> IN PER CENT  
BY VOLUME IN AIR MIXTURE

Substance in admixture with air	Optimal explosive concn.	Lower limit	Upper limit
Butadiene (pure)	3.65	2.07	11.32
Butene-2 (almost pure)	3.35	1.85	7.78
Butadiene "rectificate" (monomeric mixture): 0.02-0.04% aldehyde; 0.21-0.88% rectification residues; and 76.0-79.8% butadiene-1,3	3.58	1.57-2.20	9.80-10.87
Air-free part of gas prior to absorption: 3.2-6.7% CO <sub>2</sub> ; 40.0-44.6% total unsatd. compds.; 0.49-1.79% CO; 46.5-49.87% H <sub>2</sub> ; 0.49-2.28% CH <sub>4</sub> ; 12.15-12.4% C <sub>2</sub> H <sub>4</sub> ; and 0.40-0.53 g./l. C <sub>4</sub> H <sub>6</sub> <sup>b</sup>		3.97-4.32	19.1-23.11
Air-free part of gas after scrubbing (absorbing): 4.89-7.66% CO <sub>2</sub> ; 17.6-29.51% total unsatd. compds.; 1.15-3.83% CO; 59.2-70.6% H <sub>2</sub> ; 1.84-4.16% CH <sub>4</sub> ; 16.3% C <sub>2</sub> H <sub>4</sub> , and 0.011-0.067 g./l. C <sub>4</sub> H <sub>6</sub>		5.04-5.61	25.3-37.5 <sup>b</sup>
Gas exhausted from polymerizers (after completion of polymerization): 0.0% CO <sub>2</sub> ; 0.0% CO; 0.0% O <sub>2</sub> ; 100% unsatd. + satd. compds.; and 0.255 g./l. butadiene		2.9	13.0
Air-free gas exhausted from vacuum kneaders: 0.0% CO <sub>2</sub> ; 89.4% unsatd. compds.; 0.0% CO; and 10.89% H <sub>2</sub>		2.16	10.04
Acetaldehyde (pure)	7.69	5.78	20.02
Technical aldehyde fraction: ~67.3% by vol. aldehydes; ~25% ether; 5.4% butadiene (insol. in water, ~5%); and 2.2% water	6.34	4.42	17.25
Mixtures of butadiene "rectificate" and pure acetaldehyde:			
"Rectificate" (0.04% aldehyde)		1.81	10.25
+10% by vol. acetaldehyde		1.99	11.40
+21% by vol. acetaldehyde		2.00	11.37
Mixtures of "rectificate" and technical aldehyde (see above):			
"Rectificate"		1.57	10.79
+22.2% by vol. tech. aldehyde		1.99	12.0
+50.2% by vol. tech. aldehyde		2.59	12.40
Mixture of "rectificate" and 10% diethyl ether		1.80	10.31
Air satd. with rectification residues		5.2	20.6

<sup>a</sup> At room temperature and atmospheric pressure (740-760 mm. Hg).

<sup>b</sup> The smaller figure for C<sub>4</sub>H<sub>6</sub> relates to 25.3%, the larger figure to 37.5%.

a given volume and broadens the range in which explosion can occur, mostly by raising the upper limit. Figure II-17 (page 87) depicts the condition for rectified butadiene, and is typical. At a sufficiently low pressure, the upper and lower curves would meet, and no explosion would occur beyond this point.

Increased temperature ( $100^{\circ}$  as against  $17^{\circ}$  C.) has but a slight broadening effect upon the explosive range.

In narrow tubes (pipe lines), detonation changes to "straight burning." Copper screens (metal gauze barriers) are in most cases ineffective.

Practical conclusions<sup>124</sup> drawn from the above results dictate a careful watch over hermetic conditions of reactors and pipe lines as more than just a matter of economic prudence. It may be added, though, that no fires or explosions of major proportion have been reported in the S.K. plants.

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<sup>124</sup> N. Petropavlovskii, *Sintet. Kauchuk*, 5, No. 5, 13 (1936).



### III. POLYMERIZATION

#### A. INTRODUCTION

In recent years, considerable work has been devoted to polymerization reactions in general, and to their kinetic treatment in particular. Several authors (Chalmers, Dostal, Flory, Mark, Schulz, Simha, Gee, Eyring *et al.*) have presented mathematical theories which give a more or less quantitative treatment of the process. It would go far beyond the scope of this book to review all these attempts, especially since most of them are already adequately treated in various modern treatises.<sup>125</sup> However, introductory to the presentation of data on polymerization of butadiene it might be useful to recall in a more general way the basic ideas which have emerged to date on the kinetics of polyreactions.

As pointed out by Carothers, two fundamentally different processes can lead to macromolecules: polycondensation and polymerization. In the process of *polycondensation*, the over-all reaction consists of a sequence of individual and independent steps, each step having approximately the same kinetic frequency constant,  $A$ , and the same heat of activation,  $E^\ddagger$  (following the Arrhenius equation for the rate constant,  $R = Ae^{-E^\ddagger/RT}$ ). The first polymer to appear in this type of reaction is the dimer. Then, as the reaction progresses, the amount of dimer diminishes and the trimer appears as the dominant polymer fraction, and so on. Reactions of this type are chemically well known, and differ from ordinary condensation reactions only in the aspect that the monomer molecules are so constructed that the condensation process can repeat itself indefinitely, thus leading to a polymeric (macromolecular) product.

It should be emphasized that the term "polycondensation" includes two types of reactions: simple additions, and additions with subsequent elimination (or substitution).

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<sup>125</sup> H. Mark and R. Raff, *High Polymeric Reactions*, Interscience, New York, 1941. Also R. E. Burk, H. E. Thomson, A. J. Weith, and Ira Williams, *Polymerization and Its Applications in the Fields of Rubber, Synthetic Resins and Petroleum*, Reinhold, New York, 1937.

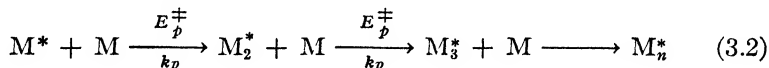
A *polymerization* reaction begins with the creation of an active nucleus—a slow, rate-determining, first step. It is followed by a very rapid, chain-like growth which continues until the chain is broken in one of several ways by a cessation reaction. At no time does the dimeric or the trimeric form predominate among the products of polymerization (except when a side reaction takes place). The distribution of chain lengths encountered at an early stage of the process is about the same as that found later. Like all chain reactions, this process is extremely sensitive to catalysts and inhibitors and can be easily altered. Hence it is safe to predict that the properties of a polymer will depend very largely on the polymerization conditions.

As already suggested, the polymerization process can be divided into three distinct steps:

(1) Initiation of the reaction, in which a monomer is activated (*i. e.*, either brought to a higher electronic state or transformed into a free radical), such activation being achieved in one of several ways. The rate will be governed by a constant,  $k_i$ , and a corresponding activation energy,  $E_i^\ddagger$ :



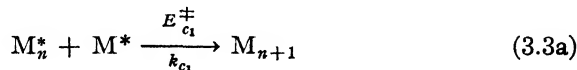
(2) Propagation of the reaction, consisting of adding of monomeric molecules to the activated monomer,  $M^*$ , or polymer,  $M_n^*$ :



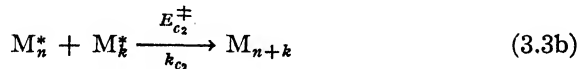
where  $k_p$  is the rate constant and  $E_p^\ddagger$  the activation energy of this step of the process.

(3) Cessation of the reaction, consisting of a deactivation (and hence a stabilization) of the activated complex brought about either:

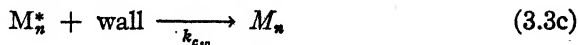
(a) by a collision with an activated monomer:



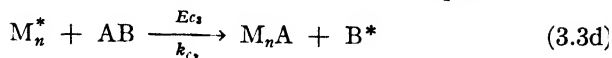
(b) by a collision with an activated or inactivated polymer:



(c) by a collision with the walls of the reaction vessel:

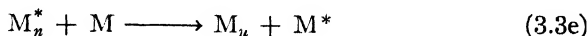


(d) by a collision with a solvent molecule, if a solvent is present:



followed by a subsequent reaction of the activated part of the solvent molecule,  $B^*$ , with other solvent molecules (as, for instance,  $M_n^* + CCl_4 \rightarrow M_nCl + CCl_3^*$ ,  $CCl_3^* + M \rightarrow Cl_3CM^*$ ,  $CCl_3^* + CCl_3^* \rightleftharpoons C_2Cl_6$ ), or finally:

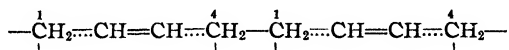
(e) by a transfer of its activation to a new molecule of the monomer or of the polymer:



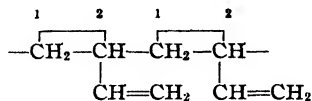
Each type of cessation mechanism calls for a different amount of activation energy ( $E_{c_1}^\ddagger$ ,  $E_{c_2}^\ddagger$ , ...) and a different probability factor,  $A$ , and hence is more or less prevalent at a given temperature and at given concentrations of different components of the system.<sup>126</sup>

In the case of diolefins, the initiation process usually requires an activation energy  $E_i^\ddagger$  of 23–25 kcal. per mole and has a large probability factor of  $A \sim 10^{10}$ . It is generally the slowest part of the whole polymerization process, and for this reason lends itself to careful study. Since the rate of propagation is about  $10^6$  times faster than the rate of initiation, this step of the reaction is more difficult to follow. In the case of butadiene-1,3, the propagation can take place in a variety of ways:<sup>127</sup>

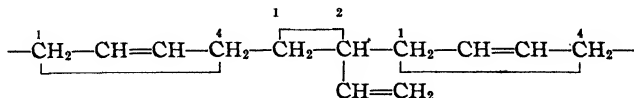
(a) as a 1,4 addition:



(b) as a 1,2 addition:



(c) as a simultaneous 1,2 and 1,4 addition in varying proportions:

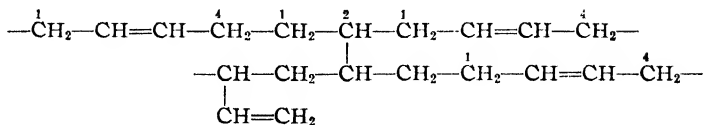


<sup>126</sup> For a more detailed discussion, see the articles of J. Abere, G. Goldfinger, H. Mark, and H. Naidus; C. C. Price; H. M. Hulburt, R. A. Harman, A. V. Tobolsky, and H. Eyring, *Ann. N. Y. Acad. Sci.*, **14**, 267, 351, 371 (1943).

<sup>127</sup> R. Hill, J. R. Lewis, and J. L. Simonsen, *Trans. Faraday Soc.*, **35**, 1067, 1079 (1939).

and finally:

(d) by a process of more or less extended branching:



The heat of activation for the propagation reaction on butadiene-1,3 has been determined for only one type of polymerization—initiation with excited mercury atoms<sup>128</sup>—and was found to be somewhat larger than 5.5 kcal./mole. This figure is close enough to the figure of 5 kcal./mole, given by Schulz and Husemann<sup>129</sup> for the activation energy of the propagation reaction in the polymerization of styrene, to be considered typical. It should, however, be noted that, for certain polycondensation mechanisms, this activation energy is different for 1,2 and 1,4 additions.<sup>130</sup>

It is generally known that the average length of the chains in the polymer decreases with increasing temperature of polymerization. This means that, with increasing temperature, the rate of cessation increases faster than the rate of propagation, that is, cessation requires a higher activation energy. We can, therefore, safely assume that the energy of activation for the fastest cessation reactions is in excess of 5 kcal.<sup>131</sup> Since the rate of a cessation reaction governs not only the growth of the main chains, but also the growth of the branches, it is readily seen why often small changes in the physical conditions can alter drastically the properties of the polymers obtained.

The effect of catalysts consists mainly in an increased rate of creation of active centers. In the case of polymerization, only the rate of the initiation reaction is affected. In the case of polycondensation, where all the steps are similar, obviously the rate of "propagation" is affected too. We shall see that this is the case for the sodium-catalyzed butadiene condensation because, in this case, the reacting part of the molecule is the part containing the catalyst itself.

The chain length,  $N$ , or the number average degree of polymerization depends generally on the three rates,  $k_i$ ,  $k_p$ , and  $k_c$  and on the concentrations

<sup>128</sup> G. Gee, *Trans. Faraday Soc.*, **34**, 712 (1938).

<sup>129</sup> G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B34**, 187 (1936).

<sup>130</sup> G. V. Schulz, *Ber.*, **B74**, 1766 (1941). See also page 152.

<sup>131</sup> See, for instance, M. W. Perrin, *Trans. Faraday Soc.*, **35**, 1064 (1939).

of both monomer and catalyst, and can be represented in the most general way by a relation of the type:

$$N \sim \frac{(k_p)^n}{(k_i)^m (\Sigma k_c)^r} \cdot \frac{[M]^s}{[C]^t [I]^u} \quad (3.4a)$$

where  $[M]$ ,  $[C]$ , and  $[I]$  are the concentrations of the monomer, catalyst, and "inhibitor," respectively,<sup>132</sup> and  $n$ ,  $m$ ,  $r$ ,  $s$ ,  $t$ , and  $u$  represent powers generally between  $1/2$  and 3, depending on the exact mechanism. It is clear from equation (3.4a) that an increase of the concentration of the catalyst,  $[C]$ , or of its "catalytic activity,"  $[k_i]$ , leads to shorter chains, as does also an increase in the rate of cessation reaction or in the concentration of "inhibitor." (In this particular case, we consider as inhibitor any substance likely to react with the growing polymer according to equation 3.3d.) The corresponding initial rate,  $R_t$ , of the polymerization is given by:

$$R_t = \frac{(k_i)^m (k_p)^n}{(\Sigma k_c)^r} \frac{[M]^s [C]^t}{[I]^u} \quad (3.4b)$$

As will be shown in the following pages, the polyreactions leading to formation of polybutadiene can be of both types, either polymerizations or polycondensations. The best possible theoretical subdivision of this chapter would be along these lines. In such a case, however, the first part, on polymerization reactions, would include both the bulk polymerization and the emulsion polymerization which, although proceeding by the same reaction mechanism, are phenomenologically fairly different. Furthermore, the photochemically induced polyreactions, as well as the polyreactions in the glow discharge, would have to be subdivided, because, in certain instances, both mechanisms are possible or present. It is therefore more suitable to sacrifice pure logic somewhat and to divide the chapter into four parts:

- A. Homogeneous and catalyzed thermopolymerization.
- B. Emulsion polymerization, which is an important specific case of heterogeneous thermopolymerization.
- C. Sodium polycondensation.
- D. Photochemical polyreactions, reactions in glow discharge, etc.

It is to be emphasized again that polymerization and polycondensation in the broad sense used in this book differ only by the ratio of reaction rates for initiation and for propagation. For polymerization,  $k_p \gg k_i$ , and for polycondensation,  $k_p \geq k_i$ .

<sup>132</sup> See, for instance, J. Abere, G. Goldfinger, H. Mark, and H. Naidus, *Ann. N. Y. Acad. Sci.*, **44**, 267 (1943).



## B. HOMOGENEOUS AND CATALYZED THERMOPOLYMERIZATION

### 1. General Remarks

Although thermopolymerization does not yield polymers of rubberlike character, it has been carefully investigated over a wide range of temperatures, for two reasons: (1) the desire to obtain information on the mechanism of polymerization of butadiene, and (2) the importance of thermopolymerization as an often unwelcome reaction accompanying certain phases of synthetic rubber manufacture. Thus, thermopolymerization at room temperature, the so-called "autopolymerization," is a problem attending the storage of butadiene. Thermopolymerization at 400–500° C. is of importance in the Lebedev process, in which the butadiene formed remains for a certain time in contact with the dehydration-dehydrogenation catalyst at about this temperature and is then cooled down. Thermopolymerization at even higher temperatures is a factor in the production of butadiene by the cracking process from petroleum products. The formation of polymer leads, on the one hand, to losses of butadiene and, on the other hand, to accumulation of resinous products, particularly in the heat exchangers, disturbing their proper functioning.

The first scientists to observe and investigate—simultaneously, though independently—the thermopolymerization of butadiene were Lebedev<sup>133</sup> and Hofman.<sup>134</sup> Lebedev observed that butadiene kept at 150° C. was well polymerized in five days and completely polymerized in a matter of ten days, yielding a viscous liquid—a solution of the polymer in the dimer—and a small amount of insoluble polymer. The dimer was distilled off at 100 mm. Hg pressure; it was found that, under these conditions, the polymer represented 14–15% and the dimer 86–85% of the total polymerization products.

### 2. Low Polymers

#### A. THE DIMER

It was Lebedev who first determined the characteristic properties of the dimer as well as its structure. The dimer, a colorless liquid with a pungent smell, produces a yellowish color with tetranitromethane. It is a fairly unstable compound, readily oxidized in air. Its viscosity increases on pro-

<sup>133</sup> S. V. Lebedev, *Zhur. Russ. Fiz.-Khim. Obshchestva*, **41**, 1818 (1909); **42**, 726 (1910); **43**, 1124 (1911).

<sup>134</sup> F. Hofman, German Pat. 235,423, issued Nov. 30, 1909.

longed heating, indicating further polymerization probably through a dissociation to butadiene. Its major physical properties are presented in table III-1. The table also shows the degree of agreement between various investigators.

TABLE III-1  
MAJOR PHYSICAL PROPERTIES OF THE DIMER

Density	Refractive index	Authors
$\rho_4^0 = 0.8484$ $\rho_4^{20} = 0.8320$	$n_D^{20} = 1.4653$	Lebedev <sup>133</sup>
$\rho_4^{20} = 0.8319$	$n_D^{20} = 1.4624$	Aschan <sup>135</sup>
$\rho_4^0 = 0.8470$ $\rho_4^{20} = 0.8304$	$n_D^{20} = 1.4628$	Lebedev and Sergienko <sup>136</sup>
$\rho_{25}^{25} = 0.837$	$n_D^{20} = 1.466-1.470$	Moor <i>et al.</i> <sup>137</sup>
$\rho_4^{20} = 0.848-867$	$n_D^{20} = 1.460-1.469$	Vaughan <sup>138</sup>
Surface tension	Parachor	Molecular refraction
$\gamma = 27.0$	$P = 296.5$	$MR_D = 35.88$
Vapor pressure		Author
$t, ^\circ\text{C.}$	$p, \text{mm. Hg}$	
50	74	Aschan <sup>135</sup>
66.5	100	Lebedev <sup>139</sup>
129.5-130.5	760	Lebedev <sup>139</sup>
Heat of combustion, cal./g. <sup>139</sup>	Heat of formation of liquid dimer <sup>a</sup> from gaseous butadiene, cal./g. <sup>139</sup>	Heat of vaporization, calcd. from vapor pressure, cal./g. 117
10.932	222	100

<sup>a</sup> Calculated assuming 11.254 cal. as heat of combustion of the gaseous monomer. If 11.300 cal. per g. (L. Hock and H. Leber, *Kolloid-Z.*, **90**, 65, 1940) is assumed, the heat of formation is 268 cal. per g.

Combustion analysis of the dimer leads to the formula,  $\text{C}_8\text{H}_{12}$ ; the dimer yields ethylcyclohexane on hydrogenation and  $\beta$ -carboxyadipic acid on oxidation, and adds four atoms of bromine. From these data, Lebedev deduced that the dimer of butadiene is 4-vinylcyclohexene-1 and was formed

<sup>135</sup> O. Aschan, *Ber.*, **57**, 1959 (1924).

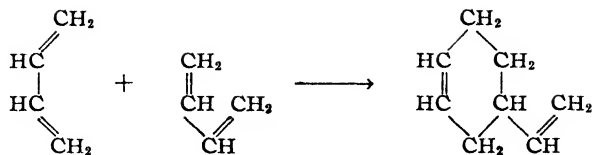
<sup>136</sup> S. V. Lebedev and S. R. Sergienko, *Zhur. Obshcheĭ Khim.*, **5**, 1839 (1935).

<sup>137</sup> V. G. Moor, N. V. Strigaleva, and L. V. Shil'fæva, *Zhur. Obshcheĭ Khim.*, **5**, 818 (1935).

<sup>138</sup> W. E. Vaughan, *J. Am. Chem. Soc.*, **54**, 3863 (1932).

<sup>139</sup> S. V. Lebedev, G. G. Koblfanskiĭ, M. A. Khokhlovkin, N. I. Kuĭbina, and M. M. Gol'dman, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B."*, **4**, 46 (1935).

by the reaction :



This structure of the dimer was fully confirmed by later investigations, both Russian<sup>136</sup> and American.<sup>140</sup> Sergienko<sup>136</sup> in particular definitely established that no aliphatic dimer with three double bonds (as was assumed by Kondakov,<sup>141</sup> Harries,<sup>142</sup> and Ostromislensky<sup>143</sup>) could be justified. A more careful fractionation of the dimer revealed the presence of a small amount of an isomeric dimer, probably 3-vinylcyclohexene-1. Below 150° C., no further polymerization of the dimer could be observed. In order to polymerize, the dimer must be broken down or brought into contact with activated monomer. Dissociation of the dimer seems to take place around 350° C.; at this temperature, Vaughan<sup>138</sup> as well as Kistiakowsky and Ransom<sup>140</sup> observed the formation of a trimer toward the end of the dimerization reaction, *i. e.*, when at least 70% of the monomer is converted. A similar observation was made by Zhavoronkov<sup>144</sup> when the thermopolymerization was effected in presence of activated charcoal at 350–450° C.

#### B. THE TRIMER

Alder and Rickert<sup>145</sup> have prepared a large enough amount of the trimer to be able to determine its constitution.

Using the fact that dimer and trimer formation are extremely insensitive to the presence of catalysts (except oxygen, the presence of which favors the formation of the high polymer) while the high polymer formation can easily be inhibited, Alder and Rickert heated in an autoclave 100 g. 4-vinylcyclohexene-1 (dimer) with 150 ml. butadiene in the presence of 0.5 g. acetylenedicarboxylic acid (as polymerization inhibitor), for 14 hours at 170–180° C. The distillation yielded 160 g. dimer and an oily liquid, which constitute a solution of the high polymer in the trimer. At 100–130° C., under 11 mm. Hg pressure, 7 g. of the trimer could be distilled off.

<sup>136</sup> G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7**, 725–735 (1939).

<sup>141</sup> I. L. Kondakov, *Synthetic rubber, its homologs and analogs*. Yuriev, 1912.

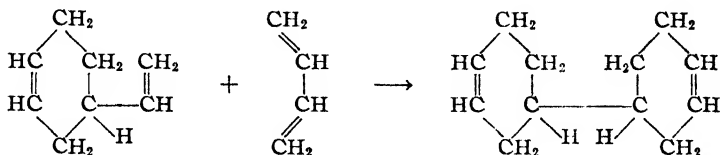
<sup>142</sup> C. Harries, *Ann.*, **383**, 205, 211 (1911).

<sup>143</sup> I. I. Ostromislensky, *Zhur. Russ. Fiz.-Khim. Obshchestva*, **47**, 1928 (1915).

<sup>144</sup> P. V. Zhavoronkov, *Kauchuk i Rezina*, **4**, No. 11, 10–14 (1940).

<sup>145</sup> K. Alder and H. F. Rickert, *Ber.*, **B71**, 873 (1938).

The trimeric form is a colorless, strongly smelling liquid with a boiling point of 230–232° C. at 760 mm. Hg. Its structure was determined through catalytic reduction and through dehydration with bromine and proved to be  $\Delta^{3,8}$ -octahydrobiphenyl, suggesting that it was formed from the dimer by way of the reaction:

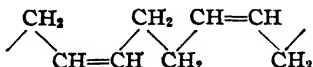


### 3. Structure of the Thermopolymer

Lebedev also investigated the structure of the higher polymer formed simultaneously with the dimer at 150° C. As already pointed out, a part of the polymer dissolved in the dimer, while another formed an insoluble swollen gel. While the structure of the soluble part could be more or less successfully determined by ozonolysis, the structure of the insoluble fraction defied investigation because it could not be dissolved in carbon tetrachloride even after prolonged boiling, and hence could not be ozonized.

This is in agreement with observations made on the polymerization of isoprene and 2,3-dimethylbutadiene where larger amounts of an insoluble form appear if the polymerization takes place at or only slightly above room temperature. But there is some difference between the upper temperature limits for the gel formation, which is 100° C. for isoprene and 2,3-dimethylbutadiene and above 150° for butadiene. No experimental proof is obtainable in this last case since, above 150°, the thermopolymerization of butadiene yields practically pure dimer.

As for the structure of the soluble polymer fraction, the hydrolysis of the ozonolysis products yields only succinic acid and succinaldehyde. Thus, the most probable configuration is the 1,4 addition polymer:



The structure of the polymer is extremely sensitive to catalyst action. For instance, in the presence of formic acid, Harries<sup>146</sup> obtained, at 110–120° C., a polymer completely soluble in chloroform, and practically no dimer.

<sup>146</sup> C. Harries, *Chem. Ztg.*, **37**, 330 (1911).

#### 4. Thermopolymerization in the Liquid Phase

##### A. AT ROOM TEMPERATURE

The kinetics of thermopolymerization of butadiene at room temperature has been studied by Lebedev and coworkers,<sup>147</sup> Khokhlovkin,<sup>148</sup> Koblîanskiĭ and Piotrovskiĭ,<sup>149</sup> and Koblîanskiĭ.<sup>150</sup> The time necessary for complete polymerization of liquefied butadiene at room temperature is of the order of 1.5 years, occasionally less. Butadiene thus occupies an intermediate position between isoprene (3.5 years) and dimethylbutadiene-2,3 (7 months).

The polymerization proceeds faster in light than in the dark, although variations (under identical conditions) are so large that only statistical comparisons can be made. Khokhlovkin<sup>148</sup> carried out two series of polymerizations: one in the light, the other in the dark. The dark series was subdivided into three groups. In the first group the polymerization was carried out excluding all oxygen, in the second the butadiene was saturated with oxygen, while, in a third group of experiments, insoluble polymer formed at room temperature was added. This last group was the first to polymerize, indicating that this polymer acted as a catalyst. The reaction is, therefore, considered as autocatalyzed, in complete analogy with observations of Lebedev<sup>151</sup> on 2,3-dimethylbutadiene and isoprene. Most of the samples of the two other groups of the "dark" series were not appreciably polymerized after 1.5 years. In contradistinction, most of the samples of the first series (kept in light) polymerized to an extent of 85–90% in the same period of time.

In the samples polymerized in the presence of oxygen, the liquid separated into two layers: a very viscous liquid polymer occupying the bottom of the test tube, and a solution of polymer in monomer above it. About 12% of the polymer formed was found in this upper layer. The presence of oxygen hence both induces the formation of low molecular weight polymer and accelerates the reaction. Both these effects are correlated.

Another effect of the oxygen is to favor somewhat the formation of the polymer over that of the dimer. (This effect of oxygen was observed also at higher temperatures.) The polymer formed under these conditions is

<sup>147</sup> S. V. Lebedev, G. G. Koblîanskiĭ, M. A. Khokhlovkin, N. I. Kuĭbina, and M. M. Gol'dman, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 46 (1935).

<sup>148</sup> M. A. Khokhlovkin, *Sinet. Kauchuk*, 5, No. 4, 12 (1936).

<sup>149</sup> G. G. Koblîanskiĭ, and K. B. Piotrovskiĭ, *Sinet. Kauchuk*, 5, No. 3, 3 (1936).

<sup>150</sup> G. G. Koblîanskiĭ, *Sinet. Kauchuk*, 5, No. 9, 3 (1936).

<sup>151</sup> S. V. Lebedev, monograph, "Issledovanie v oblasti polimerizatsii dvetilovykh uglevodorodov," St. Petersburg, 1913, reprinted in *Zhizn' i Trudy*, Moscow, 1938, pp. 115–137.

white, fairly hard, soluble, and stable in air, and contains up to 2.3% oxygen. In the absence of oxygen, one obtains some dimer and three forms of polymer; one soluble, and the other two insoluble. One of the latter forms is a soft gel; the other a hard mass of spongy appearance called "sponge polymer" or "autopolymer." This polymer was also found by Harries.<sup>152</sup> Once exposed to air it is very easily oxidized and becomes yellow and brittle. The amount of the soluble form in the total polymer obtained at room temperature was determined by Lebedev *et al.*<sup>189</sup> and varied with the nature of the solvent (Table III-2). The insoluble "sponge polymer" is formed in large amounts only at room temperature (20° C.), and practically none of it is formed at temperatures around 100° C. It is this form which acts as a specific catalyst, accelerating the reaction and directing it toward the reproduction of "sponge polymer" even at temperatures above 100°, where, as stated before, no "sponge polymer" is formed spontaneously. The heat of formation of this polymer was found, from combustion data, to be 331 cal. per g.<sup>139</sup>

TABLE III-2

SOLUBILITY OF THE POLYMER OBTAINED AT ROOM TEMPERATURE

Solvent	Per cent dissolved
Dimer.....	0
Benzene.....	9.5
Carbon tetrachloride.....	15.4
Chloroform.....	24

In the course of a polymerization, first the dimer and the soluble form of the polymer appear, and then, after at least 10% is polymerized, the autopolymer, which increases the reaction rate by the autocatalytic effect described above. This is illustrated very clearly in figure III-1, in which the degree of conversion is plotted against time for various temperatures. In the curve depicting the observations of Khokhlovkin, the rate increases sharply after 400 days. No increase in conversion rate was observed by Koblânskiĭ and Piotrovskiĭ, who discontinued their experiments at 6% conversion, before the appearance of "sponge polymer" (see Fig. III-1, curve for 20–25° C.). At higher temperatures, the "sponge polymer" seems to appear only at degrees of conversion higher than 10%, as can be seen from the curves of Koblânskiĭ and Piotrovskiĭ at 40° and 60° C.

The experiments of Khokhlovkin, referred to in the figure, were carried

<sup>152</sup> C. Harries, *Gummi-Ztg.*, **35**, 898 (1921).

out in light and in the presence of air. They are characterized by a long induction period (14.8% of polymer formed after 427 days) followed by a rapid increase of the polymerization rate as soon as the autocatalytic effect of the "sponge polymer" comes into play (97% after 505 days). A flattening out of the curve between 130 and 427 days is attributed by Khokhlovkin to the disappearance of the accelerating effect of the oxygen, due either to a change in the polymerization mechanism or to exhaustion of the oxygen which, as noted before, becomes an integral part of the polymers.

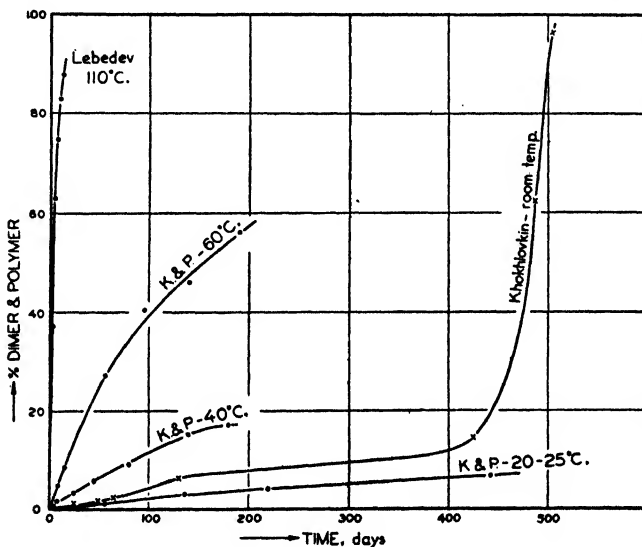


Fig. III-1.—Thermopolymerization of butadiene at different temperatures (20°–110° C.) as a function of time.<sup>148,149,154</sup>

The distinction between the "sponge polymer" and the insoluble soft gel formed concurrently (which is the only insoluble form of the polymer prepared at higher temperatures) appears markedly in the heat of formation of the latter, 554 cal. per g., compared with 331 for the former.<sup>139</sup>

A large number of catalysts and inhibitors for the autopolymerization have undoubtedly been tried out both in the U.S.S.R. and elsewhere, but little data have been published. Floridin<sup>24</sup> may be mentioned among the substances catalyzing other polymerization reactions but failing to induce the butadiene "autopolymerization" even after two years.<sup>153</sup> The inhibiting effect of certain copper salts will be discussed later.

<sup>148</sup> S. V. Lebedev and E. P. Filonenko, *Ber.*, 58, 163 (1925).

## B. AT ELEVATED TEMPERATURES

Thermopolymerization in the liquid phase above room temperature has also been investigated, in the temperature range between 25° and 164° C. (critical temperature of butadiene), by Kobljanskiĭ and Piotrovskii<sup>149</sup> at 25°, 40°, and 60°, by Lebedev *et al.*,<sup>154</sup> at 110°, 120°, 130°, and 150°, and most recently by Robey, Wiese, and Morrell.<sup>154a</sup> Their main findings can be summarized as follows:

(1) At all these temperatures, the ratio of dimer to polymer depends only on the temperature and is independent of the degree of conversion.<sup>155</sup>

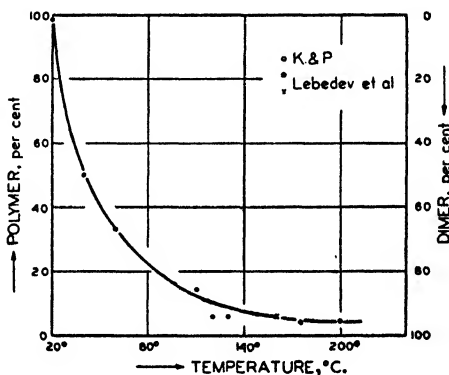


Fig. III-2.—Effect of polymerization temperature on the dimer-polymer ratio.<sup>149, 154</sup>

(2) With increasing temperature the ratio increases, more dimer being formed at higher temperatures (see Fig. III-2). Up to 200° C. this process is not reversible.

(3) The amount of “autopolymer” (“sponge polymer”) decreases with increase of temperature.

(4) The molecular weight of the polymer decreases with increasing temperature.

<sup>154</sup> S. V. Lebedev, M. A. Khokhlovkin, N. I. Kuĭbina, and A. P. Begetova, *Zhur. Fiz. Khim.*, **7**, 130 (1936); *Sintet. Kauchuk*, **5**, No. 1, 2 (1936).

<sup>154a</sup> R. F. Robey, H. K. Wiese, and C. E. Morrell, *Ind. Eng. Chem., Ind. Ed.*, **36**, 3 (1944).

<sup>155</sup> This was observed also for other diolefins by E. N. Gapon, *Zhur. Russ. Fiz.-Khim. Obshchestva*, **62**, 6, 1385 (1930), by G. S. Whitby and R. N. Crozier, *Can. J. Research*, **6**, 203 (1932), and earlier by S. V. Lebedev, see footnote 151.



(5) The reaction is homogeneous; introduction of broken glass or of steel surfaces into the reaction vessel does not affect the reaction rate.

(6) The presence of oxygen increases the reaction rate.

The per cent conversion as a function of time is given in figure III-1, containing, as indicated on page 101, the data of Khokholovkin at 25° C.,

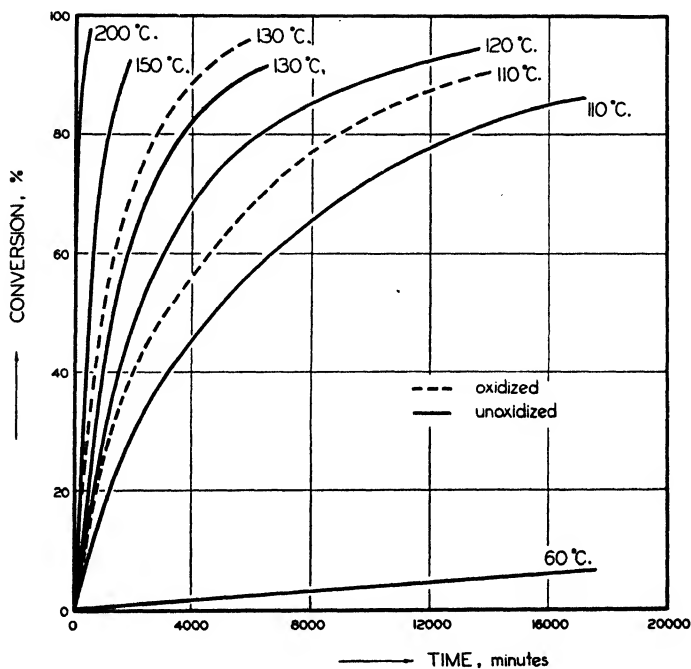


Fig. III-3.—Thermopolymerization of unoxidized and of oxidized butadiene at different temperatures (110°–200° C.) as a function of time.<sup>154</sup>

of Koblânskiĭ and Piotrovskiĭ at 20–25°, 40°, and 60°, as well as the data of Lebedev *et al.* at 110°. Figure III-3 gives on an enlarged time scale the data of the latter authors for the temperature range of 110–200°.

The data of Koblânskiĭ and Piotrovskiĭ can be represented fairly well by a second-order rate constant, with an energy of activation of about 15–17 kcal. per mole. The initial rates of reaction observed by Lebedev and co-workers can also be represented by second-order reaction constants, but with an activation energy of 12.9 kcal. per mole, corresponding to: log

$k = 3.7 - (2816/T)$ . In the presence of oxygen the reaction goes somewhat faster, although the heat of activation is at least as high,  $E_{\text{act.}} = 13.0$  kcal. per mole. The rate constant for oxidized butadiene can be represented by  $\log k = 3.9 - (2848/T)$ . However, as the reaction progresses, the second-order rate constant first decreases, then increases again, a phenomenon also observed in the gas phase by Vaughan,<sup>138</sup> who explains it by interference of side reactions due to the presence of peroxides.

Over the entire range of conversion, the results of Lebedev *et al.* can best be represented by a reaction of the order 3/2, with an activation energy of 13.1 kcal. per mole. An over-all reaction rate of the order 3/2 generally corresponds to a catalyzed polymerization reaction (see page 120). As in this case the deviation from the second order toward the 3/2 order is larger with higher temperature and higher dimer content, one would be led to assume that the dimer acts as a catalyst, a fairly improbable situation. Further checking of Lebedev's results is necessary before any such conclusion may be accepted.

Nor can this increase of the rate constant over the one corresponding to the second-order reaction towards the end of the polymerization be explained by pressure variation. The pressure decreases as the reaction progresses; and it was shown by Starkweather<sup>156</sup> that a pressure rise increases the reaction rate, an opposite effect to the one in question.

As far as the variation of the dimer-polymer ratio with temperature is concerned, one can try to explain it by assuming different activation energies for the two processes—dimerization and polymerization. In this case, assuming the frequency factors,  $A_D$  and  $A_p$ , different for both processes but independent of the temperature one would expect:

$$\frac{p(\%)}{D(\%) } = \frac{A_p}{A_D} e^{(E_D^\ddagger - E_p^\ddagger)/RT} \quad (3.5a)$$

where  $E_D^\ddagger$  and  $E_p^\ddagger$  are the activation energies for dimerization and polymerization or:

$$\ln \frac{p}{D} = \text{const.} + \frac{E_D^\ddagger - E_p^\ddagger}{RT} \quad (3.5b)$$

a relation which is not fulfilled.

Lebedev and coworkers<sup>147</sup> have extended their measurements beyond the critical point of butadiene, up to 200° C. They observed a sharp discontinuity of the activation energy, which suddenly changes to 24.9

<sup>156</sup> H. W. Starkweather, *J. Am. Chem. Soc.*, **56**, 1870 (1934).

kcal. per mole, the value it has in the gas phase. This break seems to be related to the change in the state of the butadiene, because the discontinuity disappears if the heat of activation is calculated, not from the initial rate constant, but from the rate constant at 83% conversion where the reaction always takes place in the liquid state. In this case, the heat of activation, calculated from Lebedev's data, is 18.5 kcal., of the order of the activation energy calculated from the data of Kobljanskiĭ and Piotrovskiĭ.

The effect of pressure on the thermopolymerization of butadiene was investigated by Starkweather,<sup>156</sup> who found that the rate of the reaction is greatly increased with rising pressure. At 7000 atm., 95% was found polymerized after 46 hours at 48° C. and after as little as 19 hours at 61° C., while at 1 atm. the same conversion would require several hundred days. The reaction could be represented by a first-order constant:

$$k = (1/t) \ln (1/1 - x)$$

the values of  $k$  being 0.065 and 0.158, respectively, for the two temperatures.

An analogous effect of high pressure was observed earlier by Plausen and Vielle,<sup>157</sup> who claimed that, at 25–30° C. and in an atmosphere of nitrogen, the polymerization is completed in 4 weeks at 300 atm. and in 5–6 days at 600 atm.

### C. INHIBITORS AND ACCELERATORS

The rate of polymer formation even below 100° C. is fast enough to cause trouble in the technological process. This reaction must therefore be suppressed.

As inhibitors of the polymer formation, butadiene-soluble copper salts of higher aliphatic acids proved to be fairly efficient,<sup>158</sup> as they are in the polymerization of neoprene.<sup>159</sup>

The experiments of Savel'ev and coworkers<sup>158</sup> were carried out on technical "distilled" butadiene (containing 77–90% butadiene, 0.016–0.027% acetaldehyde, and the balance, mainly butene-2) at 80° and 110° C., with copper naphthenate and copper oleate as inhibitors.

The inhibiting power seems not to depend on the anion, and the inhibition action appears to be determined only by the concentration of copper ions. The formation of the dimer seems not to be affected at all, while the

<sup>157</sup> H. Plausen and J. A. Vielle, Brit. Pat. 156,116, issued Dec. 30, 1920; Traum, German Pat. 329,593, issued Nov. 23, 1920.

<sup>158</sup> A. I. Savel'ev, O. G. Arbidan, and A. V. Zlatogurskiĭ, *Siniĭ Kauchuk*, 5, No. 4, 18 (1936).

<sup>159</sup> I. Williams and H. W. Walker, *Ind. Eng. Chem., Ind. Ed.*, 25, 199 (1933).

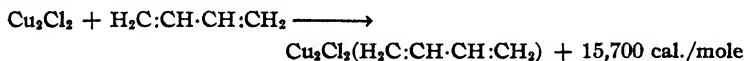
formation of the polymer is completely inhibited by as little as 0.05% copper ions for 11 days at 80° and by 0.09% for 29 days at the same temperature. The presence of copper metal increases the effectiveness of copper salts, the presence of iron seems to have no effect. This inhibiting effect of copper metals was also observed in factories.<sup>160</sup>

Table III-3 summarizes the most important results of Savel'ev *et al.*<sup>168</sup>

TABLE III-3  
EFFECT OF COPPER IONS ON THE POLYMERIZATION REACTION

Temp., ° C.	Days	Inhibitor	Copper ions, %	Metal	Dimer, %	Polymer, %	Conver- sion, %
80	11	Control	....	...	16.30	6.29	22.59
	11	Naphthenate	0.05	...	17.62	0	17.62
	11	Naphthenate	0.01	...	16.38	1.13	17.51
	11	Oleate	0.01	...	17.10	0.40	17.50
80	17	Control	....	...	27.40	7.83	35.23
	17	Naphthenate	0.0199	...	29.36	0.84	30.20
	17	Naphthenate	0.0505	...	30.90	0	30.90
	17	Naphthenate	0.0199	Cu	31.40	0	31.40
	17	Naphthenate	0.0505	Cu	30.12	0	30.12
	17	Naphthenate	0.0199	Fe	30.13	0.90	31.03
	17	Naphthenate	0.0505	Fe	30.80	0	30.80
	17	Naphthenate	0.0505	Fe	30.80	0	30.80
100	10	Control	....	...	71.10	9.13	80.23
	18	Naphthenate	0.09	...	85.50	0	85.50

The explanation of the copper salt effect probably lies in the formation of complexes of the type of those observed with cuprous chloride:<sup>161, 162</sup>



although no such complex formation was observed with cupric sulfide or sulfate,<sup>163</sup> which also seem to act as inhibitors, since no polymerization was observed after 65 hours at 100° C. and after several hours at 150° C. in the presence of these compounds. It is important to note that butadiene recovered from these solutions is easily polymerizable.<sup>168</sup>

<sup>160</sup> G. F. Lisochkin, "Reports of the S. K. Factory No. 3" (1934). Quoted from Savel'ev *et al.* (*loc. cit.*).

<sup>161</sup> M. A. Lur'e, M. N. Marushkin, N. M. Afanas'ev, and A. T. Pimenov, *Sintet. Kauchuk*, 3, No. 6, 6 (1934). M. A. Lur'e, M. N. Marushkin, V. O. Chislov, and M. A. Shlossberg, *ibid.*, 13; G. G. Koblianskiĭ, A. A. Shul'ts, and K. B. Piotrovskii, *ibid.*, 4, No. 3, 20-23 (1935).

<sup>162</sup> I. N. Bushmakin and M. M. Gol'dman, *Bull. Zavoda B*, 17, 8 (1934), quoted from an abstract in *Sintet. Kauchuk* (1935), give a heat of formation of 14.7-19.1 kcal. per mole.

<sup>168</sup> E. H. Ingold and A. Wassermann, *Trans. Faraday Soc.*, 35, 1022, 1052 (1939).

Another effective inhibitor of the polymerization process, which, like the copper salts, does not influence the dimerization is acetylenedicarboxylic acid, mentioned above.<sup>145</sup>

Berezan, Dobromyslova, and Dogadkin<sup>164</sup> have found that the polymerization process is completely inhibited or strongly retarded by phenol, primary ( $\beta$ -naphthylamine, toluidine) and secondary (diphenylamine) amines, and piperidine, in concentrations above 0.1%. Tertiary amines exhibit no inhibiting effect, and the mechanical properties of the polymer are favorably influenced by their presence.

The same authors have investigated the influence of oleate salts of different cations. Copper and manganese salts appear to inhibit the reaction completely. Potassium, ammonium, and iron oleates slow down the reaction somewhat; sodium oleate is neutral and magnesium, calcium, aluminum, lead, and zinc oleates act as catalysts. The solubilities of these salts in liquid butadiene are given in table III-4.

TABLE III-4  
SOLUBILITY OF OLEATES IN BUTADIENE

Oleates	Solubility, %	
	20° C.	65° C.
Na	Insoluble	Insoluble
K, Fe	0.05	0.05
Ca, Zn, Mg, Pb	0.05-0.01	2
NH <sub>4</sub> , Al, Cu	2	2

For calcium, zinc, aluminum, lead, and magnesium salts, the polymerization takes place in an identical manner. In most cases at 60° C. after 2-3 days, a small piece of transparent polymer is found on the bottom of the test tubes; this continues to grow while the viscosity of the liquid above constantly increases. After 25-30 days, the process comes to a standstill. At this time, about three-fourths of the butadiene is polymerized to a gel, while the rest has become a highly viscous liquid. After the same period of time in the absence of these oleates, only one-fourth of the butadiene is polymerized.

Insoluble sodium oleate acts as a polymerization center from which the polymerization starts. After a month, only one-half the butadiene has been polymerized.

The other salts, as stated above, inhibit the polymerization to a greater or lesser extent, or are neutral.

<sup>164</sup> K. Berezan, A. Dobromyslova, and B. Dogadkin, *Bull. acad. sci. U. R. S. S., Ser. VII, 1936, 409.*

Besides the oleates of the first group above, the following substances are indicated in the literature as having a catalytic effect: peroxides and pyridine (up to 10%),<sup>164</sup> glacial acetic acid,<sup>146, 165</sup> and 99% formic acid.

It appears from the work of Byzov,<sup>166</sup> Lur'e and Ignat'uk,<sup>167</sup> and Dogadkin *et al.*<sup>168</sup> that some compounds which do not act as catalysts for butadiene produced from alcohol by the Lebedev process catalyze the butadiene produced from petroleum. This is probably conditioned by traces of specific impurities present in each one of the two butadienes. The foremost example is diazoaminobenzene, which polymerizes petroleum butadiene in a relatively short time at 100° C. and 18–20 atm. pressure<sup>167</sup> but has little or no effect on the thermopolymerization of alcohol butadiene. Another example is benzoyl acetate.<sup>169</sup>

Certain substances (as the cupric sulfide and sulfate catalysts<sup>168</sup> or aluminum chloride<sup>170</sup>) which neither catalyze nor inhibit the polymerization of pure butadiene act as catalysts for mixtures of butadiene with other unsaturated hydrocarbons.

Thus aluminum chloride is said to catalyze the polymerization of butadiene containing 20–50% of other hydrocarbons, mainly butene-2, forming a grayish-white, sticky, viscous substance containing solid particles.

This behavior can be understood in the light of the general theory of polymerization catalysis developed recently by Eyring *et al.*<sup>171</sup> (see page 117).

## 5. Homogeneous Thermopolymerization in the Gas Phase

Contrary to the unclear and contradictory results for the kinetics of thermopolymerization in the liquid phase, the agreement between the various authors investigating thermopolymerization in the gas phase is very satisfactory.

### A. KINETICS

The kinetics of thermopolymerization in the gas phase has been studied by the following: Lebedev *et al.* (175–200° C.)<sup>172</sup>; Vaughan (326–436° C.)<sup>138</sup>;

<sup>165</sup> A. Dubosc, *Bull. soc. ind. Rouen*, **54**, 220 (1926).

<sup>166</sup> B. V. Byzov, *Zhur. Priklad. Khim.*, **6**, 1074 (1933).

<sup>167</sup> M. A. Lur'e and V. A. Ignat'uk, *Sintet. Kauchuk*, **1**, No. 13, 12 (1932).

<sup>168</sup> V. Balandina, K. Berezan, A. Dobromyslova, B. Dogadkin, and M. Lapuk, *Bull. acad. sci. U. R. S. S., Ser. VII*, **1936**, 423.

<sup>169</sup> B. V. Byzov, German Pat. 521,903, issued Dec. 20, 1927.

<sup>170</sup> N. D. Zelinskii, I. A. I. Denisenko, M. S. Eventova, and S. I. Khromov, *Sintet. Kauchuk*, **2**, No. 4, 11 (1933).

<sup>171</sup> H. M. Hulburt, R. A. Harman, A. V. Tobolsky, and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943).

Kistiakowsky and Ransom (173–386° C.)<sup>140</sup>; Kistiakowsky and Lacher (270–300° C.)<sup>173</sup>; Moor *et al.* (400–700° C.)<sup>137</sup>; and Volzhinskiĭ *et al.* (250–500° C.<sup>174</sup> and 250–500° C.<sup>175</sup>).

All found a strictly second-order reaction up to a fairly high conversion degree (70%) over the entire range of temperatures investigated and through a pressure range extending from 3 mm. Hg to 80 atm. The limit narrows down to 50% conversion at very high temperatures (400° C).<sup>137</sup> This is borne out not only by the absence of any drift in the rate constant when calculated from a bimolecular reaction equation but also from the dependence of the rate on the pressure and on the dilution with neutral agents like propane, nitrogen, or hydrogen.

TABLE III-5  
RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE DIMERIZATION REACTION

Temperature range, ° C.	Log $k$	$E^\ddagger$ , kcal./mole	Authors
175–200	$-\frac{5440}{T_{\text{abs.}}} + 9.83$	24.92	Lebedev <i>et al.</i> <sup>172</sup>
173–386	$-\frac{5180}{T_{\text{abs.}}} + 9.96$	23.7	Kistiakowsky <i>et al.</i> <sup>173</sup>
326–436	.....	24.7 ± 1	Vaughan <sup>138</sup>
400–700	$-\frac{6400}{T_{\text{abs.}}} + 7.32$	28.0 ± 2	Moor <i>et al.</i> <sup>137</sup>

Similar agreement prevails concerning the product of polymerization, which is chiefly the dimer with small percentages of the polymer at lower, and of the trimer at higher, temperatures. At the higher temperatures, some lower hydrocarbons are also found (see page 113).

The reaction was found to be homogeneous and independent of the surface-volume ratio of the reaction vessel. The rate is the same in reaction vessels made of glass, china, or copper. Both static and dynamic methods have been used.

<sup>172</sup> S. V. Lebedev, M. A. Khokhlovkin, N. I. Kulbina, and A. P. Begetova, *Zhur. Fiz. Khim.*, **7**, 130 (1936); *Sintet. Kauchuk*, **5**, No. 1, 2 (1936).

<sup>173</sup> G. B. Kistiakowsky and J. R. Lacher, *J. Am. Chem. Soc.*, **58**, 23 (1936).

<sup>174</sup> I. A. Volzhinskiĭ, M. K. Zhegis, L. B. Rubina, and M. S. Sheremet'eva, *Sintet. Kauchuk*, **5**, No. 1, 8 (1936).

<sup>175</sup> I. A. Volzhinskiĭ, G. M. Kogan, and O. M. Neĭmark, *Sintet. Kauchuk*, **5**, No. 11, 4 (1936).

The heat of activation,  $E^\ddagger$ , and the rate constant,  $k$ , found by the various authors are in good agreement, as may be seen from Table III-5. It seems that a slight increase of the activation energy takes place with rising temperature. This was observed by Kistiakowsky and Ransom on their results, and seems also to hold for the data of the other observers if the entire temperature range covered is taken into account. (In terms of the absolute reaction rate theory, this would mean that the entropy of activation is negative—in other words, that the entropy of the activated

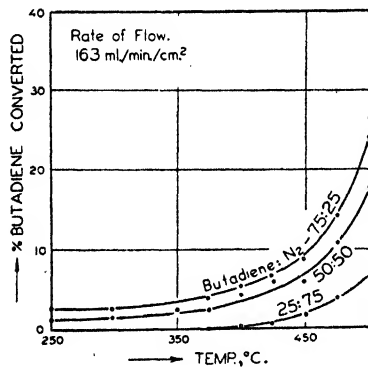


Fig. III-4.—Rate of thermo-polymerization of butadiene at different dilutions with nitrogen as a function of temperature (rate of flow 163 ml. per min. per sq. cm. cross section of reactor).<sup>174</sup>

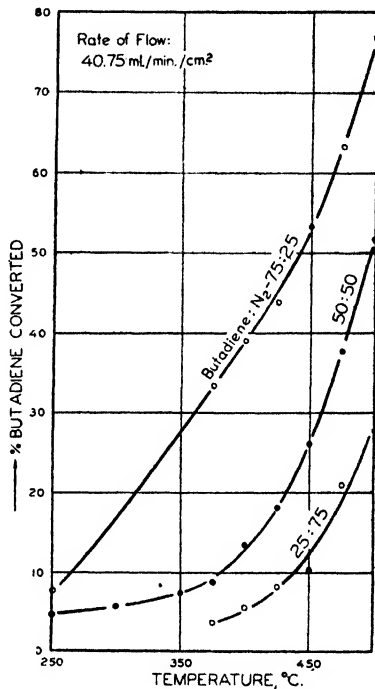


Fig. III-5.—Rate of thermo-polymerization of butadiene at different dilutions with nitrogen as a function of temperature (rate of flow 40.75 ml. per min. per sq. cm.).<sup>174</sup>

complex is lower than that of two molecules of butadiene. It will be shown on page 116 that such is really the case.)

The values of Moor and coworkers for the reaction rate constant show a definite deviation, probably due to the fact that these workers used the dynamic method and did not preheat their gas. This is probably the same reason for the strong dependence of the yield of polymer on the flow rate of gases (especially at higher rates) observed by Volzhinskiĭ, Kogan, and Neĭmark and by Volzhinskiĭ, Zhegis *et*



*al.* and reproduced in figure III-4. Vaughan's value for  $k$ , if corrected for the dead space, is only 6% lower than the values of Kistiakowsky and Ransom.

The variation of the per cent conversion with the dilution by nitrogen observed by Volzhinskiĭ *et al.*,<sup>174</sup> is shown in figure III-5.

Volzhinskiĭ, Kogan, and Neĭmark used a copper tube of 100-cm. length and 25-mm. diameter, while Volzhinskiĭ, Zhegis *et al.* used a copper tube of 60-cm. length and 17-mm. diameter.

## B. SECONDARY PRODUCTS

**The Trimer.**—As has already been pointed out, the main product of the reaction is the dimer. The main secondary product observed by Kistiakowsky and Ransom was the trimer. But while the polymer-dimer ratio was independent of the degree of conversion, the trimer-dimer ratio increased with the progress of the reaction and decreased with pressure. The variation of relative amounts of trimer and dimer with the degree of conversion eliminates the possibility that the two are formed in alternate reactions from the same intermediary product (free radicals). The formation of the trimer must be due to a reaction of the dimer with a butadiene molecule or with its free radical (see also page 99). To check this last assumption, Kistiakowsky and Ransom heated the dimer for a given time at 371° C. (644° K.) and found that the pressure remained constant. If some butadiene was then added, the pressure decreased faster than could be explained by dimerization of butadiene. The rate of reaction from this experiment was found to be 13.5 ml. mole<sup>-1</sup> sec<sup>-1</sup>.

This direct determination of reaction rate constant,  $k_3$ , for the reaction:



can be checked indirectly if one assumes that the deviation of reaction:



from the second order observed at high degrees of conversion (page 110) is due to a subsequent trimer formation. Kistiakowsky and Ransom have carried out the corresponding calculations and found an excellent agreement between the rate constant for the trimer formation determined in this way and the one observed directly (see Table III-6).

Constant  $k_3$  can be represented by the equation:

$$k_3 = 1.3 \times 10^{14} e^{-38,000/RT}$$

The frequency factor,  $1.3 \times 10^{14}$ , is very large and equal to the total number of collisions. As this trimerization process was not included in the calculation of the

dimerization rate, the rate constants given in table III-5 are too high by probably 5 to 10%.

TABLE III-6  
KINETICS OF THE TRIMER FORMATION

$T, ^\circ\text{K.}$	$t, ^\circ\text{C.}$	Initial pressure of butadiene, mm. Hg	Per cent conversion	Trimer-dimer ratio	$k_2$
644	371	336	50	0.090	13
645	372	348	86	0.308	13
572	299	326	50	0.036	0.35
		336	85	0.085	0.29
		2811	48	0.021	0.30
		2869	86	0.057	0.30

**Other By-Products**—Volzhinskiĭ, Zhegis *et al.*<sup>174</sup> have found as by-products of the dimerization reaction a certain amount of toluene and some hydrogen and methane.

Moor and coworkers<sup>137</sup> have analyzed the gaseous as well as the liquid products formed during the reaction. The gaseous products contained, in volume per cent of reacted butadiene: 0.7% hydrogen at 400° C. and 4.2% at 700°; 2.7% methane at 400° and 13.3% at 700°; and 5–8% ethylene. At 600°, about 2% propene is formed and, at 700°, also 11.2% butenes. Plotting the amount of the gaseous products against the degree of conversion by the method of Schneider and Frolich,<sup>176</sup> Moor *et al.* could show that, at 600°, the relative amount of the gaseous by-products decreases with the conversion while the relative amount of liquid products increases. In other words, the gaseous by-products come from the thermal decomposition of the liquid. From among the liquid products formed at 500°, in addition to the dimer, a fraction boiling at 22–65° can be separated (about 10% of the total). This fraction polymerizes on standing in air and yields a glassy solid. At higher temperatures (600° and 700°), fairly viscous products boiling above 130° make their appearance after 50% conversion (higher polymers). At even higher temperatures (750° C.), Staudinger, Endle, and Herold<sup>177</sup> observed the formation of a certain amount of tar, which contained aromatic compounds.

### C. THEORY OF THERMOPOLYMERIZATION

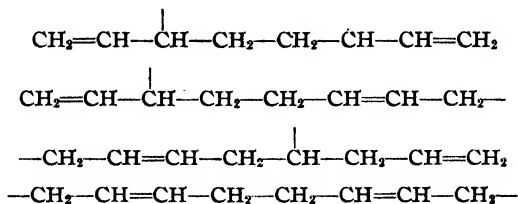
A reaction mechanism explaining all the main features of the dimer formation has been worked out by Harkness, Kistiakowsky, and Mears<sup>178</sup> and by Kistiakowsky and Ransom.<sup>140</sup> These authors assume that, on colliding, two butadiene molecules possessing the necessary activation

<sup>176</sup> V. Schneider and P. K. Frolich, *Ind. Eng. Chem., Ind. Ed.*, **23**, 1405 (1931).

<sup>177</sup> H. Staudinger, R. Endle, and J. Herold, *Ber.*, **46**, 2466 (1913).

<sup>178</sup> J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1935).

energy form as an activated complex a free radical which then may, on second activation, form the final ring structure. In the case of butadiene, the free biradical may be written in four possible resonating structures:



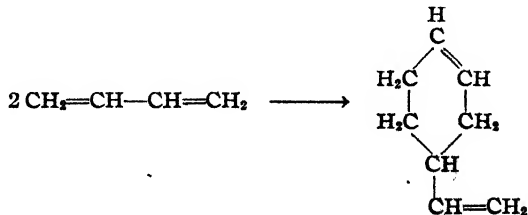
The question arises whether the observed activation energy,  $E^\ddagger$ , of about 25 kcal. per mole is sufficient to form such a radical from two butadiene molecules. In order to make the biradical formation possible the following condition must be satisfied:

The energy of opening two double bonds to two single bonds + the resonance energy in two butadiene molecules — the energy of breaking of a single bond — the resonance energy of the biradical < the activation energy.

If we designate by  $E_D$  the energy of breaking of a double bond, by  $E_S$  the energy of breaking of a single bond, and by  $R_B$  and  $R_F$  the resonance energies of the butadiene and of the free radical, respectively, we may write the above condition in the following form:

$$2(E_D - E_S) + 2R_B - E_S - R_F < E^\ddagger \quad (3.6)$$

We must now compute the different terms of this equation. The first two terms can be calculated from the heat of formation of the dimer,  $\Delta H_D$ , through the reaction:



which involves the breaking of two double bonds, the formation of four single bonds, and the disappearance of the resonance of two butadiene molecules. Hence:

$$\Delta H_D = 2E_D - 4E_S - 2R_B \quad (3.7)$$

Introducing this value in (3.6), one finds that

$$\Delta H_D + E_S - R_F < E^\ddagger \quad (3.8)$$

The heat of dimer formation,  $\Delta H_D$ , can be calculated thermochemically from accurately known heats of combustion and hydrogenation, and is found to be  $-39$  kcal. per mole.

Another more direct method of calculating  $\Delta H_D$  from the heats of combustion and evaporation of butadiene and dimer, using the data of Lebedev, is less accurate, the heat of combustion of butadiene being somewhat uncertain. From the data given in table III-1, one obtains  $\Delta H_D = -(222 - 100)$  cal. per g., or  $-13.2$  kcal. per mole. Using the data of Hock and Leber<sup>179</sup> for the heat of combustion of the monomer, together with Lebedev's<sup>136</sup> data from table III-1 (page 97) on the combustion of the dimer,  $\Delta H_D$  is calculated to be  $27$  kcal. per mole.

The resonance energy in a radical,  $\text{H}_2\overset{|}{\text{C}}-\text{CH}=\text{CH}_2$ , was computed by Coulson<sup>180</sup> to be  $15$  kcal. Since two such groups exist in the biradical, this figure must be doubled. Hence  $R_F = 30$  kcal.

The most recent value for the energy of the central C—C bond in butane is  $82.4 \pm 4.5$  kcal.<sup>181</sup> Introducing this value in equation (3.7), one sees that the condition is fulfilled:

$$-39 \text{ kcal.} + 82.4 \text{ kcal.} - 30 \text{ kcal.} = 13.4 \text{ kcal.} < 25 \text{ kcal.}$$

A somewhat higher value,  $97.6$  kcal., for the C—C bond in ethane was given by Trenner, Morikawa, and Taylor.<sup>182</sup> Equation (3.7) would be violated by introduction of this value. One must consider, however, that  $R_F$  was computed neglecting hyperconjugation, and is in reality probably higher than the  $30$  kcal. given above (see Mulliken, Rieke, and Brown<sup>183</sup>).

Assuming that, in the polymerization reaction, the slow rate-determining step is the formation of the biradical, Kistiakowsky and Ransom<sup>140</sup> made an attempt to calculate the absolute reaction rate. The rate constant,  $k$ , is given by equation (3.9) derived by Eyring:<sup>184</sup>

$$k = e^{\Delta S^\ddagger/R} e^2 \frac{k'T}{h} e^{-\Delta E^\ddagger/RT} \quad (3.9)$$

where  $E^\ddagger$  is the activation energy,  $T$  the absolute temperature,  $R$  the gas constant,  $k'$  and  $h$  Boltzmann's and Planck's constants, respectively,  $e$  the base of the natural logarithm, and  $\Delta S^\ddagger = 2S_B - S^\ddagger$ , where  $S_B$  is the en-

<sup>179</sup> L. Hock and H. Leber, *Kolloid-Z.*, **90**, 65 (1940).

<sup>180</sup> C. A. Coulson, *Proc. Roy. Soc. London*, **A164**, 383 (1938).

<sup>181</sup> E. R. Van Artsdalen, *J. Chem. Phys.*, **10**, 653 (1942).

<sup>182</sup> N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, **5**, 203 (1937).

<sup>183</sup> R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

<sup>184</sup> H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

entropy of the butadiene molecule and  $S^\ddagger$  the entropy of the activated complex.

Assuming that the dynamic properties of an activated complex are not very different from those of the associated stable molecules<sup>185</sup> (except for one degree of freedom), and using the method developed by Pitzer<sup>186</sup> for the calculation of the vibrational energy of hydrocarbons, Kistiakowsky and Ransom could easily calculate all but the rotational parts of the entropies  $S^\ddagger$  and  $S_B$ . The contribution of the rotation to the entropy of butadiene was computed by Kassel.<sup>187</sup> The rotational entropy of the biradical was estimated on the simplified assumption that the molecules were rigid and the internal rotation contributions were calculated as for rigid tops. For 600° K., the resulting total entropies are  $S^\ddagger = 117.7$  E.U. (not included is the translational contribution of the reacting bond),  $S_B = 67.4$  E.U., and  $\Delta S^\ddagger = 17.1$  E.U. Introducing this value into the frequency factor of the equation (3.9), one obtains:

$$e^{\Delta S^\ddagger/R} e^2 \frac{k' T}{h} = 10^{10.27}$$

as compared with an experimental value of  $10^{9.96}$ . This agreement can be considered as highly satisfactory.

If a cyclic activated complex is assumed, the agreement between the observed frequency factor and the factor estimated in a similar way is rather poor (a discrepancy of the order of  $10^{3.3}$ ), and this mechanism can be ruled out.

The more or less stable biradical formed in the first step of the reaction can now react in two different ways: by a monomolecular reaction requiring a new activation energy (or a redistribution of the available energy), it can go over into the dimer; or by a chain of bimolecular reactions with the monomer, it may form the polymer. The relative rates of the two reactions naturally depend on the number of collisions and the excess energy stored in the biradical at the moment of its formation, in other words, on temperature and pressure. A lower temperature and a higher pressure will favor the polymerization over the dimerization. The same influence will be exerted by any substance able to add to one end of the biradical and inhibit the ring closure, *e. g.*, oxygen, which forms peroxide-type compounds. At very high temperatures, however, this peroxide becomes unstable and the oxygen effect on the dimer-polymer ratio disappears. Both these conclusions are in agreement with experiment.<sup>138, 178</sup> It should, however, be borne in mind

<sup>185</sup> O. K. Rice and H. Gershinowitz, *J. Chem. Phys.*, **3**, 479 (1935).

<sup>186</sup> K. S. Pitzer, *J. Chem. Phys.*, **5**, 469, 473 (1937).

<sup>187</sup> L. S. Kassel, *J. Chem. Phys.*, **4**, 435 (1936).

that this does not explain the catalytic influence of oxygen on the over-all rate. This effect will be discussed on page 120.

Still another purely steric factor can influence the dimer-polymer ratio and explain why its variation with temperature cannot be simply accounted for by a difference of activation energy. There are several indications that in the butadiene, as in the case of many other compounds, there is no free rotation around the single bond; and one can distinguish between a *trans* and a *cis* form (chair and bed). At low temperatures the *trans* form appears to be stable,<sup>188</sup> while at higher temperatures both forms are present in equal amounts. The activation energy is about 200 cal.,<sup>189</sup> and a relatively rapid transition from one form to the other takes place at room temperature.

No matter how fast this *cis-trans* transition may be, it is slow as compared with the lifetime of the biradical, because it involves a motion of nuclei, while the lifetime of the biradical can contain either two butadiene groups in the *trans* form (most probable at low temperatures) or one butadiene in the *cis* and one in the *trans* form, or finally two butadienes in the *cis* form. The latter two cases become more and more probable with increasing temperature.

It may easily be seen that, while a polymer chain can be built up from any one of the three possible combinations, the dimer cannot be formed from a radical containing two *trans* butadienes without prior "isomerization." This "isomerization," as pointed out, is a "slow" process; hence the chances are fairly frequent for such a molecule to undergo further polymerization by collisions instead of a dimerization. It is perhaps worth while mentioning in this connection that the deviation of the experimental data from the relation (3.5) is particularly large at low temperatures.

Rasmussen, Tunnicliff, and Brattain<sup>190</sup> conclude, however, from the comparison of infrared and Raman spectra, that the *cis*, not *trans*, form is stable at low temperatures. If this should be confirmed, the entire argument above does not hold.

It should be noted that, although the theory of Kistiakowsky has been developed for the gas phase, it can very probably be extended to polymerization in the liquid phase.

## 6. Theory of Polymerization Catalysis

One can also approach the polymerization of butadiene from another point of view. Recently, Eyring and coworkers<sup>171, 191</sup> pointed out that two

<sup>188</sup> V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939) (electron diffraction). R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939) (intensity distribution in the ultraviolet absorption spectrum). E. Bartholomé and J. Karweil, *Z. physik. Chem.*, **B35**, 442 (1937) (comparison of infrared and Raman spectra).

<sup>189</sup> E. Bartholomé and J. Karweil, *Z. physik. Chem.*, **B35**, 442 (1937).

<sup>190</sup> R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Chem. Phys.*, **11**, 432 (1943).

<sup>191</sup> R. A. Harman and H. Eyring, *J. Chem. Phys.*, **10**, 557 (1942).

different electronic mechanisms can contribute to isomerization and polymerization of olefins.

The theoretical treatment of the ethylene molecule has shown that ten of the twelve electrons in ethylene are localized by pairs, taking up positions between carbon and hydrogen nuclei and between the two carbon nuclei; the remaining two electrons are distributed over the entire molecule. Being less tightly bound, these

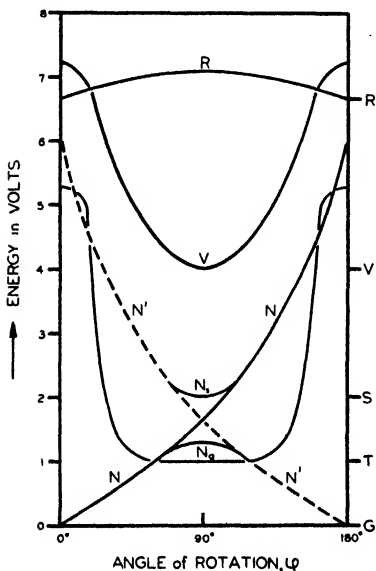


Fig. III-6.—Energy states of "unsaturation electrons" in ethylene molecules.<sup>171, 181</sup>

"unsaturation electrons" account for the reactivity of the double bond. The energy states of these electrons are shown in figure III-6, where the energy is plotted as a function of the angular rotation of one methylene group with respect to the other. In the lowest state,  $N$ , both the electrons occupy the same bonding orbital, so that they must have antiparallel spins and state  $N$  must be a singlet state. On excitation, one of the electrons is promoted to a nonbonding orbital, so that two states are possible, a singlet state,  $V$ , and a triplet state,  $T$ , which is close to ground state  $N$ . State  $V$  is the one responsible for the ultraviolet absorption. In addition to these states, there is a state,  $N'$ , in which both unsaturation electrons are in antibonding orbitals. Optical transitions to this state are forbidden by the symmetry; but it is shown that, as one methylene rotates,  $N'$  becomes lower and lower in energy and,

at  $\varphi = 180^\circ$ , becomes the ground state. Hence this ionic state,  $N'$ , interacts with homopolar state  $N$ , and the real states are linear combinations of both of them.

One can say that, just above the singlet ground state,  $N_g$ , a triplet state,  $T$ , and a singlet state,  $N_s$ , exist. State  $T$  corresponds to an internal free radical, and state  $N_s$  is largely an ionic state. The reaction of olefins can go through either one or the other of these states, so one can speak about an "ionic" and about a "free radical" mechanism. Experiment shows that, in olefins, the reactions going through the ionic mechanism have a fairly high activation energy ( $E_i^\ddagger \sim 45$  kcal. per mole) and a high frequency factor ( $A_i \sim 10^{14}$ ), while the reactions going through the free radical mechanism require a lower activation energy ( $E_r \sim 25$  kcal.) but also have a lower frequency factor ( $A_r \sim 10^6$ ). In diolefins, hence in butadiene, the fre-

quency factor is higher ( $A, \sim 10^{10}$ ). (The low frequency factor for the free radical mechanism has its origin in the fact that the singlet-triplet transition is "forbidden.") By changing the temperature, one can make the reaction of olefins go predominantly either through one or through the other mechanism. However, in the case of butadiene, the small difference in the frequency factor does not warrant a change from the free radical to the ionic mechanism. Corresponding to the two mechanisms we expect to find in general two different types of polymerization catalysts: free radical catalysts and ionic catalysts. The free radical type of catalyst changes (increases) mainly  $A$ ; the ionic type of catalyst in addition changes (decreases)  $E^\ddagger$ . The "free radical" catalysts are compounds like peroxides, persulfates, and diazoaminobenzene,<sup>192</sup> yielding free radicals on decomposition. The "ionic catalysts" are either strong acids or the so-called "generalized acids"— $\text{AlCl}_3$ ,  $\text{BF}_3$ , etc. Kinetic analysis and an abundance of experimental material<sup>174, 193</sup> have shown that dependence of the initiation, and hence of the over-all reaction rate, on the catalyst concentration is different for the two types of catalysts: for the "free radical" catalyst, the rate is proportional to the square root of its concentration, while for the "ionic" type of catalyst it is directly proportional to the catalyst concentration. This rule provides us with a very important tool for the investigation of the catalytic mechanism.

In the case of polybutadiene polymerization, as already mentioned, the ionic mechanism plays only a secondary role and all the catalysts used are of the "free radical" type. Romm<sup>194</sup> induced polymerization in the gas phase by homogeneous catalysis by free radicals. For the liquid state, the catalytic influence of free radicals has already been pointed out. The ionic catalysts have no effect on pure butadiene, but can start polymerization in the presence of impurities able to start chains by an ionic mechanism, *e. g.*, certain olefins. A certain number of such catalysts are mentioned in the patent literature.<sup>195-197</sup>

<sup>192</sup> W. Schlenk and E. Bergmann, *Ausführliches Lehrbuch der organischen Chemie*, Vol. II, Denticke, Vienna, 1939, p. 217.

<sup>193</sup> C. C. Price, *Ann. N. Y. Acad. Sci.*, **44**, 351 (1943).

<sup>194</sup> F. S. Romm, *Zhur. Obshchei Khim.*, **10**, 1784 (1940). Through *Chem. Abstracts*, **35**, 3880 (1941).

<sup>195</sup> U. S. Pat. 2,151,382, issued March 31, 1939 (du Pont) ( $\text{BF}_3$ ).

<sup>196</sup> French Pat. 835,373, issued Dec. 2, 1938 (I. G. Farbenindustrie) (anhydrous hydrochloric and hydrobromic acids).

<sup>197</sup> O. Schmidt and B. von Bock, German Pat. 504,436, issued March 22, 1929 (I. G. Farbenindustrie) (hydrazine organic derivatives and their salts; in this case, however, the free radical mechanism cannot be ruled out *a priori*).





merization of the liquid in the absence of oxygen, unless one assumes that butadiene prepared from alcohol by the Lebedev process always contains some peroxide.

## 7. Catalyzed Thermopolymerization in the Gas Phase

### A. KINETICS

Several patents<sup>199, 200</sup> claim that various substances can be used as catalysts for the polymerization of butadiene in the gaseous phase.

Zhavoronkov<sup>201</sup> has investigated the catalytic influence of charcoal. In his experiments, butadiene (96.8% pure) was passed through a quartz tube heated in a furnace to 300–500° C. with and without charcoal, and the conversion yield determined. Without charcoal at a flow rate of 75–80 ml. per min. per sq. cm. at 400–450°, about 45% of the butadiene was found polymerized; below 400°, the yield was only 10%. With charcoal, the yield was 11% at 350° and 35% at 450–460° at a somewhat higher flow rate of 100 ml. per min. per sq. cm. This yield can be increased to 50% if a more highly activated charcoal is used. The catalytic influence is, hence, not very pronounced.

The gas is first absorbed by the charcoal, and liquid products are then formed. They are all more oily than without charcoal at the same temperature, indicating a larger than usual fraction of trimer and tetramer. The effect of the charcoal is probably simply to increase the concentration of butadiene in the space where the reaction takes place. It can be presumed that the effect of silica gel, sponge iron, etc., is of the same type.

Technologically more important are the investigations of Volzhinskii, Kogan, and Neĭmark<sup>176</sup> on the effect of the Lebedev catalyst on butadiene polymerization, since, in the alcohol–butadiene process, the butadiene formed is in contact with this catalyst at high temperatures, though for a short time, and a part of the butadiene originally formed undergoes dimerization (or polymerization), decreasing the useful yield of gaseous butadiene. (This is one reason why a great number of Russian patents stress the advisability “of rapidly cooling the products of reaction” in the making of butadiene. See Chapter I.) The results of Volzhinskii and coworkers are summarized in table III-7, which shows clearly that the Lebedev catalyst, particularly the spent catalyst, greatly increases the conversion.

<sup>199</sup> Brit. Pat. 340,004, issued Aug. 12, 1929 (I. G. Farbenindustrie) (carbonyls of heavy metals such as iron, nickel, cobalt, molybdenum, tungsten, and chromium).

<sup>200</sup> French Pat. 683,284, issued Oct. 14, 1929 (I. G. Farbenindustrie) (nickel, aluminum, glass wool, silica gel, and sponge iron at 400–500° C., yielding oily, polymerized products, presumably dimer and trimer).

<sup>201</sup> P. V. Zhavoronkov, *Kauchuk i Rezina*, 4, No. 11, 10–14 (1940).

TABLE III-7  
EFFECT OF LEBEDEV CATALYST ON BUTADIENE POLYMERIZATION

No.	Catalyst layer, cm.	$t$ , ° C.	Flow rate, ml./sec./sq. cm.	Initial butadiene, %	Butadiene converted, %
1	Control	490	408	11.16	10.1
2	Control	450	408	97.65	54.94
3	100	500	870	9.62	28.5
4	200	450	870	9.89	27.20
5	200	450	870	96.07	31.2
6 <sup>a</sup>	200	450	870	97.96	53.2

<sup>a</sup> With a spent catalyst.

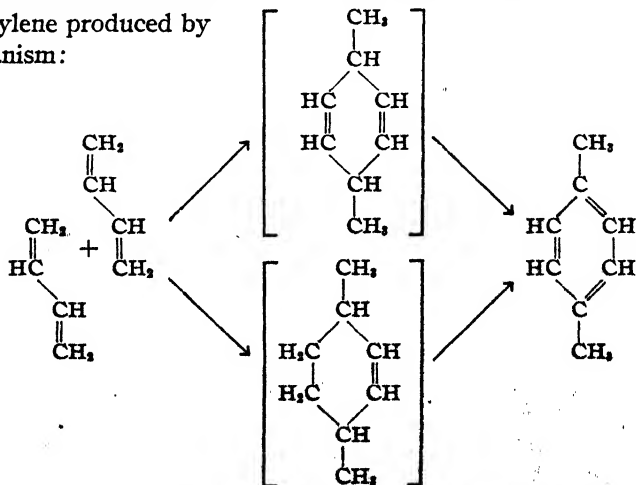
The experiments were carried out both on pure butadiene and on a mixture of 90% hydrogen and 10% butadiene. The dynamic method was used, with a reaction tube of copper and a catalyst layer, 100 and 200 cm. long, respectively.

The experiments are not precise enough to allow the calculation of the heat of activation; but as a very rough approximation it may be stated that the presence of the binary catalyst lowered the heat of activation somewhat.

### B. PRODUCTS

Slobodin<sup>202</sup> investigated the liquid formed when butadiene was allowed to polymerize in the presence of a dehydrogenating catalyst such as the Lebedev catalyst. He found that, at 450° C., a number of aromatic compounds are formed in addition to the dimer, particularly:

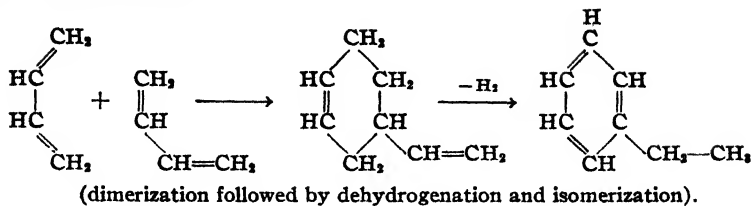
(a) *p*-Xylene produced by the mechanism:



(dimerization with isomerization followed by dehydrogenation and isomerization).

<sup>202</sup> I. A. M. Slobodin, *Zhur. Obshchei Khim.*, 5, 1414 (1935).

(b) Ethylbenzene:



(c) Toluene, a decomposition product of ethylbenzene, present only in small amounts.

(d) Even smaller amounts of styrene, a reduction product of the dimer. *p*-Xylene is the most frequent product, the *p*-xylene-(dimer + ethylbenzene + toluene) ratio being about 2:1.

## C. EMULSION POLYMERIZATION

### 1. Introduction

We have seen that the polymer obtained by mass thermopolymerization of butadiene in the liquid or gas phase is not technically satisfactory, nor is the process economical. At low temperatures the reaction is very slow, while a large amount of undesirable dimer is formed at higher temperatures. Furthermore, the heat developed during the polymerization is quite substantial, about 350 cal. per g.; and if no provisions are made for effective heat removal the continually rising temperature still further tends to favor dimer formation.

The idea of carrying out the polymerization in an aqueous emulsion suggests itself. This idea is very attractive in view of the latexlike origin of natural rubber. Dispersion of the reacting monomer in the form of minute droplets through a medium of low viscosity, in which, hence, effective stirring is possible, and of good heat conductance, is bound to create a greater uniformity and to assure a better temperature control of the system. If the diffusion of monomer through the polymer toward the active centers is of any importance, a substantial acceleration of the process is to be expected, since the size of droplets is small. (These ideas were first clarified by Ostromislensky,<sup>203</sup> but as early as 1912 patents on the emulsion polymerization were granted.)<sup>204, 205</sup> Although, or rather because, the emulsion

<sup>203</sup> I. I. Ostromislensky, *Zhur. Russ. Fiz.-Khim. Obshchestva*, 47, 1472, 1928 (1915).

<sup>204</sup> German Pats. 254,672, issued Dec. 11, 1912; and 255,129, issued Dec. 20, 1913 (F. Bayer Co.).

<sup>205</sup> K. Gottlob, U. S. Pat. 1,149,577, issued Aug. 10, 1915.

polymerization is widely used in Germany, England, and the United States, and to some extent even in the U.S.S.R. (whenever the latex can be used directly), very little information about the process is published other than in patents, which are often unclear or misleading. Most of the knowledge available outside the rubber-producing companies themselves is found in three publications of the Dogadkin<sup>206-208</sup> group which serve as the basis for this chapter and to which all the material refers unless otherwise stated. Some information pertaining to special points can be found in the papers of Fryling,<sup>209</sup> Fryling and Harrington,<sup>210</sup> Fikentscher,<sup>211</sup> and Gee, Davies, and Melville,<sup>212</sup> as well as in the articles of Trommsdorff<sup>213</sup> and Konrad.<sup>214</sup> Information concerning the analogous problems of emulsion polymerization of chloroprene has been published by Williams and Walker<sup>215</sup> and of vinyl chloride by Pavlovich.<sup>216</sup>

## 2. General Description

### A. TYPICAL FORMULATION

In addition to the two phases—butadiene and water—a simple recipe for emulsion polymerization calls for:

(a) An emulsifying agent which is essentially a compound with a more or less extended polar molecule, one terminal group of which is hydrophylic and the other soluble in the butadiene, thus being able to form a kind of skin around the butadiene droplets. Soaps, sometimes formed *in situ* (Dogadkin *et al.*), are used most extensively, though other compounds have been tried.

(b) A polymerization catalyst. The catalysts most widely used are

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<sup>206</sup> V. Balandina, K. Berezan, A. Dobromyslova, B. Dogadkin, and M. Lapuk, *Bull. acad. sci. U. S. S. R., Ser. VII, 1936, 397.*

<sup>207</sup> K. Berezan, A. Dobromyslova, and B. Dogadkin, *Bull. acad. sci. U. S. S. R., Ser. VII, 1936, 409.*

<sup>208</sup> V. Balandina, K. Berezan, A. Dobromyslova, B. Dogadkin, and M. Lapuk, *Bull. acad. sci. U. S. S. R., Ser. VII, 1936, 423.*

<sup>209</sup> C. F. Fryling, *Ind. Eng. Chem., Ind. Ed., 36, 114 (1944).*

<sup>210</sup> C. F. Fryling and E. W. Harrington, *Ind. Eng. Chem., Ind. Ed., 36, 114 (1944).*

<sup>211</sup> H. Fikentscher, *Angew. Chem., 51, 433 (1938).*

<sup>212</sup> G. Gee, C. B. Davies, and H. W. Melville, *Trans. Faraday Soc., 35, 1298 (1939).*

<sup>213</sup> E. Trommsdorff, in R. Houwink, *Chemie und Technologie der Kunststoffe.* Akad. Verlagsgesellschaft, Leipzig, 1939, pp. 304 *et seq.*

<sup>214</sup> E. Konrad in R. Houwink, *Chemie und Technologie der Kunststoffe.* Akad. Verlagsgesellschaft, Leipzig, 1939, pp. 447-448.

<sup>215</sup> I. Williams and H. W. Walker, *Ind. Eng. Chem., Ind. Ed., 25, 199 (1933).*

<sup>216</sup> P. I. Pavlovich, *Zhur. Priklad. Khim., 14, 551 (1941).*

peroxides—hydrogen peroxide, benzoyl peroxide, persulfates, but certain other compounds like diazoaminobenzene have been found to activate the polyreaction.

Dogadkin *et al.* claim that, even without any catalyst, the polymerization rate is increased merely by the emulsification. Since, however, they failed to remove the peroxides from their emulsifying agent (soap), their contention cannot be considered as proved.

(c) In later years, it became customary to add a modifier, a mercaptan,<sup>217</sup> for instance, whose function it is to direct the reaction toward the formation of macromolecules with less branching, thus permitting higher degrees of conversion without the polymer's becoming too hard or losing its solubility.

(d) In certain cases, pH buffers are added, since it was found that the quality, the rate, and the yield of the polymer depend upon the prevailing pH.<sup>218</sup> See also page 130. A typical recipe<sup>219</sup> might, for instance, consist of: monomer (butadiene), 10.0 g.; aqueous phase (water), 18.0 g.; emulsifier (sodium oleate), 2.0 g.; catalyst (ammonium persulfate), 0.03 g.; and modifier (isohexylmercaptan), 0.05 g.—at a temperature of 30° C. and a polymerization time of several days.

## B. LABORATORY TECHNIQUE

The butadiene used by Dogadkin and coworkers<sup>206–208</sup> was mainly butadiene prepared by the Lebedev process, and had the following composition: butadiene, 65–85.7%; butene-2, 14–24%; aldehyde, 0.02–0.06%; and residue boiling above 0° C., 0.16–4.0%. Although the general behavior of all the batches was fairly close, quantitative measurements on the influence of one or the other factor were made on one and the same lot of monomer.

Test tubes (or beverage bottles) of a capacity of 175–250 ml. served as reaction vessels. First, distilled water was charged into the reactor together with the necessary amount of emulsifying agent and catalyst. Then the aqueous solution was frozen out with dry ice, butadiene was added, and the test tube sealed and introduced into a thermostat containing a mechanism for rotating the tube in a plane or

<sup>217</sup> W. L. Semon, *Chem. Eng. News*, 21, 1613–1619 (1943).

<sup>218</sup> M. Luther and C. Heuck, U. S. Pat. 1,864,078, issued June 21, 1932 (I. G. Farbenindustrie).

<sup>219</sup> Recalculated and slightly modified from H. Wollthan and W. Becker, U. S. Pat. 2,281,613, issued May 5, 1942.

head-over-tail manner at about 50–70 r.p.m. A very detailed description of a similar but improved experimental technique is given by Fryling.<sup>200</sup>

### C. CHANGES OBSERVED

The following changes are observed during the polymerization:

(a) The volume of the emulsion decreases due to the difference in density between the monomer and the polymer. This volume change is a linear function of the conversion degree and can be used for kinetic investigations.

(b) The stability of the system increases markedly. A stable emulsion is hard to obtain in the initial stage of the process because of the great difference in density between butadiene and water.

(c) At a given moment, which can be considered as the end of the inhibition period and the start of the polymerization, the emulsion becomes opalescent. This opalescence is due to polymer particles of extremely small diameter formed in the early stages of the polymerization.

(d) Dogadkin observed a continuous increase of the emulsion viscosity from that of an aqueous solution of waterlike mobility up to that of a custard (and in extreme cases to that of a jelly). He found that the consistency is partly dependent on the emulsifier used. This viscosity increase is, however, not characteristic of the emulsion polymerization in general. The latex viscosity can be controlled, thus allowing an effective stirring. (It is possible that Dogadkin's observation was due to the presence of butene-2.)

(e) The color of the emulsion changes. In cases in which diazoaminobenzene is used, the yellow color often becomes more and more weakened until conversion reaches about 40–50%, at which point the dispersion becomes white and opalescent. But the reverse phenomenon was observed also, the emulsion in certain cases turning from yellow to brown.

(f) The pH varies in a complicated way (see page 131).

On opening the test tubes, the unreacted hydrocarbons evaporate rapidly, the swelling of the polymer particles recedes (this can also be due to oxidation), and the dispersion acquires a consistency similar to that of natural rubber latex.

### 3. Characteristics of the Latex

The analogy with *Hevea* latex is perhaps not quite as profound as appears on first glance. The first difference is in the size of the latex particles, most

of which are, in the case of butadiene, less than  $0.2\mu$  (Dogadkin *et al.*) (in *Hevea* up to  $3.0\mu$ <sup>220</sup> with a maximum around  $0.75\mu$ ).<sup>221</sup>

However, since the results of ultramicroscopic measurements are somewhat dependent on the technique used, it is more illuminating to compare the results for both latices obtained by the same observer. Mikhaïlova and Bass<sup>222</sup> have shown that the mean diameters of microscopic particles are  $0.99\mu$  in *Hevea* and  $0.64\mu$  in polybutadiene, not a very important difference; much the same is true for the ultramicroscopic particles, the average diameters being  $0.13\mu$  and  $0.118\mu$ . But the weight fraction of the microscopic particles is 90.5% in *Hevea* and only 0.76% in polybutadiene latex. Or, to present the same results in another way, in one gram of 35% latex there are  $2.6 \times 10^{13}$  particles in the case of *Hevea* and  $50 \times 10^{13}$  particles in the case of polybutadiene. Moreover, it seems that the larger particles in the synthetic latex are of a secondary character, being composed of smaller particles with a common emulsifier envelope.<sup>208</sup> (It has also been observed that, on standing, the number of large particles increases in polybutadiene latex and remains constant in *Hevea* latex.)

These figures are somewhat too large when compared to those of Bächle,<sup>223</sup> obtained by the same method, on *Hevea* and Buna S latices. Bächle found an average diameter of  $0.17\mu$  for *Hevea* droplets and  $0.04\mu$  for Buna S droplets. Bächle himself is in fair agreement with von Ardenne and Beischer,<sup>224</sup> who found, from electron microscopic photographs, the average diameters of  $0.5\text{--}1\mu$  for *Hevea* and  $0.05\mu$  for Buna N.

The small size of latex particles is sometimes of definite advantage as, for example, in the impregnation of fabrics.

The size of the butadiene latex particles depends somewhat on the emulsifier used, and can be influenced to a certain extent even after polymerization by addition of surface-active substances (*e. g.*, borax caseinate).

#### 4. Coagulation

The high degree of dispersion of butadiene latex makes it fairly stable. Dogadkin and coworkers found that they could store their latices for over

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<sup>220</sup> W. A. Gibbons and P. D. Brass, in C. C. Davis and J. T. Blake, *The Chemistry and Technology of Rubber*. Reinhold, New York, 1937, p. 603.

<sup>221</sup> F. F. Lucas, *Ind. Eng. Chem., Ind. Ed.*, **34**, 1371 (1942).

<sup>222</sup> K. Mikhaïlova and M. Bass, *Sbornik Trudov Opytnovo Zavoda im. S. V. Lebedeva*, **1938**, 53-74, through *Chem. Abstracts*, **34**, 3128 (1940).

<sup>223</sup> O. Bächle, *Kautschuk*, **13**, 174 (1937).

<sup>224</sup> M. von Ardenne and D. Beischer, *Kautschuk*, **16**, 55 (1940).



a year without coagulation taking place. In order to obtain coagulation, electrolytes must be added, the amount necessary depending not only on the electrolyte but also on the stabilizer used. Thus, for example, a latex stabilized by ammonium oleate and albumin is not completely coagulated even by addition of an excess of acetic acid sufficient to increase the acidity to a  $pH$  below 4. Table III-8 gives an idea of the amounts of various salts necessary to coagulate a typical latex. It is evident that the last two electrolytes are of greatest interest from a technical point of view, although coagulation by addition of sodium chloride<sup>225</sup> and acids<sup>226</sup> and by freezing<sup>227</sup> is mentioned in the patent literature.

TABLE III-8  
COAGULATION OF A TYPICAL LATEX BY SALTS<sup>a</sup>

Electrolyte	Limit of coagulation, <sup>b</sup> mole/liter
Barium chloride.....	0.603
Sodium chloride.....	0.230
Zinc sulfate.....	0.0068
Aluminum sulfate.....	0.0007
Ferric chloride.....	0.00034

<sup>a</sup> The difference between the coagulation effects of monovalent and polyvalent ions is by no means specific, and is well known in colloidal chemistry (the Schulz rule).

<sup>b</sup> Latex concentration, 25%,  $pH$  8.9. Stabilizer, ammonium oleate.

If, instead of soaps, alkylated naphthalenesulfonates or acid emulsifiers (*e. g.*, pentadecyl- $\mu$ -glyoxalidine) are used, the latex cannot be coagulated by acids, but only by salts such as potassium, sodium, or ammonium halides, carbonates, sulfates, nitrates, phosphates, etc.<sup>228</sup>

### 5. Emulsifying Agents and Stabilizing Colloids

Emulsifying agents influence the polymerization process and the resulting polymer in manifold ways:

(1) They determine the degree of dispersion and hence the action of the surface forces on the butadiene and the particle size in the latex.

(2) Some of the emulsifying agents used are soluble in butadiene and can act as catalysts for homogeneous polymerization, as, for example, certain oleates (page 108).

<sup>225</sup> French Pat. 843,903, issued July 12, 1939 (I. G. Farbenindustrie).

<sup>226</sup> Brit. Pat. 364,089, issued Aug. 21, 1930 (I. G. Farbenindustrie).

<sup>227</sup> E. Konrad and W. Siefken, German Pat. 537,032, issued Jan. 17, 1928 (I. G. Farbenindustrie).

<sup>228</sup> Brit. Pat. 346,785, issued Jan. 17, 1930.

(3) The emulsifier used seems also to influence the storage and vulcanization properties of the polymers.

The amount of the emulsifying agent used is important only if it is below the limit necessary for the production of a stable latex. In the case of such a deficiency, the rate of polymerization and the maximal degree of conversion drop sharply. Above this limit, further addition of emulsifying agent has little if any effect.

In their work, Dogadkin and coworkers used mainly ammonium oleate prepared by separate addition of oleic acid and ammonia to the emulsion. This procedure is also suggested in certain patents.<sup>229</sup> In order to obtain a better emulsifying effect at higher temperatures, a certain amount of magnesium oleate was also added.<sup>230</sup>

Dogadkin *et al.* have also investigated other emulsifying agents mentioned in the patent literature, with the following results:

(a) The soaps of stearic acid lead to a harder polymer than the soaps of oleic acid.<sup>231</sup>

(b) Active stabilizers like saponin and saponaria root extract have the same tendency.

(c) Proteins<sup>232</sup> (casein, albumin) if added alone in large enough concentrations to insure stabilization (0.8–1.0 g. per 100 ml.) act as inhibitors (perhaps due to the presence of free primary and secondary amino groups which are known to act as inhibitors; see page 171). Introduced in smaller amounts (0.2 g. per 100 ml.) in conjunction with oleic acid salts, they are claimed to influence favorably the polymer produced, which is softer and has better milling properties than the polymer obtained with oleates alone.

(d) Tar acids (vacuum-distilled pine tar and its various fractions) do not insure the desired stability.

(e) The same is true for sodium alginate. When sodium alginate is added to oleic acid, the polymers obtained are harder than those prepared with oleates.

(f) Sodium  $\beta$ -tetrasulfonate and sodium isopropyl- $\beta$ -naphthasulfonate in concentrations up to 1.5% do not insure the stability of the latex. When added to oleic acid, they yield shorter polymers in contrast to claims in the patent literature.<sup>233, 234</sup>

<sup>229</sup> U. S. Pat. 1,864,078, issued June 21, 1932 (I. G. Farbenindustrie). Brit. Pat. 318,296, issued June 1, 1928 (I. G. Farbenindustrie).

<sup>230</sup> Brit. Pat. 307,938, issued March 17, 1928 (I. G. Farbenindustrie).

<sup>231</sup> I. Williams and H. W. Walker, *Ind. Eng. Chem., Ind. Ed.*, **25**, 199 (1933).

<sup>232</sup> U. S. Pat. 1,935,733, issued Nov. 21, 1933 (I. G. Farbenindustrie).

<sup>233</sup> Brit. Pat. 312,201, 1928 (I. G. Farbenindustrie). Brit. Pat. 523,130, issued July 5, 1940 (I. G. Farbenindustrie).

<sup>234</sup> German Pat. 706,548, issued April 24, 1941 (I. G. Farbenindustrie). French Pat. 848,184, issued Oct. 24, 1939 (I. G. Farbenindustrie).

(g) Starch and dextrin alone fail to produce stable latices. Added to oleic acid they permit a reduction in the total amount of stabilizer necessary to 1.5%. The polymer obtained is soft and elastic.

(h) Natural rubber (pale crêpe), thermoplasticized or irradiated with a mercury arc, proves to be a good emulsifier. Its usefulness increases with the degree of saponification and, under certain conditions, it can replace, at least partially, the oleic acid. The properties of the polymer are not affected.

In addition, several other emulsifying agents are mentioned in the patent literature, some of an entirely different type.<sup>235-243</sup>

## 6. pH of Emulsions

### A. EFFECT ON RATE OF POLYMERIZATION

The importance of a correct choice of pH was stressed by Dogadkin *et al.*, who added to emulsions containing oleic acid varying amounts of ammonia, in order to go from a fairly acid to a definitely alkaline solution.

<sup>235</sup> Brit. Pat. 307,938, issued March 17, 1928 (I. G. Farbenindustrie) (sodium oleate). French Pat. 848,184, issued Oct. 24, 1939 (I. G. Farbenindustrie). H. Meis and R. Ludwig, German Pat. 706,548, issued April 24, 1941 (I. G. Farbenindustrie).

<sup>236</sup> Brit. Pat. 523,130, issued July 5, 1940 (I. G. Farbenindustrie).

<sup>237</sup> Brit. Pat. 522,665, issued June 24, 1940 (I. G. Farbenindustrie). (a) Salts of unsaturated carboxylic acids whose esters constitute drying oils, such as alkali salts of linoleic acid and of acids derived from China wood and Turkey red oil. See also U. S. Pat. 1,864,078, June 21, 1932 (I. G. Farbenindustrie). (b) Salts of alkylated naphthalene sulfuric acids such as the sodium salt of isopropyl naphthalene sulfuric acid and, in general, salts of products of the general formula  $R \cdot CO \cdot XR' \cdot SO_3H$ , where R stands for a chain of at least eight carbon atoms, X stands for  $-O-$ ,  $-NH-$ , or N-alkyl groups, and R' for a lower alkyl group such as  $C_2H_5$ .

<sup>238</sup> Brit. Pat. 538,639, issued Aug. 12, 1941 (I. G. Farbenindustrie).

<sup>239</sup> Brit. Pat. 496,443, issued Nov. 30, 1938 (I. G. Farbenindustrie).

<sup>240</sup> German Pat. 702,749, issued Jan. 23, 1942 (I. G. Farbenindustrie). C. Mühlhausen and W. Becker, U. S. Pat. 2,305,025, issued Dec. 15, 1942 (Jasco, Inc.). (Water-soluble acid addition salts of alkyl amines having a straight aliphatic chain of at least eight carbon atoms directly attached to the nitrogen atom, such as dodecylamine hydrochloride or octadecyldimethylamine hydrochloride, and, more generally, water-soluble salts of the type,  $X \cdot CH_2 \cdot CH_2 \cdot Y \cdot CH_2 \cdot CH_2 \cdot NZ$ , where Y is oxygen or sulfur, NZ is the residue of a secondary or quaternary ammonium compound, and X is a residue of secondary amines, acid amide, an ether, an ester, a quaternary ammonium compound, or OH, under the condition that X or Z contains at least eight carbon atoms.)

<sup>241</sup> B. Dogadkin *et al.*, *loc. cit.* (alizarin oil and tung oil).

<sup>242</sup> Brit. Pat. 521,277, issued May 16, 1940 (I. G. Farbenindustrie).

<sup>243</sup> Brit. Pat. 346,785, issued Jan. 17, 1930 (I. G. Farbenindustrie) (for emulsification in acid solutions: condensation products of ethylene oxide or glycide with water-insoluble, higher aliphatic alcohols, *e. g.*, hydrochloride of pentadecyl- $\mu$ -glyoxalidine).

The pH of the emulsion after polymerization and the yield of polymer were determined. Such a procedure is perhaps not quite unimpeachable, since the pH of the emulsion varies in the course of the polymerization, as stressed by Fryling and Harrington,<sup>210</sup> but it gives at least a fair indication. The results of Dogadkin are given in table III-9. It appears that the addition of alkali accelerates the polymerization, although the final pH is more important than is the absolute amount of alkali present. The influence of pH seems to go beyond its ability in affecting the degree of

TABLE III-9  
EFFECT OF pH ON THE YIELD OF POLYMERIZATION\*

Amount, ml.		Alkali excess over the saponification, normality	pH of the latex	Yield in per cent of monomer
Water	Ammonium hydroxide, 0.5%			
37.6	8.4	-0.02	.	32.0
34.3	11.7	-0.01	8.65	40.88
32.7	13.3	-0.0	8.90	50.88
27.6	18.4	+0.01	9.10	47.80
24.3	21.7	+0.02	9.05	50.10
17.6	28.4	+0.04	9.35	101.60

\* 50% butadiene by volume, 1.5 ml. oleic acid, 5 days.

dispersion. It has a direct bearing on the reaction rate. It is possible, through a change in alkalinity, to direct the reaction in one way or another (particularly if peroxides are used as catalysts, since their decomposition rate depends largely on the pH of the system).

An unsuccessful attempt was made by Dogadkin *et al.* to run the polymerization in acid solution, using as an emulsifier albumin dissolved in lactic acid. Nevertheless certain patents exist which claim polymerization at pH < 7.<sup>244, 245</sup> For emulsifying agents to be used under these conditions, see page 129. No indications of the quality of the polymer are given.

## B. VARIATION DURING THE POLYMERIZATION REACTION

As mentioned above, a drop in pH is usually observed during the course of polymerization. This can be attributed to oxidation products formed by the peroxides, to the formation of potassium hydrogen sulfate (KHSO<sub>4</sub>) if potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) is employed, or to adsorption of soap at the polymer interface.

<sup>244</sup> German Pat. 558,890, issued Jan. 9, 1927 (I. G. Farbenindustrie).

<sup>245</sup> Brit. Pat. 521,277, issued May 16, 1940 (I. G. Farbenindustrie).

The variation of  $pH$  during polymerization is not always simple; and unexpected examples of an increase in this value have at times been noted. Fryling and Harrington<sup>210</sup> recently pointed out one of the complications frequently encountered:

If a monomer, or for that matter any nonreactive organic liquid, is slowly added to an aqueous fatty acid soap solution, the  $pH$  drops to a sharp minimum, after which it rises on further addition of the monomer. The minimum occurs at the point where the solubility of the monomer in the soap solution is exceeded. This point is generally referred to as the "cloud point." The explanation advanced by Fryling and Harrington is based on the well-known hydrolysis equilibrium between soap, water, fatty acid, and sodium hydroxide. When monomer is added to an aqueous soap solution, solubilization with inclusion of organic molecules in the soap micelles takes place. This represses hydrolysis, and the  $pH$  drops. When the monomer is present in larger amounts as a separate phase, however, hydrolysis is favored because of solution of the fatty acid in the organic phase, and consequently the  $pH$  rises. During polymerization, the amount of the monomer present decreases and so the  $pH$  changes in an inverse way to the change observed on gradual addition of the monomer to the soap solution. This being the case and in the absence of complications noted above (namely, adsorption of the soap, formation of oxidation products, etc.), it is to be expected that an increase in  $pH$  will be observed toward the end of the polymerization reaction.

### C. BUFFER SOLUTION

From the considerations developed above, we see that it is useful to stabilize the  $pH$  value.<sup>246</sup> Luther and Heuck<sup>247</sup> and, independently, Dogadkin *et al.* introduced phosphate into the recipe. The latter workers observed a marked rise in the rate of polymerization as well as in the yield, the polymer becoming somewhat harder. (For other possible explanations of the effect of phosphate ions, see page 134.)

## 7. Catalysts of Polymerization

### A. PROMOTERS

It has already been pointed out that bulk and emulsion polymerizations are essentially free radical reactions. Hence, it is not surprising that the catalysts used are mostly unstable "per" compounds, which on decomposition yield free radicals and which are soluble either in water or in the monomer. To the water-soluble catalysts belong, for instance, hydrogen

<sup>246</sup> E. Konrad, in R. Houwink, *Chemie und Technologie der Kunststoffe*. Akad. Verlagsgesellschaft, Leipzig, 1939, p. 448.

<sup>247</sup> M. Luther and C. Heuck, U. S. Pat. 1,864,078, issued June 21, 1932 (I. G. Farbenindustrie).

peroxide, potassium peroxide,<sup>248</sup> potassium persulfate, and other salts of "per" acids as well as certain water-soluble organic peroxides (*e. g.*, urea peroxide).<sup>213</sup> Among the monomer-soluble "per" compounds are benzoyl peroxide, hexachloroethane,<sup>249</sup> and oxidized natural rubber.<sup>207</sup> To this same group of compounds, yielding free radicals on decomposition, belongs diazoaminobenzene<sup>207, 250</sup> (see page 125). Colloidal metal oxides also can be used.<sup>251</sup>

A second group of catalytic substances consists of compounds which yield oxygen readily. Oxygen then forms peroxides with the butadiene itself.<sup>252</sup>

A third group of catalysts, comprised of substances capable of several degrees of oxidation, transfer atmospheric oxygen to the butadiene in order to form butadiene peroxides.<sup>253, 254</sup>

The reaction mechanism of the fourth group of catalysts is not yet clear. To this group belong Schiff's bases,<sup>255, 256</sup> and related compounds, tertiary amines,<sup>257</sup> and certain compounds of unknown structure.<sup>258</sup>

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<sup>248</sup> A. M. Collins, U. S. Pat. 1,967,865, issued July 24, 1934 (du Pont).

<sup>249</sup> W. Bock and E. Tschunkur, U. S. Pat. 1,898,522, issued Feb. 21, 1933 (I. G. Farbenindustrie).

<sup>250</sup> B. V. Byzov, Russian Pats. 11,103, 11,275, and 11,276. C. F. Fryling, U. S. Pat. 2,313,233, issued March 9, 1943 (Goodrich). B. A. Dogadkin, K. Berezan, and M. Lapuk, Russian Pat. 46,354, issued March 31, 1936 (diazoamino compounds and oxygen-free azo dyes).

<sup>251</sup> Brit. Pat. 317,030, issued May 9, 1928; French Pat. 656,428, issued May 7, 1929; H. Meis, W. Klein, and E. Tschunkur, U. S. Pat. 1,896,493, issued Feb. 7, 1933 (I. G. Farbenindustrie). (MnO<sub>2</sub>, PbO<sub>2</sub>, Ag<sub>2</sub>O, HgO.)

<sup>252</sup> E. Tschunkur and W. Bock, U. S. Pat. 1,935,733, issued Nov. 21, 1933 (I. G. Farbenindustrie).

<sup>253</sup> French Pat. 847,878, issued Oct. 18, 1939. Brit. Pat. 542,434, issued Jan. 9, 1942.

<sup>254</sup> W. Gumlich and I. Dennstedt, German Pat. 679,587, issued Aug. 9, 1939 (I. G. Farbenindustrie) (hemin, hydrosol phthalocyanine containing iron, alkali salts of complex iron compounds of arabonic, pyrogallic, and gallic acids, as well as hydrosol complex compounds of nickel, cobalt, and copper; in this last case it is, however, necessary to add agents converting copper ions into complex compounds, *e. g.*, nitrotriacetic acid, since, as shown on page 107, copper ions usually act as inhibitors).

<sup>255</sup> German Pat. 704,039, issued Feb. 20, 1941 (I. G. Farbenindustrie) (Schiff's bases).

<sup>256</sup> R. Seidler and W. Pannwitz, U. S. Pat. 2,211,032, issued Aug. 13, 1940 (Jasco, Inc.) (organic bases containing at least one NO<sub>2</sub> group, *e. g.*, benzalnitroaniline, or other organic bases containing an open-chain with a double linkage between two carbon atoms or between a carbon atom and a nitrogen atom).

<sup>257</sup> Brit. Pat. 525,733, issued Sept. 3, 1940 (I. G. Farbenindustrie) (tertiary amines, *e. g.*, dibenzyl- $\beta$ -naphthylamine, soluble in butadiene).

<sup>258</sup> W. A. Gibbons and E. M. McColm, U. S. Pat. 1,953,169, issued April 3, 1934 (Naugatuck) ("non-rubber compound extracted by water from cortical portions of rubber trees").

## B. INHIBITORS

The effect of the cations in different oleates on the rate of the emulsion polymerization is analogous to that observed in mass polymerization.

The effect is due to the metallic ions rather than to undissociated salt molecules, since the chlorides and sulfates of the corresponding metals act much in the same way as the oleates. (An exception is to be made for stannic chloride, which forms high polymeric condensation products with butadiene.<sup>269</sup>) The following quantitative differences between the effects on the mass and on the emulsion polymerization are noted:

(a) Lead and nickel salts in emulsion slow down the polymerization when added in amounts below the threshold of coagulation, and inhibit the reaction completely in concentrations above the threshold.

(b) Zinc, chromium, and iron salts, though their deleterious action on the polymerization rate is even more pronounced at all concentrations, fail to inhibit it completely even at concentrations exceeding the coagulation threshold.

The influence of the material or surface of the reactor is in good agreement with these observations. Because metal is, to a greater or lesser degree, corroded by the soaps and the "per" compounds if these are used as catalysts, and because the polymerization process is slowed down or completely inhibited depending on the ultimate concentration of metal ions in the solution, glass-lined reactors are used in conjunction with this type of catalyst.

In order to avoid the inhibiting effect of metallic ions, phosphate ions which form insoluble salts with all the "inhibiting" metals (Dogadkin *et al.*<sup>268</sup>), have been introduced into the recipe. As already mentioned on page 132, this addition of phosphate ions to the recipe reflects very favorably on the rate and yield of polymerization. The reason for the improvement is, however, only partly due to the precipitation of inhibitor ions, which is less complete than might be expected (*e. g.*, addition of dipotassium hydrogen phosphate to an emulsion containing a large excess of ferric chloride—in amounts larger than the precipitation threshold—could not insure polymerization as would be the case if iron were precipitated as iron phosphate). The main reason is either a stabilization of pH (see page 132), or a specific catalytic activity of the phosphate ions, or a stabilization of the latex by adsorption of  $\text{PO}_4^{--}$  ions on the latex particles.

One of the advantages of diazoaminobenzene and compounds of this type as catalysts is prevention of the corrosion of the metallic surfaces so that polymerization can be carried out in metallic containers. The presence of

<sup>269</sup> G. G. Kobil'sanskii, A. A. Shul'ts, N. S. Bessmertnafa, and K. B. Piotrovskii. *Sintet. Kauchuk*, 4, No. 6, 50 (1935).

ferric chloride, aluminum sulfate, stannous chloride, and lead nitrate in concentrations above the threshold of coagulation does not inhibit the process. The only inhibitors are copper, zinc, and nickel salts in concentrations of the order of the coagulation threshold.

### C. KINETICS OF EMULSION POLYMERIZATION IN PRESENCE OF A CATALYST

The yields and rates of polymerization as functions of the catalyst concentration have been investigated by Dogadkin and coworkers.<sup>206</sup> In the case of hydrogen peroxide, they found that the rate of polymerization increases with the amount of catalyst present; and, as can be seen from figure III-7, the rate is nearly proportional to the square root of catalyst

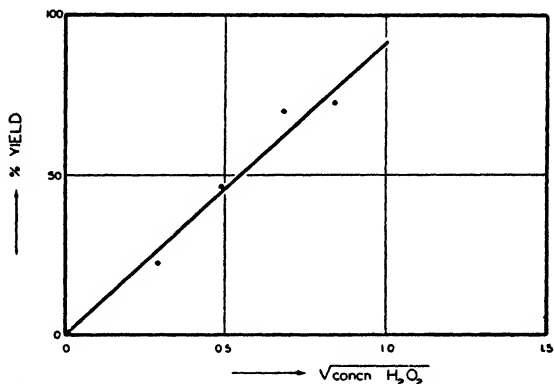


Fig. III-7.—Polybutadiene yield as a function of the peroxide catalyst concentration.<sup>206</sup>

TABLE III-10

EFFECT OF HYDROGEN PEROXIDE ON POLYMERIZATION YIELD AND RATE<sup>a</sup>

H <sub>2</sub> O <sub>2</sub> expressed as per cent of butadiene	Aspect of the system <sup>b</sup> after			Characteristics of the polymer	Yield, % butadiene
	3 days	4.5 days	7 days		
0.045	Milk	Same	...	Tacky	..
0.135	Sour cream	Same	...	Solid, elastic	29
0.38	Milk	Sour cream	...	Solid, elastic	59
0.76	Sour cream	Custard	...	Tough, elastic	89
1.14	Cream	Same	Same	Tough, elastic	92

<sup>a</sup> Butadiene (80% pure), 50 ml.; oleic acid, 1.5 ml.; magnesium oleate, 0.5 g.; excess ammonium hydroxide, 0.005 ml.; hydrogen peroxide, variable; and water, 100 ml.

<sup>b</sup> See page 126.



concentration, a distinctive characteristic of free radical catalysis (page 119). The figure is based on table III-10, given by Dogadkin *et al.*, on the assumption that the yield is proportional to the initial rate of the reaction.

In much the same manner, when diazoaminobenzene (DAB) is used as catalyst, the rate of polymerization increases with rising amounts of catalyst up to concentrations of 1.5–2.0%. On further addition of DAB, the rate and the yield decrease (Fig. III-8) and the quality of the polymer deteriorates. Instead of an elastic polymer, a tacky substance of low molecular weight is obtained (see Eq. 3.4b). Here, too, the initial rates of the polymerization calculated from the yield after 50 hours (data of Dogadkin *et al.*) when plotted *vs.* the square root of the concentration of DAB fall on a straight line, at least as long as the concentration of DAB is below its optimum value. This confirms the contention stated previously that diazoaminobenzene is a free radical catalyst (Fig. III-9).

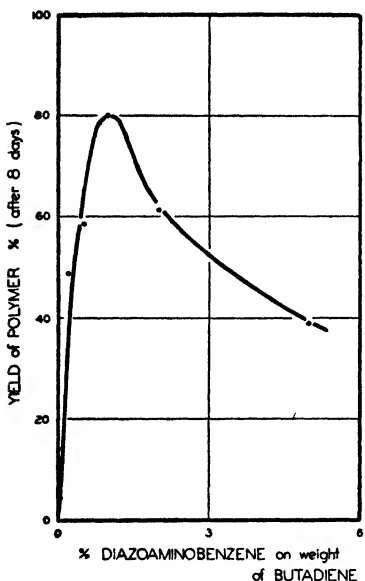


Fig. III-8.—Polybutadiene yield as a function of diazoaminobenzene concentration.<sup>208</sup>

Dogadkin and coworkers<sup>208</sup> also investigated the kinetics of emulsion polymerization in the presence of DAB.

The investigation was made on large batches polymerized in agitated autoclaves. Their technique permitted them to remove a sample periodically without interrupting the stirring. Samples were taken every six hours and the yield determined by drying.

The process shows an inhibition period of 5–10 hours (the length of the inhibition period depending on the chemical purity of the products used—the purer the products, the shorter the inhibition period). Then the rate increases, finally decreasing again near the end of the polymerization. A typical curve (for 1% diazoaminobenzene) is in figure III-10, where yield and rate are plotted against time. The general trend of the curves suggests either an autocatalytic process or a chain reaction, the latter being far more likely in light of our knowledge of the thermopolymerization of

butadiene. A formal similarity exists between the two types of reaction and in both reactions the rate constant is given by:

$$k = \frac{1}{\theta} \log \frac{x}{a - x} \tag{3.15}$$

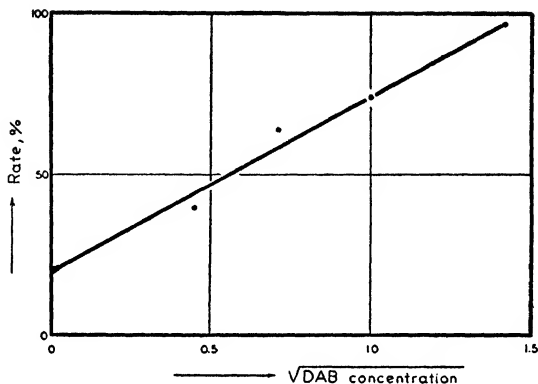


Fig. III-9.—Rate of emulsion polymerization as a function of diazoaminobenzene concentration.<sup>206, 207</sup>

where  $\theta$  is the time calculated from  $t_{\max.}$ , the moment of the maximal rate taken as 0 (inflection point on the yield curve), and  $a$  is the yield of the polymer corresponding to a time twice as long as the time corresponding

TABLE III-11  
EMULSION POLYMERIZATION WITH 1% DAB, AT  $60 \pm 2^\circ \text{C}$ .

$E$ , time from beginning of experiment, hrs.	$X$ , % yield (calcd. from contraction)	Rate of reaction in time interval $dx/dt$	$\theta$ , hrs. from time of maximal rate	$k = \frac{1}{\theta} \log \frac{x}{a - x} =$ Reaction rate constant
0	0	..	..	.....
24	5.79	0.24	-54	$2.00 \times 10^{-3}$
48	16.32	0.44	-30	$1.86 \times 10^{-3}$
72	32.4	0.67	-6	$2.25 \times 10^{-3}$
96	54.0	0.90	+18	$2.28 \times 10^{-3}$
120	64.5	0.44	+42	$1.88 \times 10^{-3}$
144	72.9	0.35	+66	$2.33 \times 10^{-3}$
168	75.0	0.09	..	.....
190	81.7	0.29	..	.....
AVERAGE:				$2.10 \times 10^{-3}$ $\approx 1.8 \times 10^{-3}$

to the maximum rate ( $t_f - 2t_{\max.}$ ). As may be seen from table III-11 this equation applies perfectly.

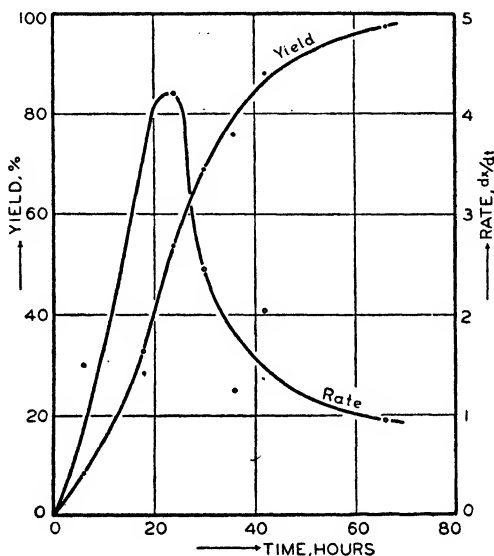


Fig. III-10.—Yield and rate of emulsion polymerization with 1% diazoaminobenzene as a function of time.<sup>208</sup>

#### D. EFFECT OF $pH$

From equation (3.4b), we can see that the initial over-all rate of the polymerization reaction is directly proportional to the rate of initiation reaction, which in turn depends on the rate of decomposition of the catalyst (formation of free radicals). In certain cases, as that of hydrogen peroxide, this rate of decomposition of the catalyst is governed to a large extent by the  $pH$  of the medium. In all cases, there is an optimum rate of decomposition of the catalyst, which corresponds to the optimum  $pH$ .<sup>212, 214, 216</sup> This explains at least in part the influence of  $pH$  and the favorable effect of buffer solutions.

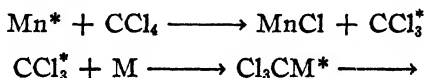
#### E. EFFECT OF THE CATALYST ON POLYMER QUALITY

Dogadkin and coworkers found that, generally, when peroxide-type catalysts are used, a cross linking of the polymer by the oxygen takes place which leads to a more or less large amount of insoluble gel. The polymers

formed with these catalysts are hard, and the treads obtained are all quite similar. The tread stocks (with 60% carbon black) have a maximum elongation of 300–800% and a low tensile strength of 570–1270 lb. per sq. inch. The polymers obtained with diazoaminobenzene are somewhat better. The amount of gel is somewhat smaller, and the tensile strength is increased. However, the maximum elongation seems to decrease.<sup>208, 260</sup>

## 8. Modifiers

Modifiers are substances which influence the properties of the polymer toward greater solubility and better working properties without affecting markedly the rate of polymerization or sacrificing yield. The mechanism of their action is unknown. However, certain guesses may be made from their nature regarding the way in which they may affect the polymerization process. For example, one of the first modifiers listed in the patent literature is carbon tetrachloride,<sup>261</sup> which we know (see page 93) can react with the growing chain corresponding to the equations:



thus interrupting one growing chain and starting a new one. We may conclude that at least certain, if not all, modifiers act by increasing the number of chain transfers.

Most of the modifiers quoted in the patent literature are organic sulfur compounds,<sup>262–264</sup> although assymetrically substituted hydrazine derivatives are also mentioned.<sup>265</sup>

These sulfur compounds, particularly the mercaptans, are known to react easily with double bonds; and some observations are made in the literature about their particular ability to "purify" the unsaturated compounds from peroxides.<sup>266</sup> Thus

<sup>260</sup> C. F. Fryling, U. S. Pat. 2,313,233, issued March 9, 1943.

<sup>261</sup> Brit. Pat. 349,499, issued Feb. 24, 1930 (I. G. Farbenindustrie) (carbon tetrachloride, *sym*-dichloroethane, chlorobenzene, trichloroacetic acid, and its sodium salt).

<sup>262</sup> Brit. Pat. 519,730, issued April 4, 1940 (I. G. Farbenindustrie) (aliphatic mercaptans containing at least six carbon atoms).

<sup>263</sup> K. Meisenburg, I. Dennstedt, and E. Zaucker, U. S. Pat. 2,248,107 (Jasco, Inc.), issued July 8, 1941 (dialkyl xanthogen disulfide, di(benzoic acid ester) tetrasulfide, tolyl di- and trisulfide).

<sup>264</sup> Brit. Pat. 520,838, issued Nov. 29, 1940 (du Pont) (compounds of the form,  $\text{RSR}_1$ , where R is an organic radical and  $\text{R}_1$  is hydrogen or ammonium, or  $\text{S}_n\text{R}_2$  groups, where  $n > 4$  and  $\text{R}_2$  are organic radicals of the same type as R).

<sup>265</sup> O. Bächle, German Pat. 702,209, issued Jan. 2, 1941 (I. G. Farbenindustrie).

<sup>266</sup> D. T. Gibson, *Chem. Revs.*, 14, 437 (1934).

butadiene peroxides, once built into the chain, are able to initiate side chains (branches) leading finally to cross links; and it is conceivable that their destruction, in addition to chain transfers, allows butadiene to polymerize to higher yields without being disturbed by excessive gel formation.

### 9. Agitation

In order to obtain high yields and fast polymerization, it is important to have as highly a dispersed emulsion as possible.<sup>214</sup> On the other hand, it is of paramount importance that the temperature of the emulsion be kept homogeneous throughout the polymerizer, and that any heat developed locally be removed as rapidly as possible. All this is effected by agitation. A number of devices for providing satisfactory agitation, even at a higher degree of conversion, have been described in the patent literature, but a discussion of them is beyond the scope of this book.

### 10. Temperature

Careful temperature control is very important because the rate of the polymerization as well as the characteristics of the polymer (average chain length) depend on the temperature. Unfortunately, the two temperature effects have opposite trends: the lower the temperature, the longer the molecular chains, but the slower the reaction, the higher the temperature, the faster the reaction but the shorter the molecules. Therefore, one must make a compromise choice.

Trommsdorff<sup>213</sup> gives the following procedure concerning the temperature variation during the polymerization and the temperature control: "A part of the emulsion is heated in the polymerizer to a certain temperature. After a short time (inhibition period) the temperature of the emulsion rises without further heating; at this moment, a cold emulsion or cold water is added to the polymerizer, until the desired temperature is reached, and the temperature is stabilized. When most of the monomer is polymerized, the temperature is maintained or even somewhat increased by heating until no monomer remains in the emulsion."

### 11. Stabilizers

If the latex is coagulated directly, as it is at the end of the polymerization process, the polymer obtained becomes insoluble and hard after a short time. This is due to the fact that the free radicals, responsible for the polymerization and the growth of chains, are not destroyed. The polymerization continues slowly and, with time, more and more cross links are formed. In order to avoid this, polymerization inhibitors are added.

They terminate the reaction and protect the product from rapid oxidative degradation. Such stabilizers are mostly compounds with hydroxyl groups capable of different degrees of oxidation: hydroquinone, pyrogallol, tannin, etc.<sup>267</sup>

## 12. Seat of the Reaction

It was very early observed that the polymer emulsion behaves differently when different (water-soluble and water-insoluble) catalysts are used. With water-soluble catalysts, a normal latex is formed. Water-insoluble catalysts, on the other hand, lead to mere suspensions of the polymer in water. A part of the polymer forms more or less large grains and crumbs, which separate from the latex.<sup>216, 268</sup> This raises the question as to the actual seat of reaction. Several have been proposed: the aqueous phase, the hydrocarbon phase, the soap micelles, the interphase. Arguments can be presented for and against each one of them.

Fikentscher<sup>211</sup> assumes that the main part of the reaction takes place in the fraction of monomer dissolved in water rather than in the droplets of hydrocarbon. This fraction is constantly used up and renewed by diffusion from the liquid droplets which thus serve simply as a reservoir. The amount dissolved is constant throughout the polymerization. The monomer is soluble in water to a certain extent, while the polymer is not; hence the polymer does not influence the equilibrium distribution of the monomer between the liquid phase and the solution.

If such is the case, one of the functions of the emulsifier would be to increase the solubility of the monomer in water. The solubility of butadiene in water was investigated by Lebedev, Kobljanskiĭ and Guljãeva,<sup>269</sup> and in water and 1% potassium oleate solutions, by McBain and O'Connor.<sup>270</sup> These results, which are in satisfactory agreement, are summarized in table III-12. The amount of butadiene soluble in water is still large enough to make Fikentscher's hypothesis feasible.

However, the solubility of butadiene in water, when compared with that of aldehydes and other impurities formed in the Lebedev process, is small enough to allow the purification of butadiene by washing in the process of its manufacture (page 67).

<sup>267</sup> E. Trommsdorff, in R. Houwink, *Chemie und Technologie der Kunststoffe*. Akad. Verlagsgesellschaft, Leipzig, 1939, p. 314.

<sup>268</sup> E. Trommsdorff, *loc. cit.*, pp. 319-320.

<sup>269</sup> S. V. Lebedev, G. G. Kobljanskiĭ, and A. I. Guljãeva, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 1, 44 (1933), quoted from *Zhizn' i Trudy*, Moscow, 1938.

<sup>270</sup> J. W. McBain and J. J. O'Connor, *J. Am. Chem. Soc.*, 63, 875 (1941).

Fryling and Harrington<sup>210</sup> have contributed several arguments in favor of initiation of polymerization in the aqueous phase:

(1) They observe that the utility of various substances as emulsifiers follows approximately the same order as their solubilizing action for propene.<sup>271</sup>

(2) The emulsion polymerization velocity of many recipes at low soap concentrations is almost linearly proportional to the soap concentration (see also page 129), which suggests that at least the initiation reaction

TABLE III-12  
SOLUBILITY OF BUTADIENE IN WATER AND IN OLEATE SOLUTION

Temp., °C.	Pressure, mm. Hg	Ml. butadiene dissolved in 100 grams of		Author
		Water	Water + 1% oleate	
0	760	87 ± 7	..	Lebedev <i>et al.</i> <sup>269</sup>
15	760	51.5	..	McBain and O'Connor <sup>270</sup>
25	100	5.8	8.4	
25	200	11.0	15.0	
25	400	20.0	28.4	
25	760 <sup>a</sup>	34	..	

<sup>a</sup> Extrapolated.

takes place in the aqueous phase with such catalysts as potassium persulfate, hydrogen peroxide, and sodium perborate, which are soluble in water but not in the hydrocarbon.

(3) It can be visually demonstrated that polymerization takes place exclusively in the aqueous phase by floating acrylonitrile quietly on the surface of a persulfate solution.

(4) Finally, " 'emulsion' polymerization takes place even though the monomer is separated from the other ingredients of the recipe by the vapor phase. The monomers evaporate, pass into the aqueous phase, and polymerize without any evidence of a monomer phase in contact with water solution. Under this condition the initiation is a homogeneous process and no part of it (*i. e.*, the initiation) can be attributed to interfacial reactions."<sup>210</sup>

The situation is naturally different if a water-insoluble catalyst, *e. g.*, benzoyl peroxide, is employed as initiator. In this case the initiation takes place in the hydrocarbon phase.

<sup>271</sup> J. W. McBain and A. M. Soldate, *J. Am. Chem. Soc.*, **64**, 1556 (1942).

The micelle theory of reaction seat can be considered as a refinement of these ideas based on the mechanism of solubilization. It is possible that a micellar structure, such as postulated by McBain, consisting of alternate layers of soap, water, soap, and organic liquid, can explain all the observations. If it is to be assumed, for instance, that the increase of the reaction rate is due to an orientation of the monomer, this orientation is as likely to occur in micelles as on the interfaces.

One may go even a step further and explain the differences existing between polymers obtained at low yields and those made at higher conversions, assuming that polymerization is initiated in the aqueous phase and that the subsequent growth occurs in the hydrocarbon phase. "Consequently those growing polymer molecules which fail to penetrate a phase interface are readily terminated, possibly by free radicals which would otherwise act as initiators and give low molecular weight products."<sup>210</sup>

A decidedly different position is taken by the advocates, such as Gee, Davies, and Melville,<sup>212</sup> of the interphase theory. They observe, in agreement with Fryling and Harrington, a slight cloudiness in the water phase on prolonged contact of the butadiene with an aqueous solution of hydrogen peroxide. Although this demonstrates well that polymerization can occur in the solution, it was remarked that the rate of this homogeneous reaction is slow when compared with the interface polymerization.

Their investigation<sup>212</sup> followed the interface polymerization by measuring, as a function of time, the variation of the surface tension of hydrogen peroxide solution brought into contact with gaseous butadiene under pressure (about 4 atm.). Two different processes seem to influence the surface tension—an adsorption of butadiene and the polymerization, the first occurring in the very beginning when the effect of the second can be neglected. The two effects can hence be separated; experience shows that their contributions are purely additive.

Adsorption was studied as a function of pressure and of temperature on the surface of a 1% (by volume) solution of hydrogen peroxide. The heat of adsorption was found to be 6.9 kcal. per mole, not far removed from the heat of dissolution in water as can be calculated from the data given in table III-12 (6.2 kcal.), and much in excess of the heat of evaporation of butadiene at the same mole temperature (50–60° C.) (about 4 kcal. per mole).

Gee *et al.* have shown that the variation of the surface tension is proportional to the amount of polymer, and the relation between them has been established. The effects of the following variables on the polymerization rate have been investigated: the pressure of butadiene, the concentration of hydrogen peroxide, its rate of decomposition (which is controlled by the  $\rho\text{H}$  of the solution), and the temperature. At low peroxide concen-



tration, the polymer time curve is nearly of first order; then it rises slightly, and is of about 1.5 order for a 12% by volume solution. The rate is said to be proportional to the concentration of peroxide and not to the square root of the concentration, although it seems from the curves published that the power is  $3/4$  rather than 1. This is somewhat peculiar, since Dogadkin found that the rate in emulsion polymerization is proportional to the square root of the catalyst concentration, as it should be for a reaction catalyzed by free radicals.

The apparent activation energy between 50° and 75° C. is 9 kcal. per mole. When corrected for the heat of adsorption (6.9 kcal. per mole), the total apparent energy of activation is about 16 kcal. It is, perhaps, noteworthy to remark that both the order of the reaction and the activation energy are close to the values given for homogeneous thermopolymerization in the liquid phase.

The experiments with variable rate of decomposition of peroxide have shown that the lifetime of the activated polymer is small, when compared with the time of the reaction. A kinetic analysis of the results leads Gee *et al.* to believe that the mechanism of the reaction consists in the reaction of one catalyst molecule with one butadiene molecule. This complex starts the polymerization chain which is terminated by some deactivating collision of the monomer, different from that for the propagation, possibly by a 1,2 addition.

Taking into account all these contradictory results, it may be stated that polymerization probably proceeds both in water and in the hydrocarbon phase (in both cases, probably, in emulsifier micelles), as well as in the interphase, a different rate governing each of the three cases. Depending on the exact conditions prevailing (which are determined by the nature of the emulsifying agent, the type of the catalyst, the pH of the emulsion, the temperature, etc.), one or the other of the concurrent processes will predominate and appear as rate determining in the over-all rate.

## D. SODIUM POLYCONDENSATION

### 1. General Remarks

The discovery that sodium acts as a catalyst for the butadiene polymerization was made simultaneously and independently by Matthews<sup>272</sup> in England and Harries<sup>273</sup> in Germany. While the noncatalyzed polymerization at room temperature requires several hundred days to reach com-

<sup>272</sup> F. E. Matthews and E. H. Strange, German Pat. 249,868.

<sup>273</sup> C. Harries, *Ann.*, **383**, 213 (1911).

pletion, Harries obtained about 90% conversion in three hours, when 9 g. pure butadiene was heated to 35–40° C. with 0.5 g. sodium wire. A rubber-like substance climbed up the wire. Only a small contraction took place on polymerization. As long as sodium was present, the color of the product was steel-gray. Upon washing with alcohol, the polymer became light yellow. The fresh polymer was readily soluble in ether, chloroform, and benzene, the solutions being highly viscous. On aging, however, particularly after milling, only limited swelling in these solvents could be observed. Ozonolysis indicated that the structure of the product was definitely different from that of the thermopolymer, although the results are too complicated to be interpreted in terms of actual structure.

It was soon recognized that sodium and potassium alkyl compounds can also be used as polymerizing agents.<sup>274</sup> But it remained for Ziegler and coworkers<sup>275–279</sup> to clarify the chemistry of the process. It was in the late twenties that the process became of industrial importance when I. G. Farbenindustrie brought out its numbered Bunas (Buna 85, Buna 115, etc.). Independently, Lebedev and his group (1926–1928) selected the sodium polymerization as the basis for their synthetic rubber process in the U.S.S.R.<sup>280</sup>

While the Germans soon abandoned this method of polymerization in favor of the emulsion polymerization, because the latter is more suitable for the production of butadiene–styrene copolymers, Buna S, and also because they apparently failed to overcome the difficulties arising from overheating due to the localized evolution of heat in the mass or bulk polymerization, the Russians retained the sodium process and, in more recent years successfully solved the problems involved (see page 184). This was accomplished mainly by changing from the batch process (“rod” polymerization, page 187) to the flow process (“rodless” polymerization, page 194) in the gaseous or liquid phase. Since the sodium process is fairly sensitive to the slightest amount of certain impurities, a very careful survey of the effects of all impurities likely to be present in alcohol and in petroleum–butadiene has been made. The actual kinetics of the process has been investigated and the closest collaboration between science and industry has been maintained.

<sup>274</sup> German Pats. 255,782 and 287,787, issued April 9, 1912 (Badische Anilin).

<sup>275</sup> K. Ziegler and K. Bähr, *Ber.*, **61**, 253 (1928).

<sup>276</sup> K. Ziegler, F. Dersch, and H. Wollthan, *Ann.*, **511**, 13 (1934).

<sup>277</sup> K. Ziegler and L. Jakob, *Ann.*, **511**, 45 (1934).

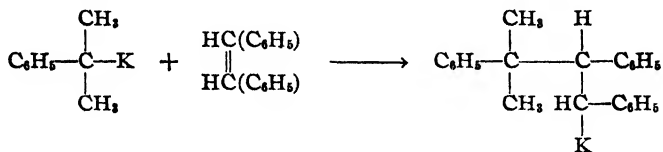
<sup>278</sup> K. Ziegler, L. Jakob, H. Wollthan, and A. Wenz, *Ann.*, **511**, 64 (1934).

<sup>279</sup> K. Ziegler, *Z. angew. Chem.*, **49**, 499 (1938).

<sup>280</sup> S. V. Lebedev, Russian Pat. 36,007, issued April 30, 1934.

## 2. Chemistry

Ziegler's starting point was his observation<sup>275</sup> that stilbene reacts very easily with potassium phenyl isopropyl, suggesting that alkali-metal-alkyl compounds can add to C=C double bonds:

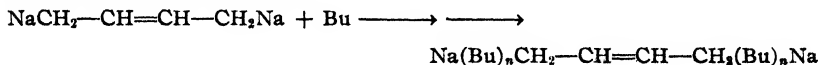


The reaction, however, proved fairly specific, since no addition compounds could be formed with other alkali-metal alkyls. This observation suggested to Ziegler that the sodium polymerization of butadiene may proceed via the formation of an organometallic compound, starting with the formation of a disodium compound of the butadiene, *i. e.*, a Schlenk's addition product ( $\text{NaCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Na}$ ), and via a continuous synthesis of organometallic compounds of increasing molecular weight—in other terms, that the process is a polycondensation rather than a polymerization:

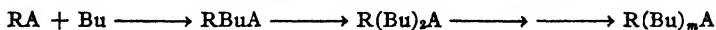
*First step:*



*Second and following steps:*



If an alkali-metal-alkyl, RA (R = alkyl group, A = alkali metal), is used as initiator, then the reaction proceeds as follows:



## A. ALKALI-METAL-ALKYL INITIATION

To substantiate this scheme, very extensive experiments proved to be necessary.

First, the specificity of the reaction had to be explained, since *a priori* the same chain reaction can be considered for all unsaturated hydrocarbons, while it is known that the polyreaction actually takes place only in a few isolated cases. The experiments of Ziegler, Crössmann, Kleiner, and Schäfer<sup>281</sup> on a very large number of substances have shown that the

<sup>281</sup> K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, *Ann.*, **473**, 1 (1929).

alkali-metal-alkyl addition to hydrocarbons is not nearly as general as their addition to CO groups. A first limiting condition found is that at least two conjugated double bonds must be present in the hydrocarbon, either in a chain or in the form of phenylethylenes (styrene, stilbene). Certain aromatic hydrocarbons (anthracene) are to be included in this group. Furthermore, the structure of the alkali-metal-organic compound to be added is also important, as very similar substances may behave differently. Thus, though the binding of potassium in potassium phenyl isopropyl and in its addition product with stilbene are very similar, the first substance is able to add to stilbene, while the second is not.

Finally, a necessary condition for a polycondensation is that the unsaturated hydrocarbon be able to add not only on the initial alkali-metal-hydrocarbon but also on *all* of its consecutively formed addition products with this hydrocarbon.

All this narrows down the field tremendously and explains the specific character of the reaction. In the case of a condensation reaction, as was stated on page 91, first the polymers of low molecular weight are formed and the solution contains chiefly the dimer, the trimer, and the tetramer. As the reaction progresses, the low polymers disappear and are replaced by the higher polymers. Ziegler, Kleiner, Dersch, and Wollthan<sup>282</sup> have shown that this is really the case if the butadiene polycondensation is initiated by potassium phenyl isopropyl, by lithium benzyl, and by lithium butyl. The experiments performed with the last-named compound are particularly clear-cut.

When butadiene is brought into contact with an ether solution of lithium butyl, the gas is absorbed with evolution of heat, and the initially colorless solution turns a light yellow. This is characteristic for compounds in which an alkali metal atom is in conjugated position with a double bond, such as:



If a sample of the solution is treated with water in order to replace lithium by hydrogen, compounds of general formula  $\text{C}_4\text{H}_7(\text{Bu})_n\text{H}$  are obtained, containing one double bond for each butadiene group. Fractional distillation shows that the numerical value for  $n$  ranges from 1 to 6. When further amounts of butadiene are added, it is found that the compounds of low molecular weight disappear in favor of compounds of higher molecular weight, until finally only resins and rubberlike polymers remain.

<sup>282</sup> K. Ziegler, H. Kleiner, F. Dersch, and H. Wollthan, *Ann.*, **473**, 57 (1929); **511**, 1 (1934).

If the alkali metal is not washed out with water, these high polymers are able to "take on" further butadiene. The introduction of additional butadiene can be interrupted for an extended period; and, provided the alkali metal compounds are not destroyed (*e. g.*, by contact with air or water), the polyreaction recommences as soon as new butadiene becomes available.

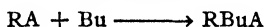
The polycondensation initiator, lithium butyl, disappears completely even in the first stages of the reaction. This also happens with potassium phenyl isopropyl, with a characteristic color change, *i. e.*, from a red to an orange, taking place almost instantaneously.

In this case the red color reappears, however, 30–50 minutes after the introduction of butadiene has been discontinued, *i. e.*, when all the butadiene has reacted.<sup>283</sup>

By contrast, the deep red color of sodium triphenyl methyl persists even on addition of a large excess of butadiene; and this substance can be almost quantitatively recovered from the solution even in fairly advanced stages of the polyreaction. At first glance, this may suggest that, in contradistinction to other alkali-metal-alkyl compounds, sodium triphenyl methyl acts as a true catalyst. This, however, is not true; and the deviation of the behavior of the latter substance from the normal can be explained quite satisfactorily by the following consideration of the reaction rates.

Actually polycondensation is a sequence of two types of reactions:

"initiation"



"growth"



The rates of the growth reactions are  $k_{g1}, k_{g2}, \dots, k_{gn}$  but they can be either slower or faster than the initiation reaction,  $k_i$ . If  $k_i \geq k_g$  then the initiator (alkali-alkyl) disappears immediately after the reaction is started. If, however,  $k_i \ll k_g$ , then all the available butadiene is built into the polymer as soon as the first active tri units, RBuA, are formed, while the rest of the initiator, *i. e.*, sodium triphenyl methyl, remains unchanged. In such a case, the polymer chains formed are fewer but longer.

This was proved by Ziegler and Jakob<sup>284</sup> by introducing diethyl amine or dicyclohexyl amine in the solution. These compounds do not react with sodium triphenyl

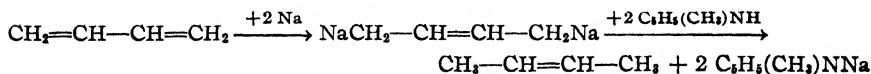
<sup>283</sup> O. Mamontova, A. Abkin, and S. Medvedev, *Acta physicochim. U. R. S. S.*, **12**, 277 (1940).

<sup>284</sup> K. Ziegler and L. Jakob, *Ann.*, **511**, 52 (1934).

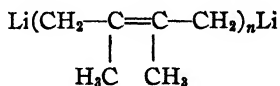
methyl, but very rapidly exchange their hydrogen atoms with the alkali-metal atom (A) of the more active compound, RBUA, forming  $(C_6H_5)_2NNa$  and  $(C_6H_5)_3C-CH_2-CH=CH-CH_3$ . The growth reaction is thus interrupted, so that the butadiene present serves uniquely to form  $(C_6H_5)_3C-CH_2-CH=CH-CH_2Na$ , in other words, the only reaction taking place is the initiation reaction. Under this condition, the "catalyzed" polymerization is changed to a stoichiometric addition and the solution is decolorized in about 24 hours.

## B. ALKALI-METAL INITIATION

It still remains to be proved that the molecule,  $A-CH_2-CH=CH-CH_2A$ , formed by direct reaction of the alkali metal (A) with butadiene, can act as initiator. Isolation of this molecule is impossible because it is formed in a surface reaction and destroyed (by addition) in a volume reaction, so that its concentration at any given moment is negligible, most of the butadiene being polymerized even before it comes in contact with the sodium surface. Ziegler, Jakob, Wollthan, and Wenz<sup>278</sup> nevertheless supplied the necessary proof by a very elegant indirect method. They added to their sodium and butadiene mixture some methylaniline, an amine which does not react directly with sodium. The experiment showed, however, that, in presence of butadiene, it adds rapidly to sodium to form sodium methylanilide, in such a way that two sodium methylanilide molecules are formed for each butadiene molecule present. The only possible explanation is the reaction sequence:



Further support of the contention that dialkali-metal butadiene acts as the initiator can be based on the similarity of the reactions of butadiene and 2,3-dimethylbutadiene. If this latter substance is used with lithium instead of sodium as catalyst, then the rate of the initiation reaction is increased and that of the growth reaction decreased as compared with the case of butadiene-sodium, and it is possible to isolate among the low molecular weight substances formed the molecule:



A further confirmation of the idea that the sodium butadiene polyreaction is a polycondensation rather than a polymerization can be found in the experiments of Bessmertnaïa and Vasil'eva.<sup>285</sup> These authors performed the polymerization in sealed test tubes, in the dark, at 24–26° C.,

<sup>285</sup> N. I. Bessmertnaïa and A. N. Vasil'eva, *Sintet. Kauchuk*, 5, No. 6, 50 (1936).



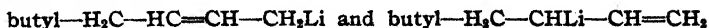
However, the yields of succinic acid and succinaldehyde found were fairly low and no formaldehyde was detected at all.

For this reason, Ziegler, Dersch, and Wollthan,<sup>276</sup> and later Ziegler, Grimm, and Willer<sup>287</sup> have investigated the problem from another angle. As stated before, if lithium butyl is used as initiator, the reaction can be conducted easily in solutions, and the rates of initiation and of growth are comparable. When small amounts of butadiene are introduced into the solution, a mixture of low polymers is formed; and by varying the amount of butadiene in a convenient way, one can obtain the predominance of molecules containing 1, 2, 3, or 4 butadiene units. These molecules of the general type  $C_4H_9(C_4H_6)_nLi$  are first treated with water and converted to  $C_4H_9(C_4H_6)_nH$  and then hydrogenated to yield the corresponding paraffins. The paraffins can be fractionally distilled and their properties compared with the properties of hydrocarbons of known structure. The results of these experiments are: when  $n = 1$ ,  $n$ -octane is obtained nearly exclusively but, if  $n = 2$ , the amount of 5-ethyldecane (for polymers prepared at room temperature) is about three to four times as large as the amount of  $n$ -dodecane. In other words, the addition of lithium butyl to the first butadiene<sup>288</sup> occurs mostly (in three cases out of four) in a 1,2 position. If this relative probability is a general rule and holds also for addition to the second and third butadiene molecules, one can reasonably expect to find small amounts of  $n$ -hexadecane, and practically none of  $n$ -eicosane or of higher  $n$ -paraffins, these normal hydrocarbons being replaced by their different isomers. Since the boiling points of these various isomers form a nearly continuous series, they cannot be separated on an ordinary distillation column. This conclusion was confirmed by observation: after the dodecanes were distilled off, a continuous distillation was observed for the higher hydrocarbons.

Ziegler, Grimm, and Willer<sup>287</sup> have also investigated the influence of external factors on the relative probability of the 1,2 and the 1,4 addition. Experiments carried out with various solvents (diethyl ether, benzene, hexahydrotoluene), with various rates of butadiene addition and with compounds containing different alkali metals (lithium and potassium) as

<sup>287</sup> K. Ziegler, H. Grimm, and R. Willer, *Ann.*, **542**, 90 (1940).

<sup>288</sup> Naturally, it is impossible to determine, after hydrogenation, the position of the lithium atom, the compounds



both yielding  $n$ -octane. Hydrogenation of the compound with two butadiene groups, however, determines implicitly the position of the lithium on the first addition compound, since, in this case, the lithium is now replaced by a butadiene group.



initiator, have shown that none of these factors has any bearing on this probability. In contradistinction, the relative probability of 1,2 and 1,4 additions is greatly influenced by the temperature, the 1,4 additions being predominant at high, and 1,2 additions at low, temperatures. In table III-13, the percentage of *n*-dodecane in the dodecane fraction, which is a measure of 1,4 additions in the polymer, is given as a function of temperature. One can readily conclude that the hexadecane and eicosane fractions obtained by hydrolyzing and hydrogenating a low-temperature polymer ought to be fairly pure 5,7-diethyldodecane and 5,7,9-triethyltetradecane and can, hence, be separated. This conclusion was confirmed by experiments.

TABLE III-13  
EFFECT OF TEMPERATURE ON 1,4 ADDITIONS

<i>t</i> , ° C.....	-70	-50	+30	+35	+60	+80	+110
<i>n</i> -Dodecane, %.....	(12) <sup>a</sup>	8	20	25	47	75 <sup>a</sup>	85

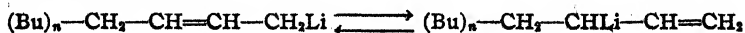
<sup>a</sup> Experiments initiated by potassium phenyl isopropyl. The others were initiated by lithium butyl.

Another prediction also borne out by experimental evidence is that polymers prepared at high temperature will yield, on ozonolysis, larger amounts of succinic acid than the polymer prepared at low temperature. The amount of succinic acid obtained from a high-temperature polymer (150° C.) was 60% of the theoretical value, calculated on the basis that all polymer was formed by 1,4 additions in the first case, as against 10% for a polymer prepared at room temperature, while in a low-temperature polymer (-70° C.) no succinic acid could be detected at all.

On the basis of these data of Ziegler *et al.*, Schulz<sup>289</sup> has calculated the difference between the heats of activation,  $\Delta E^\ddagger$ , for the two types of addition and the ratio of the frequency factors,  $A_{1,4}$  and  $A_{1,2}$ . He obtained:

$$E_{1,4}^\ddagger - E_{1,2}^\ddagger = 4.8 \text{ kcal./mole and } A_{1,4}/A_{1,2} = 2.6 \times 10^3$$

To date no such temperature effects on the ratio of 1,4 and 1,2 additions have been detected either in the thermopolymerization or in the emulsion polymerization. It is probable that, in the case of the alkali-metal polymerization, at least part of this effect is due to the allyl tautomerism of the alkali metal compound:



<sup>289</sup> G. V. Schulz, *Ber.*, **74B**, 1766 (1941).

It is also possible to formulate a mechanism without assuming tautomerism. The experimental data can be explained equally well if one merely assumes that, at a given temperature,  $X\%$  of all additions are 1,4 and  $100 - X\%$  are 1,2; and that this distribution is virtually independent of chain length. Either mechanism will explain the increase of the 1,4 type at higher temperature. In the former case, the 1,4 tautomer is more probable at high temperatures because of its higher entropy (three possible positions for the alkali-metal atom at the end of the chain, against two possible positions in the middle). In the latter case, the 1,2 addition is more likely at lower temperatures because of the lower activation energy required for its formation.

#### 4. The Sodium Polymerization in Solution

##### A. KINETICS

A careful investigation of the kinetics of the butadiene polymerization in ethyl ether solution, in the presence of potassium phenyl isopropyl,

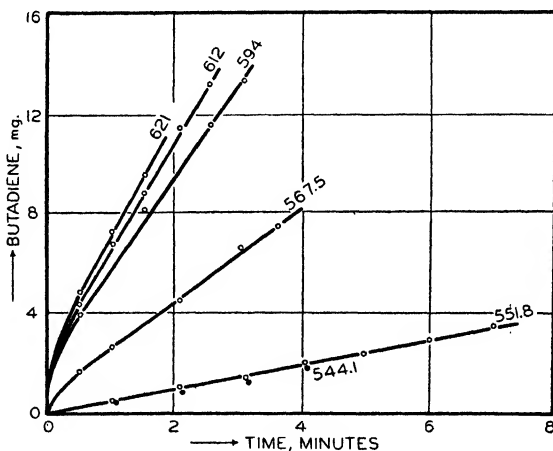


Fig. III-11.—Amount of butadiene reacted as a function of time for different values of total pressure (expressed in mm. Hg along curves) in the system.<sup>290</sup> (Initiator: potassium phenyl isopropyl.)

was carried out by Mamontova, Abkin, and Medvedev.<sup>290</sup> It confirmed the broad outlines of Ziegler's theory, but also showed that the situation is somewhat more complex than assumed by him. As will be shown, the main

<sup>290</sup> O. Mamontova, A. Abkin, and S. Medvedev, *Acta physicochim. U. S. S. R.*, **12**, 269 (1940).

difference lies in the necessity of taking into account the regeneration of potassium phenyl isopropyl.

The measurements were carried out volumetrically in a pressure of butadiene ranging from a few mm. Hg to 230 mm. (total pressure of butadiene and ethyl ether, 530–760 mm.), and at 5°, 15°, and 25° C. The compounds were prepared and mixed together in an atmosphere of nitrogen.

Measurement of the rate of polymerization began at a minimum partial pressure of butadiene. After the rate became constant, the partial pressure of butadiene was increased, and the rate was measured again, and so on. These results could be duplicated if, at the end, the pressure was lowered again and the cycle repeated.

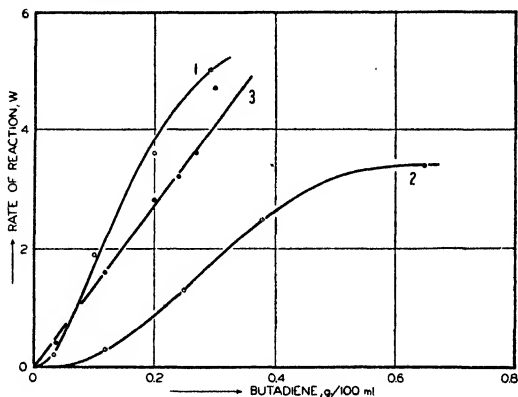


Fig. III-12.—Rate of reaction of butadiene in solution as a function of butadiene concentration (g. per 100 ml.) for different amounts of catalyst.<sup>290a</sup>

In a series of preliminary measurements, the solubility of butadiene in ether was determined. The concentration of butadiene in solution was found to be a linear function of the pressure but somewhat higher than corresponds to Raoult's law. Reproducible results could not be obtained with potassium phenyl isopropyl prepared at different times, so that the effect of the catalyst concentration cannot be expressed quantitatively.

Figure III-11 gives the amount of butadiene reacted as a function of time for different values of the total pressure. Figure III-12 shows the dependence of the rate of polymerization on the concentration of butadiene at two different concentrations of catalyst, 0.065 *N* (curve 1), and 0.019 *N* (curve 2).

The curves can be divided into three sections. At small butadiene concentrations, the rate increases more rapidly than the first power of the concentration. In the

<sup>290a</sup> A. Abkin and S. Medvedev, *Trans. Faraday Soc.*, 23, 286 (1936); and more completely in *Zhur. Fiz. Khim.*, 13, 705 (1939).

second section, rate  $k$  (ml. per min.) is proportional to the concentration. Finally, at still higher concentration, the rate varies more slowly than the concentration.

Some part of the process takes place on the surface, as may be seen from a comparison of curve 1 with curve 3 (obtained with the same catalyst concentration as curve 1 but in a vessel with twice as large a surface-volume ratio).

The results on the over-all temperature effect lead to an over-all activation energy of  $7.6 \pm 0.8$  kcal. per mole.

Four points must be borne in mind when establishing the reaction scheme:

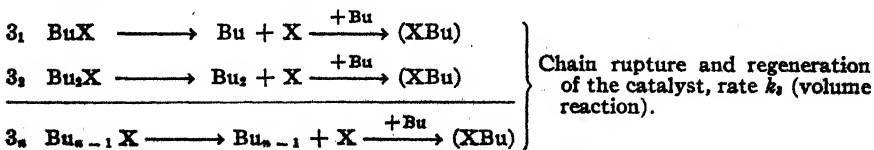
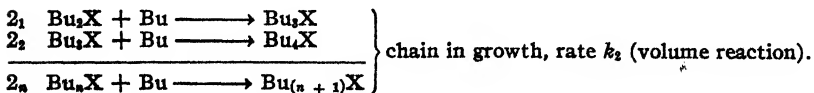
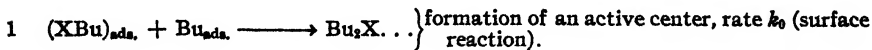
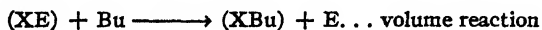
(1) Pure potassium phenyl isopropyl is colorless. In ethyl ether solution it gives the solution a cherry-red color.

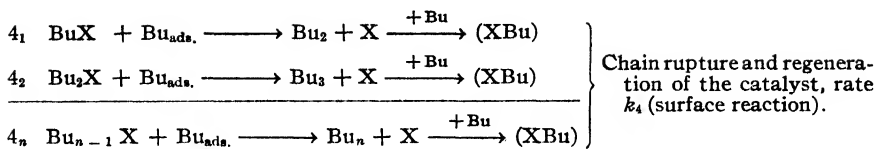
(2) This color disappears almost instantaneously when butadiene is introduced into the solution; but after the reaction has ended and all the butadiene reacted, the color reappears. In other words, the potassium phenyl isopropyl readily forms a colorless compound with butadiene, but is regenerated when the reaction chain is interrupted.

(3) When measurements are carried out while gradually increasing the butadiene concentration, the rate of polymerization increases. Upon returning to a lower concentration, the previously observed rate is reproduced. Hence, no substance influencing the polymerization rate is formed during the polymerization.

(4) Since the surface has a definite effect on the rate, a part of the process takes place on the walls.

Mamontova, Abkin, and Medvedev suggest the following reaction scheme, in which X is the catalyst (potassium phenyl isopropyl), E is the ethyl ether, Bu is butadiene, (XE) and (XBu) are their complexes with the catalyst, and  $Bu_2X$  is an active center:





The rate of formation  $k_0$  of active centers in accordance with the Langmuir adsorption theory is given by:

$$k_0 = aS_{\text{Bu}}S_{\text{X}} \quad (3.16)$$

where  $S_{\text{Bu}}$  and  $S_{\text{X}}$  are the surface fractions of the total surface occupied by the butadiene and the catalyst, and  $a$  is a coefficient which indicates what fraction of the total number of Bu and X neighbors lead to reactions.

For a state of absorption equilibrium:

$$\alpha_{\text{Bu}}Z_{\text{Bu}}S_0 = v_{\text{Bu}}S_{\text{Bu}} \quad (3.18a)$$

$$\alpha_{\text{X}}Z_{\text{X}}S_0 = v_{\text{X}}S_{\text{X}} \quad (3.18b)$$

where  $S_0$  is the free surface,  $\alpha_{\text{Bu}}$  and  $\alpha_{\text{X}}$  the fractions of Bu and X molecules striking the surface which are retained by the surface,  $Z_{\text{Bu}}$  and  $Z_{\text{X}}$  the total number of Bu and X molecules striking a unit area in a unit of time, and  $v_{\text{Bu}}$  and  $v_{\text{X}}$  the desorption rates.

Assuming  $S_0 + S_{\text{Bu}} + S_{\text{X}} = S = 1$ , the equation for  $k_0$  can be easily solved. If  $n$  is the volume concentration of active centers when equilibrium is attained, then:

$$dn/dt = 0 = k_0S - k_3S_{\text{Bu}}S - k_4n \quad (3.19)$$

and  $n$  can hence be expressed in terms of  $k_0$ ,  $k_3$ ,  $k_4$ ,  $S$ , and  $S_{\text{Bu}}$ ; and  $S_1$  in terms of  $\alpha$ 's,  $Z$ 's, and  $v$ 's.

The measured rate of the polymerization is

$$k = -d[\text{Bu}]/dt = k_2nC_{\text{Bu}} \quad (3.20)$$

where  $C_{\text{Bu}}$  is the concentration of butadiene.

Since  $Z_{\text{Bu}}$  and  $Z_{\text{X}}$  are proportional to concentrations  $C_{\text{Bu}}$  and  $C_{\text{X}}$  (proportionality factors  $\beta_{\text{Bu}}$  and  $\beta_{\text{X}}$ ):

$$k = \frac{b_1C_{\text{Bu}}^2}{1 + b_2C_{\text{Bu}} + b_3C_{\text{Bu}}^2} \quad (3.21)$$

where

$$b_1 = \frac{k_2av_{\text{X}}\beta_{\text{X}}\alpha_{\text{X}}C_{\text{X}}\beta_{\text{Bu}}S\alpha_{\text{Bu}}}{k_4v_{\text{Bu}}(v_{\text{X}} + \beta_{\text{X}}\alpha_{\text{X}}C_{\text{X}})^2} \quad (3.22a)$$

$$b_2 = \frac{v_{\text{X}}(k_3S + 2k_4)\beta_{\text{Bu}}\alpha_{\text{Bu}}}{k_4v_{\text{Bu}}(v_{\text{X}} + \beta_{\text{X}}\alpha_{\text{X}}C_{\text{X}})} \quad (3.22b)$$

$$b_3 = \frac{v_X(k_3S + k_4)\alpha_{Bu}^2\beta_{Bu}^2}{k_4v_{Bu}^2(v_X + \beta_X\alpha_X C_X)^2} \quad (3.22c)$$

Actual calculations of the results show that, since  $b_2$  is small when compared with  $b_3$ , the term  $b_2C_{Bu}$  in equation (3.21) can be neglected.

The over-all reaction rate can be adequately represented by the approximate equation

$$k = \frac{b_1C_{Bu}^2}{1 + b_3C_{Bu}^2} \quad (3.23)$$

The activation energy given above has no direct significance because it is due to a composite effect of variations with temperature of  $b_1$  and  $b_3$ , which themselves are of a very complex nature.

An attempt to disentangle these effects shows that  $b_1$  is fairly independent of temperature, while  $b_3$  decreases strongly with temperature, so that at high temperatures the reaction becomes, apparently, second order, while at lower temperatures and high butadiene concentrations, where  $b_3C_{Bu}$ , the over-all reaction rate, becomes independent of butadiene concentration and of the surface:

$$k = b_1/b_3 \quad (3.24)$$

## B. EFFECT OF SOLVENTS

Better temperature control is possible with the sodium polycondensation in solution than with the bulk reaction. Several patents<sup>291-293</sup> covering the use of certain solvents have been granted.<sup>294</sup>

An attempt was made by Hückel and Bretschneider<sup>295</sup> to run the reaction in an ether ammonia mixture which is able to dissolve both the butadiene and the sodium. In a temperature range of  $-70^\circ$  to  $-60^\circ$  C., a black deposit is formed and the initially blue solution (color of sodium in ammonia) is decolorized. On decomposition, only butene-2 and octadiene were found, the former in slightly greater amount. No higher polymers were observed, probably because sodium octadiene is insoluble in the

<sup>291</sup> Brit. Pat. 333,872, issued March 15, 1929 (I. G. Farbenindustrie) (cyclohexane, dry xylene, gasoline, and liquid polymerization products).

<sup>292</sup> French Pat. 688,593, issued Aug. 26, 1930 (I. G. Farbenindustrie) (ethyl ether cyclohexane mixtures).

<sup>293</sup> Brit. Pat. 334,184, issued May 25, 1929; French Pat. 668,790, issued Jan. 24, 1930 (I. G. Farbenindustrie) (cyclic diethers, *e. g.*, dioxane-1,4).

<sup>294</sup> See also page 139.

<sup>295</sup> W. Hückel and H. Bretschneider, *Ann.*, **540**, 157 (1939).

solution and is precipitated before a further addition of butadiene can be made.

## 5. Sodium Butadiene Polycondensation in Gaseous and Liquid Phases

### A. KINETICS

The physicochemical mechanism of sodium polymerization in liquid and gaseous states was investigated by Abkin and Medvedev.<sup>296</sup> In the first case, sodium wire, and in the second, thin sodium films produced by evaporation, were used as catalysts. Experiments with "technical" butadiene produced by the Lebedev process (79% butadiene, 19.5% butene-2, and some 0.1% acetaldehyde) gave no reproducible results; but with highly purified butadiene and with the same batch for all the comparative measurements, a reproducibility within 3% was obtained, provided the experiments were carried out in the dark and that the same sodium wire sample (or film) was used. Mercury vapor and oxygen acted as poisons and had to be carefully excluded. The butadiene was therefore prepared from its tetrabromide in an atmosphere of pure nitrogen, and the mercury vapors (from the measuring devices) were stopped by a layer of gold-asbestos wool. The main findings of Abkin and Medvedev can be summarized as follows:

(1) In contradistinction to thermopolymerization, sodium polycondensation definitely does not proceed through free radicals. The polyreaction passes through metastable sodium butadiene molecules like the ones assumed by Ziegler.

(2) The reaction in the liquid state is heterogeneous.

(3) At equal pressures, the rates of the reaction in the gas phase and in the liquid phase are identical.

(4) The rate-determining process is the initiation reaction (formation of sodium butadiene molecules), although the rate of diffusion cannot be altogether neglected.

(5) The apparent order of the reaction depends on the temperature.

(6) The heat of activation (corrected for the heat of activation of diffusion) is 12.2 kcal. per mole.

In figure III-13, the degree of conversion is plotted as a function of time. The similarity of this curve, which is typical, with the curve obtained by Khokhlovkin (Fig. III-1, page 102) for thermopolymerization at room temperature, and in general with a chain reaction with branching, is

<sup>296</sup> A. Abkin and S. Medvedev, *Trans. Faraday Soc.*, **23**, 286 (1936); and more completely in *Zhur. Fis. Khim.*, **13**, 705 (1939).

striking; but this similarity is only superficial. A mechanism going through free radicals which generally underlies branched chain reactions must be ruled out because the reaction, once interrupted by cooling of the system or by elimination of the butadiene, restarts (as soon as the original conditions are restored) with the rate it had at the moment of interruption, while

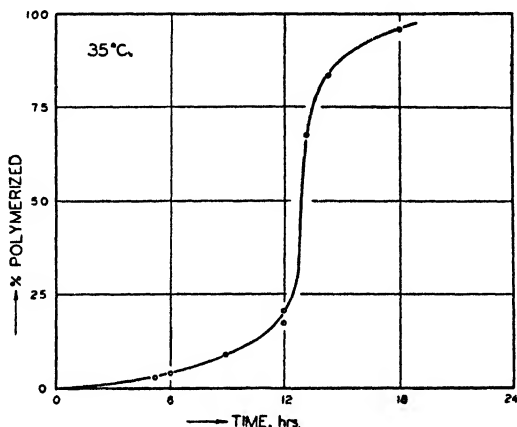


Fig. III-13.—Sodium polymerization at 35° C. as a function of time.<sup>296</sup>

in the case of a free radical mechanism a new induction period necessary for the recreation of the free radicals would follow.

The same observation was also made by Bushmarin and Ivanova.<sup>297</sup> The polymer prepared in this way had a lower plasticity and solubility than normal sodium polybutadiene.<sup>298</sup>

Therefore, the intermediary products must be stable and must be able to withstand cooling, which the free radicals are unable to do. Furthermore, a free radical mechanism is accelerated by oxygen, while, in the case of sodium butadiene polycondensation, the oxygen acts as a poison. The existence of sodium butadiene molecules, considered by Ziegler, would be in agreement with these observations because they are stable at low temperatures and are decomposed by oxygen.

The formal analogy with a chain process is merely due to the fact that the active centers in this case are the products of the reactions themselves. Since the rate of formation of the sodium butadiene molecules is slower than

<sup>297</sup> N. I. Bushmarin and E. I. Ivanova, *Bull. Zavoda. Litera "B,"* No. 15/16, 58 (1934), quoted from an abstract in *Sintet. Kauchuk* (1935).

<sup>298</sup> See also German Pat. 250,690, issued June 9, 1912 (Badische Anilin).



the rates of the subsequent steps, the formation of a few such molecules leads to the reaction of a large number of butadiene groups. As long as free sodium is present, a nonstationary state prevails, as in "degenerated explosions," where the branching is determined by the slow side reactions.

In order to ascertain whether the reaction is homogeneous or heterogeneous, two experiments were performed within the reaction vessel shown in figure III-14:

(1) Shank *a* of the reaction vessel was charged with sodium wire and liquid butadiene, while shank *b* remained empty. Polymerization was

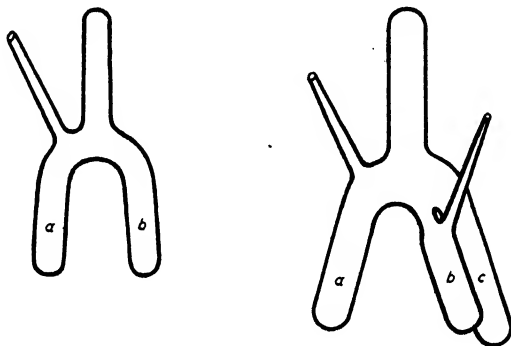


Fig. III-14.—Reaction vessels.<sup>299</sup>

started in shank *a* and allowed to progress for a certain time. Then the unreacted liquid was separated from the sodium and the growing polymer by pouring it over into shank *b* communicating with *a*. After a certain time, the liquid disappeared from *b*, while the polymer in shank *a* continued to grow at the same rate that would have prevailed if all the liquid had remained in *a* in contact with the catalyst. In other words, the polymerization rates from the gas and in the liquid were the same.<sup>299</sup> Even if an homogeneous reaction in the liquid phase did take place, it was completely overshadowed by the heterogeneous reaction.

The existence of an homogeneous reaction can be ruled out completely in the light of the results of the second experiment.

(2) After the segregation of the liquid butadiene from the growing polymer, as in the previous experiment, the two shanks of the reaction vessel

<sup>299</sup> The possibility of polymerization of butadiene in the gas phase under technical conditions was pointed out by G. G. Kobljanskiĭ, N. A. Fermor, and A. V. Zlatogurskiĭ, Russian Pat. 44,673, issued Oct. 31, 1935.

were sealed off separately. In this case no polymerization could be detected in shank *b* even after several months.

Both the monomer and sodium must be present in the same phase if the reaction is to progress. If the rate-determining step is the formation of a sodium butadiene molecule, it is reasonable to assume that the rate is given by an essentially bimolecular mechanism and is proportional to the concentration of the monomer in the polymer and to the concentration of sodium in the same phase.

Experiments show that the concentrations of butadiene in the gas phase,  $C_{\text{gas}}$ , and in a stabilized polymer,  $C$ , are related through:

$$C_{\text{gas}}/C^n = \text{const.} \quad (3.25a)$$

or, since  $C_{\text{gas}}$  is proportional to the pressure,  $p$ , of the monomer:

$$p/C^n = a \quad (3.25b)$$

or else:

$$C = (p/a)^{1/n} \quad (3.25c)$$

where  $a$  and  $n$  are constants. The isotherms of the absorption of the monomer by the polymer have been measured at several temperatures and the values for  $n$  determined graphically. The results are summarized in table III-14.

TABLE III-14

VALUES OF EXPONENT  $n$  FOR DIFFERENT TEMPERATURES

$t, ^\circ\text{C} \dots\dots\dots$	30	40	50	60
$n \dots\dots\dots$	0.54	0.75	0.94	0.94

The distribution of sodium throughout the polymer can be considered as uniform and constant over relatively long periods of time; its concentration,  $C_{\text{Na}}$  can be determined analytically. The variation of the pressure of the monomer as a function of time is then given by:

$$\frac{dp}{dt} = kC_{\text{Na}}C = \frac{kp^{1/n}}{a^{1/n}} \quad (3.26)$$

Introducing the numerical values for  $n$  in equation (3.26), one can see that the apparent order of the reaction varies from second order at  $30^\circ\text{C}$ . to first order at  $50^\circ$ . Abkin and Medvedev have actually shown that,

at 30°, the reaction rate can be represented by a second-order mechanism with a constant,  $k$ , equal to  $1.05 \times 10^{-6}$  ml. per min.

A more exact treatment requires the establishment of a relation between the reaction rate and the rate of diffusion of monomer into the polymer.

Assuming that the process is stationary, and considering a layer of thickness  $dx$  at a distance  $x$  from the surface in contact with the monomer, we may state that, at each moment, the amount of the monomer leaving the layer and diffusing toward the interior is equal to the amount entering the layer minus the amount reacting in the layer. If the reaction constant is designated as  $k$ , the diffusion constant as  $D$ , the concentration of the monomer in the polymer as  $C$ , the concentration of sodium as  $C_{Na}$ , the gradient of the concentration as  $dC/dx$ , and the thickness of the polymer layer through which the monomer has already diffused as  $x$ , one has, per cross section  $q$ :

$$kCC_{Na}q \cdot dx \cdot dt = - \left[ Dq \frac{dC}{dx} dt \right] - \left[ -Dq \left( \frac{dC}{dx} + \frac{d^2C}{dx^2} \right) dx \right] dt \quad (3.27a)$$

or, after simplification:

$$kCC_{Na} = D \frac{d^2C}{dx^2} \quad (3.27b)$$

Assuming that  $C = e^{mx}$ , where  $m$  is a constant, equation (3.27) can be solved.

The rate of disappearance  $W$  of butadiene, is given by:

$$W = C_0q \sqrt{DkC_{Na}} \tanh \left[ \sqrt{\frac{kC_{Na}}{D}} \cdot a \right] \quad (3.28)$$

where  $C_0$  is the concentration of the monomer on the surface, and  $a$  the total thickness of the polymer. Two simple limiting cases are possible:

$$\text{if } \sqrt{\frac{kC_{Na}}{D}} \cdot a < 0.5, \text{ then } \tanh \left[ \sqrt{\frac{kC_{Na}}{D}} \cdot a \right] \simeq \sqrt{\frac{kC_{Na}}{D}} \cdot a$$

and:

$$\text{if } \sqrt{\frac{kC_{Na}}{D}} \cdot a > 2, \text{ then } \tanh \left[ \sqrt{\frac{kC_{Na}}{D}} \cdot a \right] \simeq 1$$

In the first case, equation (3.28) becomes:

$$W = C_0q \sqrt{DkC_{Na}} \cdot \sqrt{\frac{kC_{Na}}{D}} \cdot a = C_0qkC_{Na} \cdot a \quad (3.29a)$$

and  $W$  is independent of  $D$ . In the second case:

$$W = C_0q \sqrt{DkC_{Na}} \quad (3.29b)$$

The experiments show it is the second case which is realized in the butadiene polymerization.

Hence, the necessity arises of determining  $D$  in a separate set of measurements. This can be done on the basis of the theory developed by Ward<sup>800</sup> of the initial rate of absorption. The amount absorbed,  $S$ , is given as a function of time and the equilibrium concentration,  $C_0$ :

$$S = \frac{2}{\sqrt{\pi}} q \sqrt{D} C_0 \sqrt{t} \quad (3.30)$$

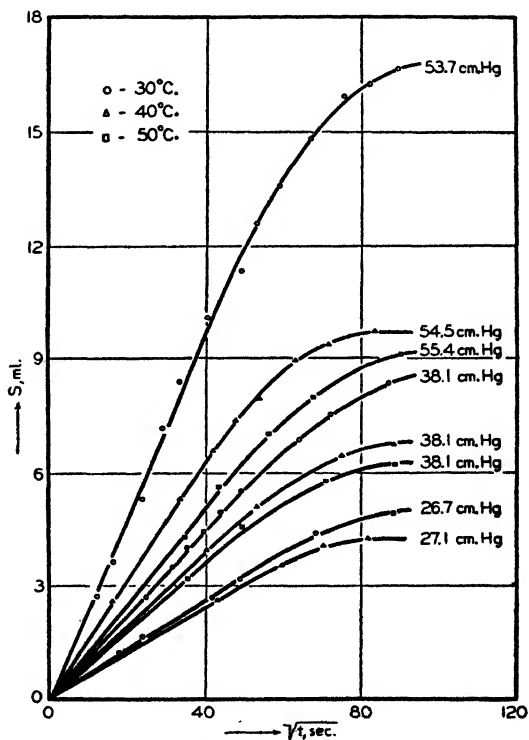


Fig. III-15.—Initial rate of absorption of gaseous butadiene by the polymer.<sup>808</sup>

Figure III-15 gives the results of experiments on the rate of initial absorption of the monomer by the deactivated polymer as a function of time. Table III-15 gives the values for  $D$  calculated from these experiments as a

<sup>800</sup> A. Ward, *Proc. Roy. Soc. London*, A133, 524 (1931).

function of temperature, together with the rates of polymerization reaction and the deduced value of the activation energy. The values for  $D$  determined by this method are of the right order when compared with the values

TABLE III-15

RATE OF DISAPPEARANCE OF BUTADIENE AND ACTIVATION ENERGY

Temp., ° C.	$D \times 10^7$ , sq. cm. per sec.	$W$ , ml. per min.	$C_0$ , ml. buta- diene per ml. polymer	$W^2/C_0^2 D =$ $qC_{Na}^2$	$E$ , kcal. per mole
30	3.92	0.143	10.0	518.7	} 12.2
40	4.98	0.167	8.0	875.7	
50	9.46	0.255	5.80	1885.7	

of Barrer<sup>301</sup> on the diffusion of argon and nitrogen in Buna S, as may be seen from table III-16.

TABLE III-16

DIFFUSION OF GASES IN DIFFERENT POLYMERS

A in Buna S-I <sup>a</sup>		N <sub>2</sub> in Buna S-II <sup>a</sup>		Butadiene in polybutadiene <sup>b</sup>	
$t$ , ° C.	$D \times 10^7$ sq. cm./sec.	$t$ , ° C.	$D \times 10^7$ sq. cm./sec.	$t$ , ° C.	$D \times 10^7$ sq. cm./sec.
30.3	6.8	20.0	2.37	30	3.92
40.7	11.1	35.5	5.06	40	4.98
51.2	17.5	50.0	9.5	50	9.46
$E = 9.0$ kcal./mole		$E = 8.9$ kcal./mole		$E = 9.3$ kcal./mole	

<sup>a</sup> Data of Barrer.<sup>301</sup>

<sup>b</sup> Data of Abkin and Medvedev.<sup>296</sup>

## B. EFFECT OF THE ALKALI SURFACE

It is clear from the preceding discussion that, for a given quantity of butadiene, the amount and quality of the sodium surface determine not only the rate of polymerization but also the properties of the polymer. If the surface is large, the number of chains started will be large, the rate will be high because of the large number of initiations, and the length of each chain will be shorter.

The amount of sodium and its surface are in a certain sense equivalent to the concentration of catalyst (Eqs. 3.4a and 3.4b, page 95); but to make the analogy more precise we must compare the amount of sodium with the concentration of a free

<sup>301</sup>R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628 (1939).

radical catalyst in the emulsion polymerization, and the surface of sodium with a factor (*e. g.*, pH) determining the rate of decomposition of the catalyst.

The polymer formed is expected to be softer, more plastic, and less cross linked, *i. e.*, containing less insoluble gel. This corresponds exactly to the results of Bessmertnaia and Vasil'eva<sup>285</sup> already mentioned (page 149). One must expect, then, that if colloidal sodium is used much larger amounts of harder polymer will be obtained in a shorter time than if the same amount by weight is present in a bulk form.

The use of colloidal sodium dispersion, in the form of suspension in neutral solvents or paste, was considered by Lebedev in his pilot-plant work. Experiments were carried out with sodium dispersions in kerosene. Molten sodium and kerosene were fed simultaneously into a "colloid mill" (Hurrell homogenizer) and the resulting emulsion used as catalyst.<sup>302</sup> Although the results obtained with this emulsion were unsatisfactory, the question was further investigated and several publications and patents deal with more complicated mixtures. For example, Chafanov<sup>303</sup> has polymerized butadiene in the presence of a dispersion consisting of sodium and potassium and of calcium, magnesium, aluminum oxide, and talc, using as solvents paraffins and 1% rubber solution in kerosene and adding oleic acid soap, palmitic acid, and stearic acid. Chafanov obtained the best results and a quiet reaction by using a catalyst corresponding to the following recipe: 2.5 g. magnesium carbonate, 12.5 g. 1% rubber solution in kerosene, 2.5 g. paraffin, 2.5 g. sodium, and 0.25 g. oleic acid. The paste was spread on a cotton gauze (0.6 g., first dried with sulfuric acid) draped in the liquid monomer. When 400 g. pure butadiene was added to this mixture, 99% conversion was obtained after 63 hours. (The tread prepared with this polymer is said to have highly satisfactory physical properties.) Kobl'anskiĭ, Fermor, and Zlatogurskiĭ<sup>304</sup> claim, for gas phase polymerization, a mixture of sodium and a substance which remains incorporated in the synthetic rubber. This patent will be described in more detail in connection with the technology of rodless polymerization.

In another direction, use of colloidal deposits of sodium on solid surfaces points to the work of Zel'manov and Shalnikov,<sup>305</sup> who also offer experimental proof for the accelerating effect of large sodium surfaces. They

<sup>302</sup> N. A. Fermor, *Polimerizatsiia divinila v proizvodstve sintet. kauchuka*, Onti, Leningrad, 1934, pp. 64 *et seq.*

<sup>303</sup> N. A. Chafanov, *Sintet. Kauchuk*, 4, No. 1, 28 (1935).

<sup>304</sup> G. G. Kobl'anskiĭ, N. A. Fermor, and A. V. Zlatogurskiĭ, Russian Pat. 44,673, issued Oct. 31, 1935.

<sup>305</sup> I. L. Zel'manov and A. I. Shalnikov, *Zhur. Fiz. Khim.*, 4, 353 (1933).

prepared the catalyst by simultaneous condensation of sodium and butadiene on a cooled surface. With 0.001–0.3% sodium (by weight) in 2–36 hours at 10–15° C., a solid polymer was obtained, while with bulk sodium about 0.5% sodium was generally required and the reaction was much more time-consuming. If this method could be used industrially, the resulting economy in sodium would easily become appreciable. The patent granted Vekshinskiĭ<sup>306</sup> points in the same direction, but suggests a somewhat different way of preparing colloidal sodium, namely, by bringing butadiene into contact with a flow of inert gas saturated with the vapors of the metal.

Scientifically more interesting are the results of Dankov and Krasnobaeva,<sup>307</sup> who have investigated the variation of the rate of polymerization on thin sodium layers condensed on a glass wall at different temperatures. At room temperature, polymerization was completed in two hours with layers condensed at –180° C., in 25 hours with layers condensed at –68°, and in 48 hours when the condensation of the layer took place at 0°. This rate difference is either due to a difference of the grain size or related to the observation made by Beeck and coworkers<sup>308</sup> that metal deposits obtained by evaporation are crystallographically oriented if the condensation takes place at sufficiently low temperatures, and are not oriented if condensation takes place at higher temperatures.

Obviously the reaction at the surface is facilitated if only the electrons have to move during the reaction process, the sodium atoms already being at the distance at which they are separated in the final compound. It is probable that this spacing of sodium atoms occurs only in certain faces and that the reaction is slowed down if, instead of oriented faces, a mixture of faces, some of which do not contain the required spacing, is exposed to the butadiene.

It is possible that the same explanation applies to the observation of Bushmarin and Zlatogurskiĭ<sup>309</sup> that the induction period is reduced from 34–37 hours to 2–8 hours when sodium–potassium alloy is used instead of pure sodium, since it is well known that the atomic distances in mixed crystals are intermediary between those of the pure components. However, in this case, other explanations can also be offered.

The use of such sodium–potassium mixed catalysts would have the advantage of faster operation, but this use is precluded by the increased danger of fire.

<sup>306</sup> S. A. Vekshinskiĭ, Russian Pat. 32,723, issued Oct. 31, 1933.

<sup>307</sup> P. D. Dankov and P. Krasnobaeva, *Zhur. Fiz. Khim.*, **4**, 346 (1933).

<sup>308</sup> O. Beeck, A. E. Smith, and A. Wheeler, *Proc. Roy. Soc. London*, **A177**, 62 (1940).

<sup>309</sup> N. I. Bushmarin and A. V. Zlatogurskiĭ, *Bull. Zavoda Litera "B,"* 20/21, 29 (1934), quoted from an abstract in *Sintet. Kauchuk*, (1935).

The use of alkali amalgams has been patented by Luther and Heuck,<sup>310</sup> who suggest a two-stage polymerization: butadiene is treated with a sodium amalgam at 0–6° C. for two days; the temperature is raised to 30–40°; more sodium is added; and the mass is allowed to stand for several more days.

This claim, however, is not quite clear, since Abkin and Medvedev have observed a poisoning effect of mercury on the sodium polycondensation.

The replacement of sodium by sodium hydride has also been proposed.<sup>311</sup> In general, however, the road taken by German industry was less original. No serious attempt was made to prepare a colloidal dispersion, although preparation of highly dispersed sodium by grinding it along with a diluent (*e. g.*, sodium chloride) in an atmosphere of nitrogen<sup>312</sup> was considered. Other patents concern the means of obtaining a more or less uniform distribution of sodium.<sup>313, 314</sup>

As has already been stated, the influence of the sodium surface is not confined to the rate of the reaction—the properties of the ultimate polymer also strongly depend upon the ratio of the sodium surface to the butadiene. Thus, Koblânskiĭ, Ozerov, Rokitiânskiĭ, and Lekakh<sup>315</sup> observed that, when the sodium surface was increased, maintaining the butadiene concentration constant in a butadiene–butene-2 mixture, the viscosity of the polymer solution of a given concentration was lowered—in other words, the average chain length of the polymer decreased. On the other hand, if the ratio of sodium surface to butadiene becomes too small, an insoluble gel is formed, the amount increasing when the sodium surface is decreased.<sup>316</sup> Since it proved impossible to use sodium wire for large-scale polymerization, and since a colloidal dispersion did not yield satisfactory results in the beginning, Russian industry used, for several years, the “rod” method of polymerization (page 187), in which a thin layer of sodium is deposited

<sup>310</sup> M. Luther and C. Heuck, German Pat. 533,886, issued April 25, 1929 (I. G. Farbenindustrie).

<sup>311</sup> French Pat. 677,416, issued June 25, 1930 (I. G. Farbenindustrie).

<sup>312</sup> Brit. Pat. 342,107, issued Jan. 9, 1929 (I. G. Farbenindustrie).

<sup>313</sup> French Pat. 696,149, issued May 17, 1930 (I. G. Farbenindustrie) (use of catalyst in form of particles of uniform size).

<sup>314</sup> Brit. Pat. 333,872, issued March 15, 1929; French Pat. 688,592, issued Jan. 21, 1930 (stirring mass or rotating the polymerizer containing butadiene and dispersed sodium).

<sup>315</sup> G. G. Koblânskiĭ, S. Ozerov, I. V. Rokitiânskiĭ, and M. Ī. Lekakh, *unpublished work*, quoted from I. V. Rokitiânskiĭ and M. Ī. Lekakh, *Sintet. Kauchuk*, 5, No. 9, 6 (1936).

<sup>316</sup> N. I. Bessmertnaĭa and A. N. Vasil'eva, *Sintet. Kauchuk*, 5, No. 6, 50 (1936).



on iron rods. It was therefore important to investigate the effect of the presence of other metals and metallic oxides, such as ferric oxide, which may be present in reaction vessels or on the supports of sodium "rods."<sup>317</sup> The experiments were carried out with 0.5% of the two following catalysts:

A = sodium + 10% precipitated ferric oxide

B = sodium + 10% magnesium oxide

Rectified butadiene (78%) was used. The reaction was inhibited in neither case, but was faster with catalyst A. Starting at the bottom of the reaction vessel this last compound formed a tree in the polymer. The same problem was investigated on an industrial scale by Zavalkov,<sup>318</sup> who could not detect a beneficial effect of iron oxide, but confirmed the observation that the presence of rust had no deleterious effect either on the rate of polymerization or on the properties of the polymer obtained. We can perhaps sum up these results by stating that a decided technological advantage can be derived from increased dispersion (increased surface) of the sodium. However, precautions are necessary in order to keep the rate of the initiation reaction within reasonable limits because of the danger of fire and the decrease in the chain length of the polymer. This decrease of the chain length occurs long before the surface is large enough to lead to hazards. The rate can be controlled by addition of modification agents and by careful determination of the amount of sodium necessary. It is apparently along such lines that catalysts for rodless polymerization have been developed in the U.S.S.R.

### 6. Effect of Impurities and Additions

Impurities or added substances can affect the reaction in four different ways.

(1) They can act simply as diluents.

(2) They can react with sodium, either covering the surface with an adsorption layer or using all or a part of it to form more or less stable compounds.

(3) They can react with the first or one of the subsequent sodium butadiene compounds and so destroy it.

(4) They can occasionally react with the growing polymer, either forming polymers or breaking up the reaction chain.

As far as possible, we shall consider separately the impurities or additions showing the four different effects.

<sup>317</sup> V. E. Kravets, *Sintet. Kauchuk*, 4, No. 1, 36 (1935).

<sup>318</sup> V. M. Zavalkov, *Sintet. Kauchuk*, 3, No. 2, 15 (1934).

## A. DILUENTS

The only effect that may be expected with impurities of this group is a certain decrease of the reaction rate when compared with the rate obtained at the same total pressure with pure butadiene, since Abkin and Medvedev<sup>296</sup> have shown that the reaction rate is determined by the

TABLE III-17A  
COMPOUNDS ACTING AS DILUENTS IN THE SODIUM POLYMERIZATION PROCESS

Addition agent	Concentration range, %	Chemical characteristics	Ref. No.
Nitrogen, hydrogen	....	"Inert" gases	312, 319, 320
Isobutane	....	} Saturated hydrocarbons	{ 321 322 323
Pentane	....		
Cyclohexane	....		
Butene	....	Olefin	324
Benzene	} 4-5%	Aromatic <sup>a</sup> compounds	325
Toluene			
Ethylbenzene			
Xylene			
Trimethylbenzene			
CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub> Biphenyl			
Ethyl ether	....	} Ethers	321
Lower aliphatic ethers	....		319

<sup>a</sup> In all the experiments of Ākubchik,<sup>325</sup> except if otherwise specified, the following recipe was used: "rectified" butadiene (tech.) containing 20-23% butene-2, 0.2-0.3% acetaldehyde, 3% residue boiling above 0° C.; polymerized with 1% sodium wire, 0.5 mm. in diameter, in sealed ampoules, 20-25 g.

concentration of the monomeric butadiene in the polymer, which in turn depends on the pressure (concentration) of butadiene in the gaseous phase or solution, respectively. The compounds belonging to this class are listed in table III-17A.

<sup>319</sup> E. Tschunkur and W. Bock, German Pat. 575,371, issued April 27, 1933 (I. G. Farbenindustrie).

<sup>320</sup> Brit. Pat. 363,810, issued Dec. 11, 1930 (I. G. Farbenindustrie).

<sup>321</sup> V. N. L'vov, *Zhur. Obshcheĭ Khim.*, 7, 928 (1937).

<sup>322</sup> I. V. Rokitiĭanskii and M. Ī. Lekakh, *Sintet. Kauchuk*, 5, No. 9, 6 (1936).

<sup>323</sup> M. Müller-Conradi and W. Daniel, German Pat. 677,433, issued June 26, 1939 (I. G. Farbenindustrie); Brit. Pat. 490,366, issued Aug. 10, 1938.

<sup>324</sup> French Pat. 658,652, issued Aug. 7, 1928 (I. G. Farbenindustrie).

<sup>325</sup> A. Ākubchik, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 2 (1935).

## B. SUBSTANCES REACTING WITH METALLIC SODIUM

To this group belong compounds which can react with sodium faster than can butadiene. These are aldehydes and ketones (or, more generally,

TABLE III-17B  
SUBSTANCES DELAYING THE START OF POLYMERIZATION AND INCREASING  
POLYMERIZATION TIME

Addition agent	Concentration range, %	Procedure: characteristics of butadiene	Effect on polymerization	Ref. No.
Carbon monoxide*	0.01-0.06	.....	Process delayed up to one month	332
Acetylene*	0.01-1.6	.....	Process delayed up to one month, even at lowest concentrations	332, 333
Dimethyl acetylene	0.4-1.6**	.....	} Process somewhat delayed	325 <sup>b</sup>
<i>tert</i> -Butylacetylene	0.4-1.6	.....		
Phenyl acetylene	0.4-1.6	.....		
Phenanthrene	0.4-1.6**	.....		
Acetaldehyde*	0.2-0.3	.....	Process delayed	326
Butyraldehyde*	.....	*	Process considerably delayed	334
			POLYMERIZATION TIME INCREASED:	
Isobutyraldehyde	0.1-0.5	Purified butadiene <sup>a</sup>	1.5-3 times	} 334
Benzaldehyde	0.1-0.5	"	1-2.5 times	
Salicylaldehyde	0.12-0.58	100 g. butadiene <sup>a</sup>	2-6 times	
Furfural	0.12-0.58	100 g. butadiene <sup>a</sup>	1.5-2.5 times	
Acetone*	0.08-0.40**	"	.....	} 334
Methyl ethyl ketone*	0.08-0.33**	"	2-5 times	
Methyl propyl ketone	0.08**	"	.....	} 334
Acetonyl acetone	0.20	"	4 times	
Dimethyl acetyl acetone	0.40	"	Induction period over 2 months	
Acetophenone	0.50	"	10 times	
Menthane	0.09-0.36**	"	2 times	
Ethanol*	0.24-0.40	"	1.5-4 times	
<i>n</i> -Butanol*	0.5	"	2 times	
Amyl alcohol*	0.4	"	2 times	
<i>sec</i> -Octanol	0.1	"	2 times	} 334
Allyl alcohol*	0.44	"	3 times	
Pyrrole	.....	} (See table III-17A (measurements by the same author)	Strong delay	325
Pyridine	.....		.....	.....

\* 0.5 g. sodium wire, 1 mm. diameter in all these cases except for pyrrole, where 0.2% sodium was used. <sup>b</sup> See footnote, a, table III-17A.

(See page 171 for numbered footnotes)

compounds containing C=O groups), alcohols, acetylenes, and possibly certain aromatics. They delay the beginning of the reaction until completely reacted with sodium and diffused back into the liquid or gaseous monomer. In extreme cases, the reaction can be completely inhibited. When present in very small amounts, they can have a beneficial effect on the process by lowering the rate and so avoiding overheating of the system. The use of small amounts of such inhibitors is claimed in a series of patents.<sup>326-331</sup> Table III-17B summarizes the available data on compounds belonging to this second group. The compounds formed by side reaction in the Lebedev process (impurities) are marked by an asterisk. In certain cases (marked by a double asterisk), liquid polymers are formed at the highest concentration of the inhibitor used. These compounds really belong in both table III-17B and table III-17C.

### C. SUBSTANCES REACTING WITH SODIUM BUTADIENE

To this group belong compounds which do not react with metallic sodium but do react with the sodium hydrocarbons, with the exception of water. These are, chiefly, primary amines and halogen and cyano derivatives.

As this reaction can take place at any stage of polymerization, initiation excepted, one may not expect to observe a delay for the beginning of

<sup>326</sup> S. V. Lebedev, Russian Pat. 36,007, issued April 30, 1934 (acetaldehyde).

<sup>327</sup> French Pat. 695,441, issued May 12, 1930 (I. G. Farbenindustrie) (acetals, particularly unsaturated acetals).

<sup>328</sup> Brit. Pat. 340,008, issued Aug. 19, 1929 (I. G. Farbenindustrie) (cyclic acetals, aldehydes, ketones, acids; it is claimed also that a more or less tough or soft polymer can be obtained by varying the concentration of these inhibitors).

<sup>329</sup> G. Ebert, F. A. Fries, and P. Garbsch, German Pat. 575,439, issued April 28, 1933 (I. G. Farbenindustrie); French Pat. 695,299, issued May 8, 1930 (unsaturated ethers soluble in butadiene, *e. g.*, vinyl ethyl ether).

<sup>330</sup> German Pat. 520,104, issued Jan. 29, 1929 (I. G. Farbenindustrie); G. Ebert and P. Garbsch, U. S. Pat. 1,953,468, issued April 3, 1934 (I. G. Farbenindustrie) (unsaturated compounds in which at least two valences of the same carbon atom are saturated by oxygen, *e. g.*, ethylene acetal).

<sup>331</sup> G. Ebert and P. Garbsch, U. S. Pat. 1,953,468, issued April 3, 1934 (I. G. Farbenindustrie) (same description as given in preceding footnote).

<sup>332</sup> A. V. Lazarevskaja, *Sintet. Kauchuk*, 5, No. 2, 17 (1936).

<sup>333</sup> G. G. Kobljanskij, I. A. Livshits, L. Kh. Khristiansen, and I. V. Rokitsanskij, *Sintet. Kauchuk*, 3, No. 4, 3 (1934).

<sup>334</sup> N. A. Chafanov and Z. N. Nemtsova, *Kolloid. Zhur.*, 2, 487 (1936). These authors have also fractionated the impurities present in the butadiene prepared by the Lebedev process and have shown that the polymerization delays observed were due mainly to traces of butyraldehyde and acetone.

polymerization, but may expect a decreased rate of polymerization and more plastic and, eventually, liquid polymer. Small amounts of these compounds can be added in order to avoid overheating, to facilitate a quiet and uniform polymerization, and to obtain softer polymers.<sup>335-338</sup> In table III-17C are listed the compounds belonging to this group. But it must be noted that the compounds given in table III-17B as leading to liquid or soft polymers in reality should be listed here also, their action being of a twofold nature: a direct attack on metallic sodium and an exchange reaction with sodium polybutadiene molecules.

TABLE III-17C  
SUBSTANCES DECREASING THE CHAIN LENGTH OF THE POLYMER

Addition agent	Concentration range, %	Sodium, %	Effect on polymerization	Ref. No.
<i>unsym.</i> -Dimethyl allene	0.4-1.6	0.54 <sup>a</sup>	No delay; liquid polymer	325
Aniline	}5	0.2 <sup>a</sup>	Polymerization proceeds slowly and in some cases is stopped	325
Xylidine				
Piperidine	.....	0.2 <sup>a</sup>	No delay; liquid, viscous polymer	325
Water <sup>b</sup>	.....	...	See table III-18	339

<sup>a</sup> For further details on the polymerization procedure and butadiene used, see table III-17A, measurements by the same author.

<sup>b</sup> Secondary and tertiary amines have no effect.<sup>325</sup>

Because the effect of moisture is of great technical importance, further details are given below:<sup>339</sup>

The butadiene used in these experiments was the dehydrated technical "rectificate" composed of 83-86% butadiene, 0.01-0.02% acetaldehyde, and the remainder mainly butene-2. Before drying, 0.03-0.04% moisture was present and, in certain cases, as much as 0.1%. The polymerization was carried out at 20-25° C. in beverage bottles containing iron rods 6 mm. in diameter covered with an 0.5-mm. layer of sodium.

<sup>335</sup> G. Ebert, F. A. Fries, and P. Garbsch, U. S. Pat. 1,921,867, issued Aug. 8, 1933 (I. G. Farbenindustrie) (chloride derivatives of hydrocarbons, *e. g.*, ethylene chloride).

<sup>336</sup> French Pat. 702,784, issued Sept. 30, 1930 (I. G. Farbenindustrie) (halogenated hydrocarbons, *e. g.*, dibromocyclohexane-1,2,-dichloro(or bromo)naphthalene-1,2).

<sup>337</sup> G. Ebert, F. A. Fries, and P. Garbsch, German Pat. 592,096, issued Feb. 1, 1934 (I. G. Farbenindustrie) (cyanides, *e. g.*, hydrogen cyanide, ethylene cyanide, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CN; thiophene, acetylenic hydrocarbon, *e. g.*, MeC≡CH, which act in a manifold way).

<sup>338</sup> Brit. Pat. 326,869, issued Dec. 20, 1928; French Pat. 678,305, issued July 11, 1929 (ammonia and primary, secondary, and tertiary amines are also claimed in this patent, but experiments of Ākubchik—see table III-17C—have shown that the latter have no effect whatever).

<sup>339</sup> A. P. Krūchkov and V. P. Shatalov, *Sintet. Kauchuk*, 5, No. 2, 15 (1936).

As may be seen from table III-18, the induction period is lowered (probably because of the heat developed by the reaction between sodium and water), the reaction rate is decreased, and the plasticity is increased as with all the substances of group C. But, at the same time, a tendency for the polymer to "blow," *i. e.*, to increase its size (up to 200%), after removal from the polymerizer is noted. This tendency is measured conventionally by the volume increase 10 minutes after the polymer is taken out of the bottle.

#### D. MODIFIERS AND COMPOUNDS FORMING COPOLYMERS

The compounds of this group are, to a certain extent, built into the polymer, either with or without termination of the chain. Since the reaction takes place comparatively infrequently, the rate of the polyreaction is not greatly affected. The only effects are to shorten the chain length somewhat, to decrease branching, to increase the percentage of the soluble fraction, and to yield softer polymers. To a certain extent these compounds act as diluents (group A), stabilizing the reaction and helping to avoid overheating. Their action is somewhat analogous to the action of modifiers in emulsion polymerization.<sup>340</sup> All the compounds of this group are olefinic hydrocarbons. In certain cases, for instance, in the presence of isobutylene,<sup>341</sup> polymers of low molecular weight can be isolated which contain one isobutylene molecule for  $n$  butadiene molecules, the lowest of these being 2-methylheptadiene-2,5.

TABLE III-17D  
COMPOUNDS FORMING COPOLYMERS OR ACTING AS "MODIFIERS"

Addition agent	Concentration range, %	Effect on polymerization	Ref. No.
Isobutylene	...	.....	341, 342, 345
Butene-2*	20-90	.....	340-343
Trimethylethylene (Pentene-2)	} 0.02	Slight acceleration { Slight acceleration; a viscous, red polymer is obtained	} 325 <sup>a</sup>
Styrene			
Stilbene			
<i>as</i> -Diphenylethylene			

\* See footnote *a*, table III-17A.

<sup>340</sup> S. V. Lebedev, Russian Pat. 36,007, issued April 30, 1934. See also equation (3.3d), page 93.

<sup>341</sup> V. N. L'voy, *Zhur. Obshchei Khim.*, 7, 928 (1937).

TABLE III-18

EFFECT OF MOISTURE ON THE POLYMERIZATION

Moisture in butadiene, %	Induction period, hrs.	Reaction time, hrs.	Volume increase, %	Karrer plasticity
0.00	58	43	2	0.06
0.04	43	55	5	0.08
0.10	42	66	29	0.28
0.50	41	108	80	0.48
0.80	41	136	204	0.72
1.00	41	196	"	Liquid polymer

<sup>a</sup> In this case, the polymer is ejected from the polymerization bottle by the gas pressure.

This ability of sodium polybutadiene molecules to add isobutylene or its polymer, yielding a product that can be vulcanized, is utilized in a patent granted Müller-Conradi and Daniel.<sup>342</sup> The results are summarized in table III-17D.

Since butene-2 is the main impurity present in the butadiene made from alcohol by the Lebedev process, and since its separation from butadiene is by no means easy (see page 78), its effect on the polymerization was carefully investigated by Rokitiĭanskiĭ and Lekakh.<sup>343</sup> Their experiments were carried out at 60° C. and the concentration of butadiene in the mixture was varied between 10 and 36%. In agreement with the results previously observed by the same authors together with Koblĭanskiĭ and Ozerov,<sup>344</sup> if the ratio of butadiene to the surface of sodium was kept constant, the relative viscosity of the polymer solutions decreased when the concentration of butadiene was lowered. Low polymers of the form  $(C_4H_6)_nH_2$ , with  $n = 2, 3$ , or 4, could be isolated. (No attempt was made to isolate polymers of higher degree of polymerization than  $n = 4$ .) The fraction of the low polymers varied between 16 and 42% of the total amount of polymers. The lower the percentage of butadiene in the mixture, the more low polymers were present. The total yield of polymers was about 116 to 135% of the butadiene initially present, the highest value occurring at the lowest

<sup>342</sup> M. Müller-Conradi and W. Daniel, German Pat. 677,433, issued June 26, 1939; Brit. Pat. 490,366, issued Aug. 10, 1938; French Pat. 830,633, issued Aug. 4, 1938 (I. G. Farbenindustrie).

<sup>343</sup> I. V. Rokitiĭanskiĭ and M. Ū. Lekakh, *Sintet. Kauchuk*, 5, No. 9, 6 (1936).

<sup>344</sup> G. G. Koblĭanskiĭ, S. Ozerov, I. V. Rokitiĭanskiĭ, and M. Ū. Lekakh, *unpublished work*, quoted from I. V. Rokitiĭanskiĭ and M. Ū. Lekakh, *Sintet. Kauchuk*, 5, No. 9, 6 (1936).

<sup>345</sup> I. I. Ostromislensky, *Zhur. Russ. Fiz.-Khim. Obschestvo* 48, 71 (1916).





has reacted. An analogous observation was also made by Kobljanskij and Ivanova,<sup>347</sup> who found that the initial stage of conversion of technical butadiene consists almost exclusively in the formation of a low molecular

TABLE III-19

YIELD OF POLYMER AND PERCENTAGE OF SUBSTANCES OF LOW MOLECULAR WEIGHT FORMED IN BUTADIENE-BUTENE-2 MIXTURES<sup>a</sup>

Per cent by wt. of the total mixture, butadiene + butene-2, of:		Yield of polymer (calcd. on butadiene), %	Per cent low mol. wt. polymers distilled at 100° C. and 3 mm. pressure
Butadiene	Sodium		
10.14	1.31	133.5	42.4
20.77	1.35	126.3	32.7
30.05	1.68	120.6	26.8

<sup>a</sup> 48 hours at 60° C.

weight polymer, soluble in the monomer; in the next stage, the process proceeds with the formation of a predominantly high molecular weight polymer, insoluble in the monomer, which in later stages builds in the low-

TABLE III-20

EFFECT OF ACETALDEHYDE ON POLYMERIZATION TIME AND THE PLASTICITY OF THE POLYMER

Composition <sup>a</sup>			Time of polymerization, days	Karrer plasticity
Butadiene, %	Acetaldehyde, %	"Bottoms," %		
20.4	Traces	2.4	43	0.70
44.0	0.057	0.74	11	0.24-34
51.0	0.025	1.17	9	0.67-0.60
53.4	0.033	0.65	8	0.46
66.9	0.041	0.21	7	0.53-0.54
71.1	0.041	0.21	5	0.40-0.50
77.1	0.026	0.53	4	0.35-0.43
84.5	0.035	0.21	3	0.24-0.38

<sup>a</sup> The balance, *i. e.*, 100% - (% butadiene + % acetaldehyde + % "bottoms") is represented by butene-2.

molecular polymer from the solution. The polymer of high molecular weight consists of a benzene-soluble and a benzene-insoluble fraction.

As mentioned previously, the presence of impurities also influences the plasticity of the polymer. Table III-20 and figure III-16, given by Zaval-

<sup>347</sup> G. G. Kobljanskij and E. I. Ivanova, *Sintet. Kauchuk*, 4, No. 3, 11 (1935). Sodium-covered iron rods were used as catalyst.

kov,<sup>348</sup> are based on laboratory data (bottle experiments) and illustrate the points more quantitatively. Technical butadiene was used.

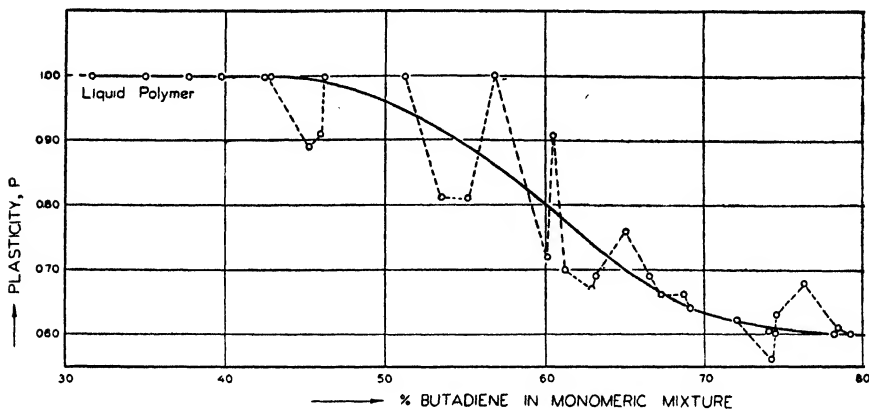


Fig. III-16.—Karrer plasticity of polymer as a function of butadiene concentration in the monomeric mixture.<sup>348</sup>

#### E. EFFECT OF IMPURITIES AND OF BUTADIENE CONCENTRATION ON POLYMER QUALITY

Zavalkov's paper also sheds some light on the effect of the composition of the monomeric mixture on such technologically important properties

TABLE III-21  
EFFECT OF FRACTIONATION BOTTOMS

"Bottoms," %.....	0.2-0.4	1	3	10	15	} Liquid polymers
Average plasticity (Karrer).....	0.34	0.43	0.51	0.81		
Average polymerization time, days	5.7	6	8	10.8		

TABLE III-22  
EFFECT OF ACETALDEHYDE

Acetaldehyde, %... ..	0.005	0.012	0.03	0.037	0.043
Average plasticity (Karrer) .....	0.46	0.63	0.68	0.68	0.69
Average polymerization time, days	9	9	10	10	10
Yield, % . . . . .	86.4	81.0	85	83	84.4

as plasticity of the polymer, total time of polymerization, and ultimate yield of polymer. As outlined elsewhere, the trend rather than the numerical values are of significance.

<sup>348</sup> V. M. Zavalkov, *Sintet. Kauchuk*, 3, No. 2, 15 (1934).

Figure III-16 shows the effect of the butadiene concentration in the monomeric mixture on the plasticity of the rod polymer (see page 187) obtained on an industrial scale. This graph only summarizes the effects of all the impurities present. The effects of the individual impurities are given in the tables III-21 and III-22. Table III-21 illustrates the influence of rectification bottoms by laboratory results with fractionated butadiene containing 70–82% butadiene and 0.02–0.045% acetaldehyde. In table III-22, presenting the effect of acetaldehyde, the butadiene in the gas varied between 74 and 78% and the percentage of "bottoms" from 0.2 to 0.8. Water has a very deleterious effect. In the presence of about 2–4% water, the plasticity increased to 0.78.

### 7. Carbon Dioxide Polymer

The effect of carbon dioxide must be treated separately because its presence leads to a different kind of polymer. The observations of various authors seem, at first glance, to be contradictory. While Badische Anilin und Soda Fabrik<sup>349</sup> and I. G. Farbenindustrie<sup>350</sup> recommend the addition of carbon dioxide as leading to insoluble polymers of higher technical value, and add that the sodium-carbon dioxide polymer can be used to promote further polymerization,<sup>351</sup> Lazarevskaja<sup>352</sup> found that, although 0.04% of carbon dioxide had no noticeable delaying effect, addition of 0.09–0.1% delays the polymerization by as much as 800 hours. A similar observation was made by Kobljanskij *et al.*<sup>353</sup>

If considered more carefully, however, this discrepancy disappears. Holt<sup>354</sup> was the first to observe that, in the presence of carbon dioxide, the formation of sodium polymer is delayed and that, instead, a new polymer, sodium-carbon dioxide-polybutadiene, makes its appearance. This polymer is not soluble in ordinary rubber solvents and shows very little, if any, swelling. It cannot be vulcanized, as pointed out by Kobljanskij and Rokitjanskij,<sup>355</sup> to whom we owe most of the information on this subject. This polymer is rather frail, can be easily powdered, oxidizes rapidly in air, becoming yellow and brittle, does not give a smooth film on milling and, if added to ordinary sodium polybutadiene, has an adverse effect on its mechanical properties. On the other hand, it can induce a polymerization even after the sodium has been washed out (also mentioned by Holt<sup>354</sup> and in a German patent<sup>351</sup>).

<sup>349</sup> German Pat. 287,787, issued April 9, 1912.

<sup>350</sup> Brit. Pat. 363,810, issued Dec. 11, 1930.

<sup>351</sup> German Pat. 294,816, issued July 11, 1912 (Badische Anilin).

<sup>352</sup> A. V. Lazarevskaja, *Sintet. Kauchuk*, 5, No. 2, 17 (1936).

<sup>353</sup> G. G. Kobljanskij, I. A. Livshits, L. Kh. Khristiansen, and I. V. Rokitjanskij, *Sintet. Kauchuk*, 3, No. 4, 3 (1934).

<sup>354</sup> A. Holt, *Z. angew. Chem.*, 27, 153 (1914).

<sup>355</sup> G. G. Kobljanskij and I. V. Rokitjanskij, *Sintet. Kauchuk*, 5, No. 6, 2 (1936).

The analogy with the "autopolymer" ("sponge polymer," page 101) is so striking that the identity of the two types of polymer, or at least a similar parentage, may be assumed. As far as the sodium-polybutadiene polycondensation is concerned, the addition of small amounts of carbon dioxide is sufficient to decrease the rate of polymerization (or to delay the polymerization) through the reaction:

$$(C_4H_6)_nNa_2 \xrightarrow{+2CO_2} (C_4H_6)_n(COONa)_2$$

This effect will continue until all the carbon dioxide present has reacted far enough so as not to interfere with the normal course of the reaction. During the inhibition period, reaction products of the type  $(C_4H_6)_n(COONa)_2$  and the sodium-CO<sub>2</sub> polymer are deposited on the sodium surface which disintegrates and gives a sodium powder. When the normal reaction starts, it will proceed very fast and energetically because of the large sodium surface of the sodium powder. In this case, all three types of polymer are formed simultaneously. If, however, the amount of carbon dioxide present is sufficient to inhibit the normal process completely, the only polymer formed is the sodium-CO<sub>2</sub> polymer. The rate of the reaction leading to this polymer is increased by temperature increase and by the large sodium surface.

## E. OTHER METHODS OF POLYMERIZATION INITIATION

Several other methods of polymerization initiation—photochemical,  $\alpha$ -particle, electrical discharge—have been investigated without giving any results which can be useful technically. From a theoretical standpoint, the most important series of investigations concerns photopolymerization.

### 1. Photopolymerization

If carried out quantitatively at different temperatures, photopolymerization could yield the activation energy for the propagation reaction. Indeed, if the reaction is started with light and carried on in the darkness, the rate of the dark reaction depends chiefly on the rate of the growth of chains, the process of active center formation (which is generally slower) being eliminated. Determination of the rate at different temperatures should yield the activation energy of the growth process. Unfortunately, this experiment is hard to perform, since pure butadiene has an absorption (and hence activation) threshold at 2300 Å.,<sup>356</sup> at shorter wave lengths than the mercury resonance line, 2537 Å., and intensive sources of light of these higher frequencies are not easily available. It is because they did not use light of sufficiently short wave length, that Nikiforov and Runtso<sup>357</sup> failed to observe any photopolymerization when using

<sup>356</sup> G. Scheibe and H. Grieneisen, *Z. physik. Chem.*, **B25**, 24, 52 (1934).

<sup>357</sup> V. K. Nikiforov and P. M. Runtso, *Acta physicochim. U. S. S. R.*, **3**, 335 (1935).

a mercury arc and quartz vessels. This was also confirmed by Bolland and Melville.<sup>358</sup>

Khokhlovkin<sup>359</sup> has observed an effect of visible light on the polymerization of liquid butadiene (page 102), but probably this effect is entirely due to traces of impurities.

Kublifskii<sup>360</sup> used an intensive cadmium arc and a quartz vessel. He observed the formation after 20 hours of a certain amount of polymer on the walls facing the arc. This polymer was fairly easily soluble in the liquid monomer. No polymer was formed in a glass vessel containing the same amount of butadiene and irradiated simultaneously in a position symmetrical to that of the quartz vessel so that thermopolymerization was excluded. The experiment was continued with frequent shaking, and it was observed that polymerization proceeded and that the polymer formed became less and less soluble. The shaking was necessary because the absorption threshold of the polymer lies at longer wave lengths (over 2540 Å.) than that of the monomer, and all the active radiation was absorbed in the polymer film if the film was not immediately redissolved or peeled off mechanically. Analysis after 15 days for a total irradiation of 100 hours at 40–50° C. gives the results in table III-23.

TABLE III-23

## PHOTOPOLYMERIZATION OF BUTADIENE

Component	Quartz vessel	Glass vessel
Butadiene, %.....	92.95	97.60
Dimer, %.....	1.70	1.30
Polymer, %.....	5.35	1.10

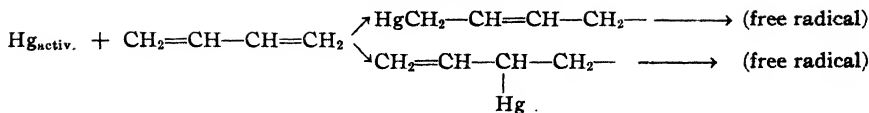
Some polymerization also takes place on irradiation with a mercury arc, due to the presence in its spectrum of a few weak lines of shorter wave length than 2537 Å. In order to be able to use 2537 Å. as the exciting line, Gee<sup>361</sup> added to butadiene some mercury vapor as a sensitizer; although, formally, the polymerization he observed was induced photochemically, in reality his investigations refer to gas polymerization catalyzed by activated mercury atoms. The initiation reaction in this case can best be represented by:

<sup>358</sup> J. L. Bolland and H. W. Melville, *Rubber Tech. Conference*, London, 1938, p. 239

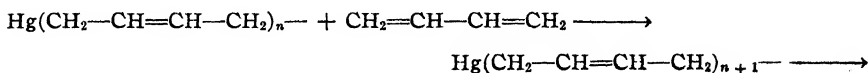
<sup>359</sup> M. A. Khokhlovkin, *Sintet. Kauchuk*, 5, No. 4, 12 (1936).

<sup>360</sup> A. M. Kublifskii, *Sintet. Kauchuk*, 5, No. 7–8, 30 (1936).

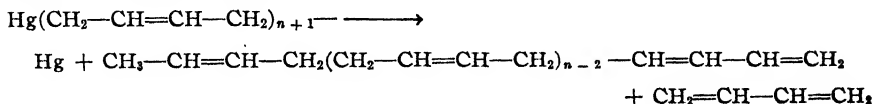
<sup>361</sup> G. Gee, *Trans. Faraday Soc.*, 34, 712 (1938).



the propagation reaction by:



and the termination reaction by an isomerization:



Gee's experiments were carried out at 15° and 100° C. In addition to the polymer some hydrogen, butane, and dimer were formed; but, as may

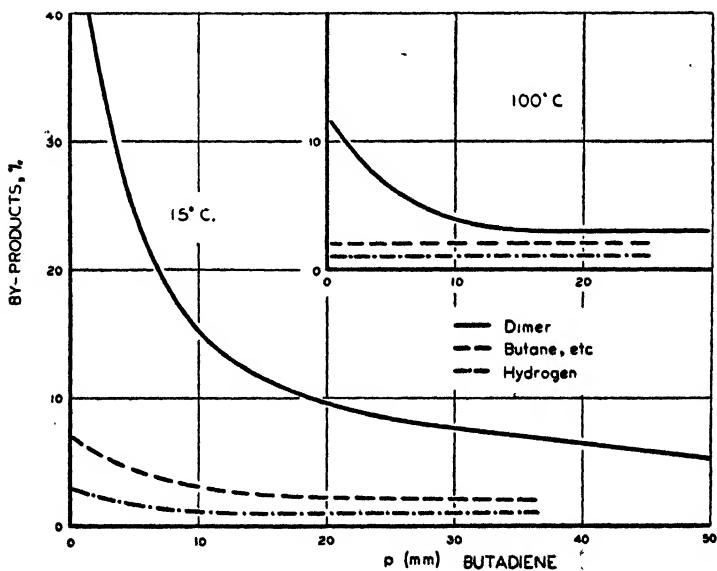


Fig. III-17.—By-products of the photochemical polymerization of butadiene.<sup>358</sup>

be seen from figure III-17, in contradistinction to what was observed in pure thermopolymerization (page 103), less dimer was formed at 100°

than at 15°. With increasing pressure, the amount of by-products decreased.

As shown in figure III-18, the reaction starts slowly and then increases, reaching a constant value which allows calculation of the quantum yield (the number of butadiene molecules polymerized by a quantum of light), and finally decreases again because of the absorption of the exciting line 2537 Å. by the polymer film on the walls. The quantum yield increases strongly with pressure in the low pressure range and then levels off, reaching the maximum values of 0.6 at 100° C. and 35 mm. Hg; 0.2 at 15° and

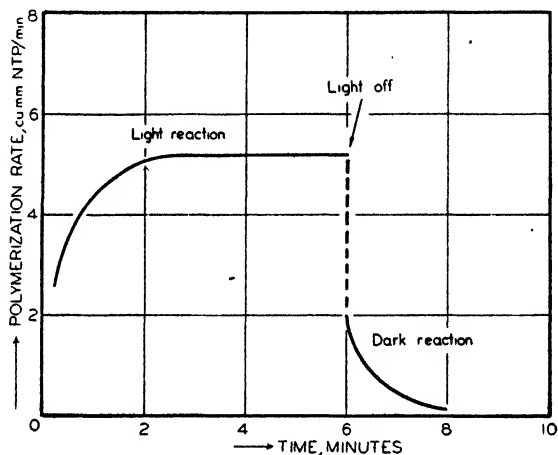


Fig. III-18.—Rate of photochemical polymerization of butadiene.<sup>861</sup>

10 mm. Hg. The main effect of the temperature on the polymerization seems to be an increase of the mercury vapor pressure.

A change of the surface-volume ratio does not influence the quantum yield; hence the reaction must be an homogeneous gas phase process. Nor does addition of hydrogen have any effect on the polymerization rate. When the light is switched off, the reaction rate first drops sharply and then decreases exponentially (see Fig. III-18)—in other words, the photochemical reaction is followed by a dark reaction. This dark reaction is characterized by a half-life,  $\tau$ , independent of the density and by  $R_0$ , the initial dark reaction rate. If the maximum rate of the photochemical reaction,  $R_i$ , is reached, ratio  $R_0/R_i$  is independent of the intensity but decreases with increasing pressure and increases with the surface. The dark reaction is, hence, at least partly a surface reaction. Probably it

corresponds to the growth of free radical polymers that reach the wall without being deactivated. Since the reaction mechanism involved is different from the reaction mechanisms involved in the technical processes of polymerization, it is not useful to reproduce here in detail the kinetic analysis of the experimental data. It may be mentioned, however, that the energy of activation for the propagation reaction,  $E_p$ , is in this case  $E_p \geq 5.5$  kcal., of the same order as given by Schulz and Husemann<sup>362</sup> for the growth reaction in styrene polymerization (see page 94).

## 2. Polymerization in the Glow Discharge

The polymerization of butadiene in a glow discharge was investigated by Rubanovskii,<sup>363</sup> who observed, at low pressures ( $10^{-3}$  to  $10^{-1}$  mm. Hg), an increase of pressure in the discharge tube corresponding to a cracking of butadiene. At pressures above 0.1 mm. Hg, the pressure decreases because of the polymerization, an effect also observed when butadiene-hydrogen mixtures were used instead of pure butadiene, the polymerization being started in this case probably by the collision impact of hydrogen atoms. (If, however, hydrogen ions or hydrogen molecule ions are formed in the glow discharge, other mechanisms can be proposed.) In all cases in which polymerization was observed, an induction period of 3-7 minutes was found, suggesting that the polymerization is a chain reaction corresponding to the process:



where  $C_4H_6^*$  is an activated end of a polymer, perhaps a radical. The fact that hydrogen atoms are as effective as electrons indicates that the polymerization is not due to an "ionic catalysis" but to an activation of butadiene in a collision. The breaking of chains would occur mainly on the walls, since the reaction is about 20% faster in a tube of 10-cm. diameter than in a tube of 1.5-cm. diameter. This conclusion is confirmed by the fact that the polymerization is accelerated by addition to butadiene of argon and oxygen, which hamper the diffusion toward the wall. For oxygen, the effect already mentioned of favoring polymerization over dimerization probably must be taken into account.

The process is not affected either by the characteristics of the glow discharge or by the material of the electrodes.

<sup>362</sup> G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B34**, 187 (1936).

<sup>363</sup> L. Rubanovskii, *Zhur. Fiz. Khim.*, **4**, 431 (1933).



### 3. Polymerization under $\alpha$ -Particle Impact

This question was investigated by Heisig,<sup>364</sup> who found that butadiene polymerizes under  $\alpha$ -particle impact to form a light-colored mobile liquid (probably the dimer) which in turn undergoes further polymerization and becomes waxlike and a light yellowish brown. The evolution of hydrogen and methane is rather small. There seems to be an indication of a break in the constancy of the velocity constant when the pressure of hydrocarbon drops to about 60–70% of the original value. The yield (the number of hydrocarbon molecules reacting per ion pair formed) is moderate, about 9.0 when compared with 18 for acetylene and 4.8 for ethylene.

## F. TECHNOLOGY OF SODIUM POLYMERIZATION

In the over-all picture of the world's production of synthetic rubber from butadiene, emulsion polymerization occupies first place, particularly for the manufacture of copolymers with styrene and acrylonitrile. For valid reasons, specific information on the industrial technology of the polymerization process in emulsion is still restricted. In contradistinction to American and German practices, the main and most widely used method of polymerization in the U.S.S.R. is the mass polycondensation with sodium. It is to the technological aspects of the latter process that the following pages are devoted.

### 1. General Remarks

Summarizing and extending the laboratory experience outlined in preceding sections, one can formulate a few basic requirements necessary for translating the sodium process into a successful industrial operation.

(1) Certain compounds present as by-products in butadiene (*e. g.*, produced by the Lebedev process) are strong inhibitors. Either they must be completely eliminated or at least their concentration must be reduced below certain limits. This is accomplished by "rectification" of the crude butadiene, described in detail in Chapter I. In particular, the concentration of carbonyl compounds must be kept below 0.03%, that of "rectification bottoms" (see page 177) below 1%, that of carbon monoxide or of moisture below 0.04%, and that of certain acetylenic and ethylenic hydrocarbons at an absolute minimum.

(2) The presence of other compounds, such as butene-2, arising as companion substances with the butadiene, is harmless and, in moderate

<sup>364</sup> G. B. Heisig, *J. Am. Chem. Soc.*, 55, 2304 (1933).

concentrations, can actually be beneficial. Butene-2 acts as a "regulator" or "modifier" of the reaction, leading to softer or more completely soluble polymers.

(3) If, however, the concentration of butene-2 is too high (in other words, if the butadiene content in the monomeric mixture falls below certain limits), the beneficial effect of the butene disappears. The polymers resulting are too soft, and sometimes liquid. Practical experience (see page 177) has shown that the best rubber is obtained from monomeric mixtures containing from 75–85% butadiene.

(4) The quantity of volatile substances, *i. e.*, compounds with a boiling point below that of butadiene, must be kept down to reduce the vapor pressure prevailing above the monomeric mixture which has been liquefied by compression.

(5) The temperature must be controlled very closely. At low temperatures the reaction "freezes" and the yield remains low, while at high temperatures only low molecular weight polymers are produced, on the one hand, and, on the other, the reaction may get out of control, leading to a carbonization of the polymer. Polymerization vessels must be provided with a means for rapidly supplying or withdrawing heat.

(6) The ratio of butadiene to the surface area of sodium must be selected judiciously, because too small a sodium surface leads to hard, insoluble polymers, while too large a surface leads to polymers of low molecular weight and sometimes to very violent reactions, in which case "modifiers" must be added. It will be shown later that rubber technological advantages are derived from keeping to a minimum the amount of sodium used per unit of butadiene.

(7) The sodium surface must be clean (not oxidized) and must be uniformly distributed throughout the monomer if inhibition periods are to be reduced.

(8) Hazards due to the contact of sodium with moisture or due to the formation of explosive hydrocarbon-air mixtures must be prevented. The polymerization vessels should be fully hermetic, and the air contained therein must be evacuated or displaced with inert gas prior to their being filled with the monomeric hydrocarbon material.

(9) Since it was shown that the construction material of the polymerizer proper has no effect on the reaction, the reactors can be conveniently made of welded iron plate.

(10) Provisions must be made for easy removal of polymer when formed, and for the filling and stripping operations.

## 2. Monomer Phase and Catalyst Distribution

In a preceding discussion, it was shown that sodium polycondensation is equally feasible with the monomer in the liquid state and with the monomer in the gaseous state.

As already outlined, the surface area of the sodium catalyst is of paramount importance. It is advantageous to distribute as little sodium as possible as uniformly as possible through a given quantity of butadiene. For this purpose three main methods have been employed:

(1) By extruding sodium through a fine mesh sieve into kerosene (or directly into the polymerizer), whereby a fine sodium wire is obtained ("wire polymer").

(2) By coating rods of 5-6-mm. diameter with molten sodium, protecting the coating with a layer of wax and suspending such rods at uniform spacings into the monomeric mixture ("rod polymer").

(3) By making a suspension or dispersion of sodium in an inert solvent like kerosene, preferably with the aid of a protective colloid ("dispersion polymer)."

Table III-24 compares the area deployed by 1 kg. sodium (1030 ml.) in the various forms described.

TABLE III-24  
SURFACE AREA OF ONE KILOGRAM OF SODIUM

Dimensions and quantities	Wire, 0.1-mm. diam.	Wire, 0.3-mm. diam.	Dispersion of 0.1-mm. particle size	Dispersion of 1-mm. particle size	Sodium-coated rods, <sup>a</sup> 5-mm. diam.
Area, sq. meters	41.2	13.75	62	6.2	2.06
Length, miles	82	9.2	..	...	.....
Quantity Na required for 1600 l. liquid monomeric mixture, kg.	..	2.0-2.5	..	...	3.6-4.4

<sup>a</sup> Thickness of coating, approximately 0.5 mm.

An equally important factor is uniform distribution of the polymerization catalyst, whereby the difference in density of sodium and monomeric mixture (0.97 vs. 0.62) mitigates the desired effect.<sup>865</sup> Sodium wire, in spite

<sup>865</sup> Alloys of lithium ( $d = 0.534$ ) and sodium ( $d = 0.97$ ) or lithium and potassium ( $d = 0.83-0.86$ ) could, in principle, be made to have the same density as the monomeric liquid.

of its great length per unit weight, cannot be relied upon to distribute itself uniformly. Convection currents, etc., may tend to create local accumulations of the fine wire, causing overpolymerized regions. Since the presence of wire precludes the use of agitation devices, the wire method, although extensively used in the laboratory, has not found its way into factory practice. For a number of years the method employing coated rods immersed in the liquefied monomer dominated the S.K. industry; but, beginning with 1935, it has been gradually displaced by the "rodless" method. This is the result of the combined use of the gas-phase polymerization and of a finely dispersed sodium catalyst, mostly spread thinly over metal shelves or trays. The "rodless" gas-phase method has been shown to produce superior polymers.

### 3. "Rod" Polymerization

The technology of "rod" polymerization was described in considerable detail by Zavalkov,<sup>366</sup> who summarizes the experience of early operations in S.K. plant No. 1. The following discussion is based largely on his article.

#### A. THE POLYMERIZER

In order to understand the choice of equipment for the original "rod" polymerization method, it is necessary to recall that the chemical apparatus industry in the U.S.S.R. was very much in its infancy in the early thirties, and was then not able to undertake the task of constructing rapidly several thousand hermetic vessels provided with agitators. As a compromise, a "static" unit was selected as the "basic polymerizer."

A typical basic polymerizer of this type is shown schematically in figure III-19. It is a vertical autoclave of 1350-mm. internal diameter and about equal total depth (excluding the lids). The autoclave is provided with a jacket (later divided into a lower and an upper part) through which steam, water, or brine can be circulated alternatively. The lid is bolted (using pneumatic wrenches) over a gasket made of cardboard impregnated with a mixture of glue, glycerin, and chromalum. Butadiene is filled, and un-polymerized gas is withdrawn, through a rubber hose attached to a flanged tube in the lid. Thermometers are provided in wells extending from the lid. To facilitate the unloading of the polymer, a removable, vertical, cylindrical liner made of 3-4-mm. iron plate is inserted in the autoclave. The liner must be liquid-tight to prevent unreacted butadiene or viscous polymer from leaking out and thus making removal of the liner very

<sup>366</sup> V. M. Zavalkov, *Sintet. Kauchuk*, 3, No. 2, 15 (1934).

difficult, besides impairing the heat transfer. The liner is coated inside with a mixture of talcum and glycerin (the composition of the lubricant is of no special significance for the polymerization process).

A ring is placed over the rim of the liner which supports, in radial distribution, a number of "combs" carrying the sodium-coated rods suspended vertically. The number of rods and their size, which together

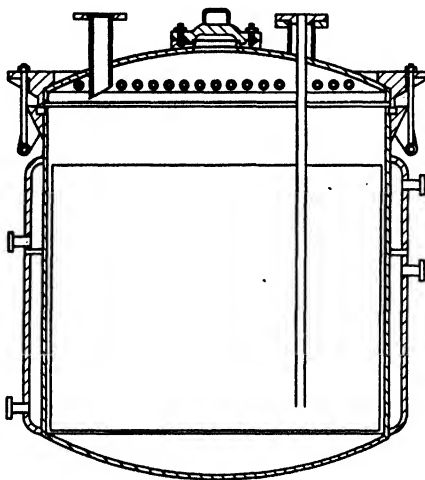


Fig. III-19.—Reaction autoclave for "rod" polymerization.<sup>366</sup>

determine the sodium surface available, as well as the homogeneous distribution of the surface, are fairly critical, since the quality of the polymer depends on the sodium surface. The optimum was found to be, for a charge of 1600 liters butadiene, 648 rods of 5–6-mm. diameter, covered with sodium over a length of 95–110 cm., the weight of the sodium being about 0.5% that of butadiene, *i. e.*, the thickness of the sodium layer was about 0.5–0.8 mm., and the sodium surface available was about 45 sq. cm. per liter butadiene.

#### B. PRÉPARATION OF "RODS"

Although it was found, on both a laboratory and a factory scale, that iron oxide has no adverse effect either on the rate of polymerization or on the mechanical properties of the final product, it is advisable to have the rods "rust-free" because rust included in the polymer makes it unsuitable for

certain applications, as, for instance, for wire insulation. In addition, if the rods are clean, the sodium layer is more uniform and its adhesion is better.

Generally, the rods are freed from residual polymer by burning, pickling, washing, and drying in an autoclave. They are transferred while still warm to the sodium room, where they are dipped first in molten sodium and then immediately into molten paraffin wax. The sodium bath is maintained at about 120° C. and the paraffin bath at 70°. Sodium deposition occurs by cooling of the metal on the rods. The thickness of the layer will decrease with longer immersion time. Rods prepared in this manner are promptly placed in the polymerizer, and the autoclave is closed.

The total weight of paraffin is 0.7% of the weight of butadiene, and the thickness of the wax deposit is about 0.5 mm. Thicker paraffin layers may delay the beginning of the polymerization by as much as 24 hours.

### C. PREPARATION OF THE AUTOCLAVE AND TESTING

The bolted autoclave is first tested for tightness with a carefully dried inert gas under a pressure of 8 atm. No pressure drop must be detected in the course of two hours. When the tightness of the autoclave is found satisfactory, the pressure is slowly released, and a vacuum created in the polymerizer. The empty autoclave is then connected to the butadiene supply system. The butadiene flows under its own pressure from the storage tank through a number of measuring tanks and into the autoclave. A charge of 1600-1700 liters was used with autoclaves of the dimensions given above at the time of Zavalkov's publication. The batch was later successfully increased to 2000 liters.

Much of the data presented in Zavalkov's work is completely outdated, mainly because the monomeric feed stock was not pure enough. One consequence was that the polymerization process often required 10 to 12 days to reach completion; another, that only in a few cases did a polymer of a plasticity of <0.60 result. In later years, the polymerization time was successfully reduced to less than 4 or 5 days and a plasticity of 0.40 became a common standard for the "rod" polymer. Nevertheless, some of the trends revealed by Zavalkov's figures are quite significant, and have in principle retained their validity despite the considerable change in actual numerical value.

### D. TEMPERATURE CONTROL

The maintenance of correct temperature conditions is essential. It can be safely stated that, everything else being equal, the quality of the polymer

produced will depend mainly on the skill of the operator controlling the temperature. This "skill" becomes almost an "art" if we consider that changes in the rate of reaction may occur very suddenly and that the quantities of heat evolved may be very large. Such changes must be "anticipated" to some extent if the reaction is to be kept under control.

**Preheating.**—The polymerization cycle begins with a preheating step designed to shorten the "induction period." The temperature of the charge is raised as rapidly as possible to about 30° C. The preheating period should not exceed 6 hours and, to avoid local overheating, is accomplished by intermittent admission of steam to the jacket. It is important not to overheat the monomer during the induction period because a rubber of high plasticity is likely to result, as may be seen from the following experimental series:

Temperature of preheating, ° C.....	20	25	30	40	50
Plasticity of polymer.....	0.62	0.64	0.65	0.80	0.82

CONDITIONS: *Factory runs.* Charge, 1600 l.; butadiene, 71.4 ± 1.7%; butene-2, 28%; acetaldehyde, 0.03%; rectification residues, 0.6%; and sodium, 3.36 ± 0.32 kg.

A temperature of 30° C. is not an absolute value. For a more pure monomeric stock, it can be raised to about 40° with a corresponding shortening of the induction period and without sacrificing the quality of the resulting polymer. The polymerizer is maintained at the induction temperature until the start of the reaction, which manifests itself by the fact that temperature and pressure begin to rise spontaneously. At this point, heating of the jacket is discontinued.

**First Reaction Period.**—In the following first 6–8 hours, the reaction progresses slowly, the temperature may increase by 0.5–0.8° C. an hour, and the pressure increment may be 0.5–0.7 atm. per hour. Thereafter, the temperature and the pressure increase are more rapid, and it becomes necessary to circulate water or brine through the jacket. The pressure and temperature in the polymerizer are only partially correlated, since their "normal" relation can be upset by variations in the amounts of highly volatile impurities in the monomer.

On the basis of over 100 factory runs performed in order to determine the best temperature and pressure conditions for the main polymerization period, Zavalkov came to the conclusion that a temperature of 65° C. and a pressure of 8 atm. are optimum if both yield and quality of the polymer are taken into account. If we were to postpone cooling until the optimum temperature is reached, the reaction would become uncontrollable. Cooling

must begin long before the temperature of 65° is attained. It is this initial reaction period which offers particular difficulties, because of its unpredictable nature.

Zavalkov distinguishes three types of reaction (during the initial period), and attributes them to small variations in the activity and distribution of sodium on the rods and also to small fluctuations in the amounts of impurities in the butadiene.

The first type, the so-called "top-heavy" reaction, is characterized by a very rapid pressure increase requiring premature cooling as soon as the temperature reaches 33–35° C. and the pressure 5 atm. As a result of such early cooling (and if no provisions are made to cool independently the upper regions of the polymerizer), the temperature in the lower part of the autoclave may drop to 15–20°, and the reaction may temporarily become dormant at the bottom of the vessel, while the temperature in the upper part continues to increase. Only after an extended time period does the temperature equalize itself so that the reaction region is broadened to include also the lower parts of the polymerizer. From there on the process proceeds normally. Zavalkov believes that this type of reaction occurs when the sodium covering on the rods extends above the liquid level of the butadiene. It can also be due to forced preheating.

In the second type of reaction, which we may call "normal," the temperature and pressure increase almost as rapidly as in the first type. However, there is no significant lag between the temperature at the bottom and at the top of the vessel. What difference exists never exceeds 4–5° C., and completely disappears toward the later stages of the process. In the case of the "normal" reaction, the beginning of the cooling can be postponed until the temperature of the polymerizer has reached 37–40° and the pressure 6 atm. This type of reaction seems to be favored when the rods are sheathed with sodium to less than their normal height.

While the above two types of reaction are most frequently encountered, a third type, the "slow" reaction, occasionally occurs. With the first two types, a cooling of the system with cold water or brine solutions or even by releasing some of the gas pressure must be practiced long before the final reaction temperature is reached; no such premature cooling is necessary with the "slow" reactions. The occurrence of this third type seems to be conditioned by the excess of certain impurities in the butadiene; it is characterized by a slow temperature increase, the temperature scarcely reaching 55–58° C. and the pressure 8 atm. The slightest cooling during the first reaction period brings about an immediate and significant drop of pressure and temperature. In this case, cooling must be started



only 1–2° below the upper temperature limit and 0.5 atm. below the upper pressure limit, whichever is reached first.

In all instances, the cooling must be carried out gradually and must be carefully watched in order to avoid a "freezing" of the reaction, on the one hand, or a "burning" of the polymer as the result of the reaction's becoming uncontrollable.

**Second Reaction Period.**—By varying temperature between the limits of 45 and 70° C., and pressure between 7 and 9 atm., it was found, as already outlined, that the optimum temperature for the main reaction period is 65° and the optimum pressure, approximately 8 atm. A lowering of the temperature decreases the yields; a temperature rise above 65° may lead to an uncontrollable reaction. Again, it should be remembered that Zavalkov's data have only relative value. In particular, with the introduction of the low-temperature "epuration" in the process of butadiene rectification (see page 66), the pressure corresponding to 65° is lowered below 8 atm.

**Duration of the Reaction. Afterpolymerization.**—A normal reaction used to take 90–120 hours, if the end of the reaction is conventionally considered to be the moment when the heat generated has mostly spent itself and the temperature drops to 40° C. A gas analysis at that moment should show no more than 10% butadiene. Nevertheless, it was found useful not to strip the butadiene immediately, but to continue the process for several days by keeping the polymerizer at 40° and to release the gas only when its butadiene content remained constant over a period of two days. The afterpolymerization normally extended over a period of 4–5 days, so that the entire polymerization process required 10–12 days. This time was greatly reduced in subsequent years.

The variation of the temperature between 30–50° C. in the afterreaction period affected neither the yield nor the properties of the polymer; the temperature of 40° was chosen because it is convenient for the next operation, the stripping.

### E. STRIPPING

It will be recalled that technical butadiene contains a number of substances which do not take part in the polymerization to any noticeable extent. These gases and the remaining butadiene must be removed from the polymer.

The temperature of the polymerizer is raised to about 45° C. and the pressure to 6 atm., whichever is reached first; the valves are slowly opened;

and the gases are discharged through a pump and a brine-cooled condenser into a storage tank. Here the major part of the butene-2 is liquefied. If the time necessary to reach this stage exceeds 24 hours, the stripping is considered to be finished as soon as a pressure of 0.8 atm. at 25° C. is reached.

The uncondensed gas is returned to the absorption bay (see page 61). The final stage of the stripping, *i. e.*, the evacuation, takes place under intensive heating. The temperature is never allowed to fall below 12°, in which case the evacuation is interrupted and the temperature allowed to rise. The evacuation is considered to be finished if under a vacuum of 600 mm. (pressure of 160 mm.) the temperature remains constant and equal to 15° for three hours.

This operation completed, a stream of dry nitrogen is re-admitted until atmospheric pressure is reached; the autoclave is opened; and the liner is lifted out with the aid of a pneumatic hoist and placed upside down on a truck.

#### F. VACUUM KNEADING

The "combs of rods" are withdrawn from the blocks of polymer and the liner removed. The blocks are dissected into a number of segments of convenient size and are charged into a vacuum kneader (Werner and Pfeleiderer type). Here, under continuous evacuation, the still occluded quantities of butene-2 and other volatile substances are removed. Simultaneously, some 0.5% of an antioxidant is added. Often the vacuum kneading operation is utilized to blend blocks of varying plasticity.

#### G. REFINING

The final operation is mill refining, a process step familiar from the reclaiming industry. It is in this operation that overpolymerized strands (tendons) are removed or dispersed.

In the earlier days, some of the polybutadiene S.K. was subjected to mill washing to reduce polymer alkalinity resulting from unused sodium. This practice was later discontinued. For specific applications, as that of wire insulation requiring a very low alkalinity, selected lots of S.K. are assigned which, according to analysis *a priori*, show a low content of sodium hydroxide. While no official specifications for S.K. rod polymer seem to have been published, some tentative specifications<sup>367</sup> suggest that one general-purpose grade of the rod polymer should have less than 0.5%

<sup>367</sup> I. A. Livshits, *Zhur. Resinovoĭ Prom.*, **10**, 199 (1934). F. Merzlikin, *ibid.*, **12**, 826 (1935). F. Vergiles, *ibid.*, **11**, 423 (1934).

volatile substances, less than 0.3–0.8% sodium hydroxide (alkalinity), approximately 0.3% ash, and a Karrer plasticity of 0.4–0.6.

#### H. CONCLUSIONS

We may conclude that, although "rod" polymerization gives, with an inexpensive installation and in good yield, a polymer of more or less satisfactory quality, this method presents certain disadvantages:

(1) The polymerization time is long, even though it no longer takes 8–10 days, as indicated by Zavalkov (1934). The equipment is immobilized for a long time and a large number of polymerizers is required.

(2) It is difficult to obtain rubber of uniform quality.

(3) The plasticity of the polymer produced varies not only from one batch to another, but also locally within the same batch.<sup>368</sup>

(4) The heating and cooling present a complicated problem.

(5) The amount of sodium necessary for a successful polymerization is high, affecting the cost and the technological and electrical properties of the vulcanizates.

(6) Cleaning the rods is a time-consuming operation.

All these disadvantages, when considered jointly, point toward another solution—"rodless" polymerization.

#### 4. "Rodless" Polymerization

Polymerization with dispersed sodium was suggested by Fermor in the early thirties.<sup>369</sup> In its original form, the method was not found suitable for industrial exploitation. It involved the use of colloid mills to which were fed simultaneously molten sodium and hot kerosene, each at a temperature of about 125–130° C. (to forestall congealing in the mill). The dispersion, consisting of two parts kerosene to one part sodium, was charged into the polymerizer filled with the monomer under pressure from a specially designed funnel. The charge was made in discrete quantities of 0.1–0.4 kg. sodium at time intervals of several hours.

As already noted, early polymerizations took between 7 and 12 days, and the polymerization equipment had no agitation devices. In the induction period preceding thickening of the monomer, ample opportunity existed for the sodium particles to settle out, and the method was not a success. It remained confined to cases of "doctoring up" a wire polymer whose

<sup>368</sup> P. I. Fedorov, L. E. Smolenskaja, and I. A. Levitin, *Sintet. Kauchuk*, **3**, No. 2, 32 (1934).

<sup>369</sup> N. A. Fermor, see Ref. 302.

reaction had "frozen" and which could be reactivated by a "shot" of sodium dispersion. Besides, it is gleaned from scanty disclosures in the literature that the dispersion could not be made of too fine a particle size or the sodium area deployed became too large and adversely affected the product. The colloidal stability of the suspension was therefore not adequate.

An advance in the art was introduced by Chaňanov,<sup>370</sup> who incorporated certain soaps and other substances as protective colloids and modifying agents, and, following an earlier suggestion of Dumanksiĭ, spread the catalyst so prepared on dried cotton wool or gauze. The textile carrier (0.1% on the polymer) suspended or draped in the polymerizer was not removed at the end of the process; it seemed, though, to mill apart satisfactorily in the polymer. Other, and more effective, dispersed sodium catalysts have been disclosed in patents and have been discussed on pages 165 *et seq.* They are generally attributed to Koblĭanskiĭ and his coworkers. In particular, Chaňanov reported that the gel resulting from dispersing 5 parts sodium in 10 parts kerosene (or 1% rubber solution in kerosene) with 1 part palmitic or stearic acid (or alternatively 0.1 part oleic acid) is sufficiently stable to be stored without deterioration in a humid atmosphere. He reported that polymerization with his catalyst was completed in 3 days with a yield of 96-98% on the butadiene content in the monomer. The temperature of a factory run was 30-35° C. and the pressure, 3-3.5 atm.

In 1935, Koblĭanskiĭ, Fermor, and Zlatogurskiĭ<sup>371</sup> were granted a patent claiming a method of polymerizing butadiene in the gas phase. This became the basis of the "rodless" method. According to very scanty disclosures, a dispersed sodium catalyst is spread thinly on removable trays or shelves placed in a polymerization chamber of several tons' capacity. The gas is continuously circulated. It is withdrawn from the chamber, passes a cooling unit, and is recycled. The polymerization time is counted in hours rather than days, and the polymer stripped in sheet form from the trays is of a plasticity as low as 0.16 to 0.25. The main advantage of the method seems to lie in the more efficient temperature control made possible by the circulation of the gaseous monomeric mixture.

### 5. Sodium Polymerization Technique in Germany

No detailed description of German numbered Buna process, equivalent to that in the paper of Zavalkov<sup>366</sup> has ever been published. Some informa-

<sup>370</sup> N. A. Chaňanov, *Sintet. Kauchuk*, 4, No. 1, 28 (1935).

<sup>371</sup> G. G. Koblĭanskiĭ, N. A. Fermor, and A. V. Zlatogurskiĭ, Russian Pat. 44,673, issued Oct. 31, 1935.

tion can, however, be obtained in an indirect way from the patent literature. For a long while, a batch process was used which was probably fairly analogous to the Russian "rod" polymerization, with the difference that rotating autoclaves were employed. All the difficulties encountered by the Russians in the rod polymerization seem to have been experienced also in the German factories<sup>372</sup>: local overheating, long polymerization time, nonuniformity of the product, etc.

Fairly early attempts were made to replace the batch process by a continuous one which would allow at the same time a better dissipation of the heat developed. For example, in an early patent a sodium polymerization in ether solution flowing over sodium metal was suggested.<sup>373</sup>

Real progress—combining the continuous polymerization and the use of colloidal dispersions—seems to have been achieved by Ebert *et al.*<sup>372</sup> at about the same time as the Russians introduced their rodless method. The polymerization (or copolymerization with, for example, styrene) is carried out in tubes, in which the material to be polymerized is moved forward during the course of polymerization while being thoroughly mixed with the catalyst, and from which the polymerization product is withdrawn at the end. The forward movement is effected by a conveyor worm, strong enough to move the already polymerized material and to force it out of the tube. The catalyst is made from a colloiddally dispersed sodium (or sodium-potassium alloy) mixed into viscous substances like soft paraffin or even polybutadiene of low degree of polymerization. The catalyst is prepared by heating fused alkali metal and the fused binding agent together and by stirring it very vigorously and cooling. The grain diameter is generally below 0.01 mm.; only 0.2% sodium based on the butadiene weight is required. The main advantages of the process are the ease of temperature control, which in turn permits employing higher temperatures (65–70° C.), and the use of the colloidal alkalies already mentioned. The reaction time is greatly reduced—the reaction is finished in hours instead of days. The catalyst and the butadiene can be fed in continuously; the remaining free alkali can be destroyed while the material is in the tube. The patent even suggests introducing together with the catalyst the necessary amount of antioxidant, softeners, fillers, etc.

The total production for a given space is said to be 100 times larger than in the batch process, at least on a pilot-plant scale. The amount of non-

<sup>372</sup> G. Ebert, P. Heidebroek, and P. Orth, U. S. Pat. 2,209,746, issued July 30, 1940 (Jasco, Inc.).

<sup>373</sup> G. Ebert, F. A. Fries, and W. Reppe, Can. Pat. 300,674, issued Nov. 11, 1930 (I. G. Farbenindustrie).

polymerized butadiene is about 4% or less. The vulcanizate in standard tread recipe has better properties than the block or batch polymer. Thus, the tensile strength is 140 kg. per sq. cm. instead of 80 kg. per sq. cm. Much the same, the modulus increases from 26 to 33 kg. per sq. cm.

No indications are available as to how extensive a large-scale use was made of this patent.<sup>372</sup>



## IV. PHYSICOCHEMICAL PROPERTIES OF THE POLYMER

### A. GENERAL PROPERTIES

#### 1. Description

The appearance of the polybutadiene depends largely on the polymerization conditions. The emulsion polymer is a crumbly substance, easy to tear, colored by the antioxidant added. The fresh sodium polymer is steel-gray. Its mechanical strength depends on the exact conditions of polymerization and varies from a viscous or plastic substance to a rather tough rubbery product. On standing in air without antioxidant it grows harder and becomes brittle, at times recalling macrocrystalline agglomerates. Characteristic for polybutadiene, as for all the butadiene-base synthetic rubbers is the absence of "tack." In contradistinction to *Hevea* rubber, the tensile properties of the raw polymer are rather low and the material becomes industrially useful only when compounded with active or reinforcing fillers.

#### 2. Physical Properties

Very few data are available on the physical properties of raw polybutadiene.

##### A. DENSITY

The density of sodium-polymerized butadiene lies between 0.86 and 0.90.<sup>374</sup> That of the emulsion-polymerized polymer<sup>375</sup> is  $d_{20}^{20} = 0.894$  for the sol fraction and  $d_{20}^{20} = 0.906$  for the gel fraction.

##### B. DIELECTRIC PROPERTIES

No data have been published on the dielectric properties of the raw polymer, but from that ( $\epsilon = 2.9$  at 50 cycles per sec.)<sup>376</sup> given for pure gum

<sup>374</sup> A. Ermolaev and I. Telkov, *Zhur. Rezinovoi Prom.*, 8, 147 (1932).

<sup>375</sup> B. A. Dogadkin, D. M. Sandomirskii, and P. Sharkevich, *Kolloid. Zhur.*, 6, 199 (1940).

<sup>376</sup> K. H. Meyer, *High Polymeric Substances*. Interscience, New York, 1942, p. 187.



stocks it may be inferred that it is fairly low, *i. e.*, between 2.0 and 2.8, as is to be expected for a compound containing no polar groups. The electric conductivity of a sodium polymer carefully freed from sodium is said to be less than that of natural rubber.<sup>377</sup>

The dielectric constant of raw *Hevea* rubber is  $\epsilon = 2.37$  (at 1 kilocycle per sec.),<sup>378</sup> while the dielectric constant of *Hevea* pure gum stock was reported<sup>376, 378a</sup> as  $\epsilon = 2.69$  (at 1 kilocycle per sec.) and  $\epsilon = 2.52$  (at 1 megacycle per sec.).

### C. THERMAL AND OPTICAL PROPERTIES

No data are given on the specific heat of the sodium polymer. The heat-insulating properties are said to be better than that of *Hevea* rubber.

TABLE IV-1  
INFRARED AND RAMAN SPECTRA OF BUTADIENE AND POLYBUTADIENE<sup>a</sup>

Infrared		Monomer			Polymer
$\nu$ , cm. <sup>-1</sup>	Intensity	$\nu$ , cm. <sup>-1</sup>	Intensity	Polarization <sup>b</sup>	Infrared
					$\nu$ , cm. <sup>-1</sup>
..	..	340	0	..	..
520	5	513	4	..	..
665	1	..	..	..	..
914	10	906	2	D	..
			(doublet)		
988	2	..	..	..	..
1014	9	..	..	..	..
..	..	1202	4	P	1135
1280	3	1276	4	P	1160
1302	1	1303	2	P	1335
1388	5	..	..	..	1390
1432	1	1436	4	P	..
1490	2	..	..	..	1460
1603	7.5	1634	10	P	1680
1821	6.5	..	..	..	1820
2725	1	..	..	..	..
3021	7.5	3000	5	..	2920
..	..	3090	2	..	..

<sup>a</sup> The italicized figures have been found by several authors, or are particularly strong.

<sup>b</sup> P = polarized; D = depolarized.

No data are given in the literature on the refractive index of the sodium polymer. For the emulsion polymer, Dogadkin and coworkers<sup>375</sup> found  $n_D^{20} = 1.518$  for the sol fraction and  $n_D^{20} = 1.520$  for the gel.

<sup>377</sup> M. A. Lur'e, *Sintet. Kauchuk*, 1, No. 3, 21 (1932).

<sup>378</sup> A. H. Scott, A. T. McPherson, H. L. Curtis and A. D. Cummings, *J. Research Natl. Bur. Standards*, 11, 173 (1933).

<sup>378a</sup> L. B. Sebrell, *Ind. Eng. Chem., Ind. Ed.*, 35, 736 (1943).

Ultraviolet absorption begins at wave length  $\lambda \geq 2540 \text{ \AA}$ .<sup>379</sup>

Infrared absorption of polybutadiene was investigated by Williams.<sup>380</sup> His data on the absorption frequencies of polybutadiene are listed together with the infrared<sup>381, 382</sup> and Raman spectra<sup>383</sup> of the monomer in table IV-1.

#### D. PERMEABILITY

Quantitative data on the permeability of the polymer to gases have been obtained only with respect to the monomer; these<sup>384</sup> are summarized in table III-16, page 164. Qualitatively, permeability to gases is said to be smaller than that of natural rubber,<sup>377, 384a</sup> while permeability to water depends on the alkalinity. ✓

#### E. MECHANICAL PROPERTIES

No quantitative data are available concerning the mechanical properties of the raw polymer. However, Lomakin<sup>385</sup> has investigated the relative mechanical strength of polybutadiene films prepared from polymers of different plasticity. He found that, in the plasticity range of  $P = 0.70-0.90$  (Karrer), which corresponds to relative viscosities of 2% benzene solutions ( $\eta_{\text{rel.}} = 5-6$ ), an increase in  $\eta_{\text{rel.}}$  gives rise to a pretty strong linear increase in the film strength. In the plasticity range of  $P = 0.42-0.70$  ( $\eta_{\text{rel.}} = 5-15$ ), the increase in the strength of the film is still linearly proportional to the viscosity, but the slope is smaller. Somewhere between  $P = 0.42$  and  $P = 0.22$ , the slope is reversed; the film prepared from a polymer with  $P = 0.22$ , ( $\eta_{\text{rel.}} > 15$ ) is weaker than a film prepared from a polymer of  $P = 0.42$ . ✓

Differences in mechanical film strength of polymers of varying plasticity persist, or are even magnified, after incorporation of reinforcing compounding ingredients (carbon

<sup>379</sup> A. M. Kublitskiĭ, *Sintet. Kauchuk*, 5, No. 7/8, 30 (1936).

<sup>380</sup> D. Williams, *J. Applied Phys.*, 7, 399 (1936). The mode of preparation of the polymer is not given.

<sup>381</sup> R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Chem. Phys.*, 11, 433 (1943).

<sup>382</sup> J. Turkevich and W. W. McCarthy, *private communication*.

<sup>383</sup> *Tables Annuelles de Constantes*, Vol. 12, Chapter 15.

<sup>384</sup> A. Abkin and S. Medvedev, *Zhur. Fiz. Khim.*, 13, 705 (1939).

<sup>384a</sup> J. P. Haworth and F. P. Baldwin, *Ind. Eng. Chem., Ind. Ed.*, 34, 1301 (1942), showed that a synthetic rubber may be superior as a barrier for one gas and inferior for another.

<sup>385</sup> B. A. Lomakin, *Kolloid. Zhur.*, 2, 281 (1936); 5, 335 (1939). B. A. Lomakin and Z. N. Nemtsova, *ibid.*, 3, 597 (1937).

black) and after vulcanization. Gorbunov<sup>386</sup> showed that the tensile strength of a polybutadiene stock containing 60 parts semireinforcing carbon per 100 parts polymer was *two* times higher when made with a polymer of plasticity  $P = 0.25$  as compared with a polymer of plasticity  $P = 0.65$ . The increase in tensile strength as a function of plasticity was practically rectilinear.

Talmud *et al.*<sup>387</sup> failed to observe on compounded polybutadiene a reversal in trend (suggested by Lomakin) when going from medium- to low-plasticity polymers. On the contrary: they consistently obtained higher tensile properties in tread stocks prepared from a polymer of plasticity  $P = 0.17$  than from a polymer of Karrer plasticity  $P = 0.29$ .

A difference from the *Hevea* rubber appears on freezing of stretched rubber. Polanyi has shown that the tensile strength of raw *Hevea* rubber is markedly increased if the rubber is stretched and then frozen, when compared with the tensile strength of rubber frozen without stretching. Glagolev<sup>388</sup> found that with polybutadiene this effect is very small. The reason for this difference lies in the fact the polybutadiene does not crystallize on stretching (see also page 205).

## B. STRUCTURE OF THE POLYMER

### 1. General Remarks

It is now generally assumed, on the basis of x-ray, thermodynamic, ozonolytic, and viscometric evidence, that natural rubber consists of thread-like molecules built from isoprene units, all of them added head-to-tail in a *cis* configuration. The only difference between the different molecules is the number of isoprene units contained in each one, that is, their molecular weight. Subsequent experiments show that the distribution of the molecular weight possesses a fairly sharp and pronounced maximum at at least 600,000 for a good quality of plantation rubber smoked sheet. These molecules are held together by van der Waals' forces, as are all the liquids and all the molecular crystals, and can be separated (dissolved) when brought into contact with a solvent.

In the unstretched state, the rubber molecules are more or less coiled (configuration corresponding to the maximal entropy); on stretching they are straightened out so that they come to lie together in a crystal-like manner. (It is their tendency to "coil up" which is responsible for the rubber-type elasticity, as was suggested by Meyer, von Susich, and Valkó<sup>389</sup> and

<sup>386</sup> L. Gorbunov, *Zhur. Resinovoĭ Prom.*, 9, No. 2, 110 (1933).

<sup>387</sup> S. Talmud and G. Ūzhenko, *Kauchuk i Rezina*, 3, No. 7, 15 (1939). S. Talmud and Ū. Vassil'eva, *ibid.*, 2, No. 8/9, 34 (1938).

<sup>388</sup> M. M. Glagolev *et al.*, from I. I. Zhukov, V. A. Komarov, and S. L. Talmud, *Bull. acad. sci. U.R.S.S., Ser. VII*, 1938, 775.

<sup>389</sup> K. H. Meyer, C. von Susich, and E. Valkó, *Kolloid-Z.*, 59, 208 (1932).

shown by Mark, Guth, Flory, Wall, and others.) Hence natural rubber exhibits on stretching a "crystalline" x-ray diagram and an optical birefringence.

In synthetic polymers, particularly in the butadiene-base polymers, the situation is somewhat different. In contradistinction to natural rubber, the polymer molecules are not differentiated by their length only—the structure law for the individual molecule is not unique. We find in one and the same molecule certain butadiene units connected by 1,4, others by 1,2 additions. Some of them have *cis*, others *trans*, configurations. In certain places we find branch chains of different length growing from the

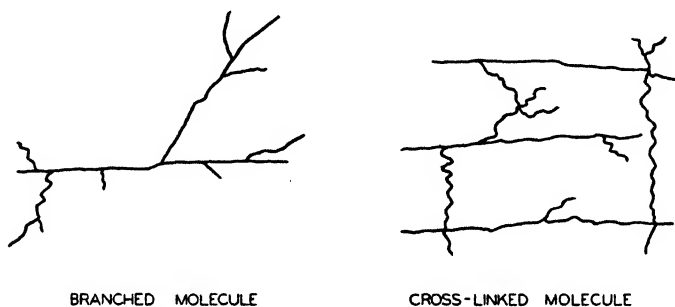


Fig. IV-1.—Branched and cross-linked molecules.

main chain. Moreover some of the chains are cross linked, *i. e.*, held together by primary C—C bonds, which are not broken in the presence of solvents, so that a part of the molecular chain forms an insoluble gel which exhibits only limited swelling (Fig. IV-1).

Thus we have not only a mixture of homologues of different molecular weight but a mixture of isomers as well. The number of possible isomers is very high, depending on both the chain length and the relative probability, that is, on the reaction rates of all the different reactions possible and hence on the exact conditions (temperature and concentration) under which the polymerization process has been carried out. Schulz<sup>800</sup> has calculated the number of isomers possible under different assumptions concerning the relative rates of 1,2 and 1,4 addition processes, the relative rates of branching *versus* straight addition, etc., and arrives at the conclusion that  $10^{80}$  isomers for a polymer of molecular weight of 50,000 is a fairly conservative estimate. This number is tremendous even when compared with the number of molecules  $6 \times 10^{23}$ , in one mole. It can be stated that it is extremely improbable that two absolutely identical polymer molecules have ever been produced.

<sup>800</sup> G. V. Schulz, *J. Makromol. Chem.*, **1**, 35 (1943).

Even less likely is the chance of finding two identical molecules in two particular samples. The question therefore arises: How far are we entitled to speak about polymers as definite substances rather than as mixtures? One should, however, consider that the polymeric substances are not mixtures of different compounds but mixtures of molecules, that these molecules are formed in one process and obey the same structural laws, and that the properties of polymeric substances are reproducible.

The difference between them and ordinary chemical compounds is mainly the impossibility of assigning to the polymer molecules of a definite structural formula. The structural formula is replaced by the following characteristics, which determine the polymer completely and knowledge of which is all that is necessary for its adequate description:

(1) The monomer from which the polymer is derived; in the case of mixed polymers, the different monomers and their ratio.

(2) The law determining the addition of the monomer; if several types of addition are possible, as in the case of polybutadiene 1,2 and 1,4 additions, their relative frequency.

(3) The degree and the type of branching (long or short branches) and the way the branches are distributed along the main chain.

(4) The molecular weight distribution.

(5) The amount of the insoluble (cross-linked) material (gel) and the number of cross links per given chain length.

Given these data, the polymer (but not an individual molecule) is completely described.

The question may arise as to how it is possible for two polymer samples to have identical properties without any two of the molecules of which they are composed being identical. The following explanation has been advanced by Schulz<sup>500</sup>: Let us consider three or more properties (density, hardness, elasticity, refractive index, etc.) as coordinates. For each possible isomer there is a corresponding point in this space. If we plot the points for all the possible  $10^{50}$  isomers, we find that all together they occupy a finite volume. Indeed, for each property there exists one isomer which has a maximal and another which has a minimal value, the points corresponding to all the other isomers being situated in between these two limits, thus defining a "property body." The properties of a mixture of all the possible isomers are given by the coordinates of the center of gravity of this "property body." If only a fraction of the possible isomers, let us say  $10^{10}$ , are realized, the only difference, *viz.*, the "property body" of *all* the  $10^{50}$  isomers, is the difference in the density (number of points), the center of gravity (the properties of the mixtures) being the same as long as the choice of the isomer existing in the sample is determined by chance alone.

## 2. X-Ray Structure

Since it is to be expected that locally two adjacent regions of two different molecules have a different structure, it is not astonishing at all that no crystalline structure of the polymer can be observed on stretching, in contradistinction to the more regularly built *Hevea*. Glagolev<sup>388</sup> has stretched sodium polybutadiene three to five times at  $-35^{\circ}$  C. and fixed it in this stretched position by cooling it down to  $-50^{\circ}$ . No crystalline spots of the fiber diagram could be observed, the diffraction picture showing only an amorphous ring. The diameter of this ring varied somewhat from one sample to another, as well as for fractions of different molecular weight.

In much the same way the thermopolymer and the oxidized polybutadiene yielded only diffraction rings. However, these rings are thinner and less diffuse than in the case of the sodium polymer, and resemble greatly the rings observed on unstretched *Hevea*.

As far as the emulsion polymer is concerned, Meyer<sup>391</sup> claims that spots observed on the fiber diagram indicate this polymer is built up mainly by 1,4 additions of butadiene molecules in *trans* form. The identity period is of 5.0 Å. However, this result has not been confirmed by other authors.<sup>392</sup>

## 3. Optical Birefringence

When subjected to a stress, sodium-polymerized butadiene, like rubber, exhibits a positive birefringence, the index of refraction for the ordinary

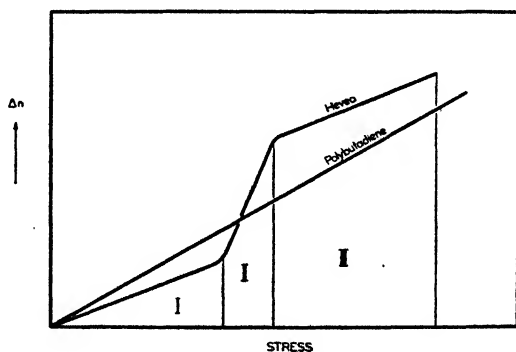


Fig. IV-2.—Stress birefringence of *Hevea* rubber and polybutadiene.<sup>388</sup>

<sup>391</sup> K. H. Meyer, *loc. cit.*, p. 183.

<sup>392</sup> L. B. Sebrell, *Ind. Eng. Chem., Ind. Ed.*, 35, 736 (1943).

ray being larger than for the extraordinary. However, the dependence on the stress is different in the two cases. While for *Hevea* rubber the relation between birefringence and stress is represented by an S-shaped curve, for sodium polybutadiene the relation is linear (see Fig. IV-2).<sup>388</sup> This observation can be explained if one assumes that the second part of the S-curve for *Hevea* is due to a crystallization process. Since no crystallization can occur in the case of polybutadiene, this part of the curve is absent.

#### 4. Chemical Structure

The most important information we possess on the structure of the polymer is that derived from ozonolysis, since catalytic hydrogenation yields results which are somewhat uncertain because of cyclization reactions which may occur in the hydrogenation process.

##### A. OZONOLYSIS

Ozonolysis generally consists of dissolving the rubber to be investigated in an unoxidizable solvent, treating the solution with ozone, and determining the products formed, sometimes after treatment with water. It is based on the observation that ozone very easily attacks and ruptures double bonds.

The first polybutadiene whose structure was investigated by ozonolysis was the soluble fraction of the thermopolymer<sup>393</sup> which, according to Lebedev, yields only succinic acid and succinaldehyde (see the scheme on page 150) and is consequently built up mainly by 1,4 additions. Lebedev made no ozonolysis of the "sponge polymer" ("autopolymer"), since it is not soluble in carbon tetrachloride or in other solvents.

The ozonolysis of the emulsion-polymerized polymer was carried out by Hill, Lewis, and Simonsen,<sup>394</sup> who prepared their polymer themselves. The polymer was insoluble in all the common solvents and the ozonolysis had to proceed without dissolution.

The volatile aldehydes were removed in steam, the nonvolatile residue further oxidized, the acids so formed isolated and esterified, and the methyl ester separated by fractionation.

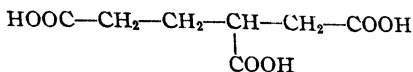
The following compounds have been isolated:

(1) Succinic acid and aldehyde (identified as the dimethyl ester and 2,4-dinitrophenylhydrazone). These compounds correspond to 1,4 addition sequences.

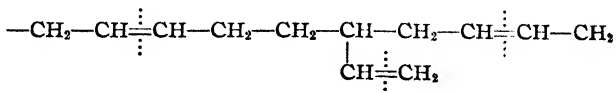
<sup>388</sup> S. V. Lebedev, *Zhur. Russ. Fiz.-Khim. Obshchestva*, **41**, 1818 (1909); **42**, 726 (1910); **43**, 1124 (1911).

<sup>394</sup> R. Hill, J. R. Lewis, and J. L. Simonsen, *Trans. Faraday Soc.*, **35**, 1067 (1939).

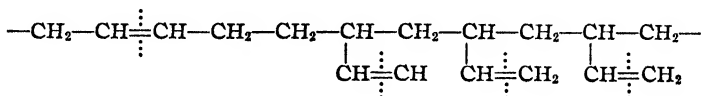
(2) Butane-1,2,4-tricarboxylic acid (identified as the trimethyl ester), which corresponds to the formula:



This acid can only be formed where 1,4 and 1,2 additions are followed by 1,4 additions:



(3) A neutral higher ester residue resulting from sections of the polymer where 1,2 additions predominated, that is:



or where branching occurred.

(4) A resinous acid which did not esterify completely under the conditions of experiment. This corresponds to regions where 1,2 additions predominated even more than in the structure considered under (3).

Furthermore, some formaldehyde, carbon monoxide (corresponding to 1.3% of all CH<sub>2</sub> groups present), and formic acid were found. But since their amounts are small and at least a part of them have been formed in secondary processes, they can be disregarded.

TABLE IV-2

## OZONOLYSIS OF EMULSION-POLYMERIZED POLYBUTADIENE

Compound	Type of addition responsible	Per cent
Succinic acid and succinaldehyde	1,4 addition sequence	21.7
Butane-1,2,4-tricarboxylic acid	Mostly 1,4, 1,2, 1,4 addition sequence	10.6
Resinous acid	At least two 1,2 additions per one 1,4 addition	21.2
Neutral esterification products	Almost purely 1,2 additions	18.4

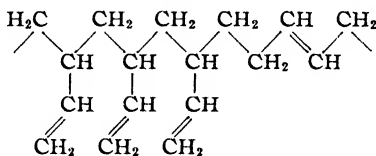
From the relative amounts of the four products observed, some indications on the relative frequency of 1,4 and 1,2 additions can be drawn. These results are summarized in table IV-2. Comparing this with the results of Ziegler and coworkers (page 151) and the following results of Pum-



merer and of Ākubchik on the ozonolysis of sodium-polymerized butadiene, one may conclude that, in emulsion polymerization, there are more 1,4 additions than in low-temperature, sodium-polymerized butadienes.

As far as the ozonolysis of the sodium polymer is concerned, it has already been stated (page 150) that the first experiments of Ziegler and Bähr<sup>395</sup> led to unclear and inconclusive results. Later experiments of Ziegler, Grimm, and Willer,<sup>396</sup> Pummerer,<sup>397</sup> and Ākubchik, Zhabina, and Mal'fseva<sup>398</sup> have been somewhat more successful. All the authors agree that the amount of succinic acid and succinaldehyde formed from polymers prepared at low temperature is fairly small. Ziegler and coworkers and Pummerer give 6–10% as the amount of 1,4 addition sequences. This amount increases with increasing temperature (see page 152). Furthermore, it represents the lower limit, since succinic acid is formed only in the case of at least two consecutive 1,4 groups; the sequence 1,2—1,4—1,2—1,4—leads to butane-1,2,4-tricarboxylic acid. Ākubchik *et al.* do not give explicitly the amount of succinic acid found, but state that it was small. They found, besides succinic acid, the following compounds: formaldehyde; formic acid; carbon dioxide; insoluble products of the formula  $(C_4H_6O_2)_n$ , where  $n$  is large; a fraction of acids of molecular weight 122–124; a fraction of acids of molecular weight 264–272.

The interpretation generally agreed upon is that sodium polybutadiene prepared at room temperature is a nearly pure 1,2 addition polymer with only occasional 1,4 additions, corresponding to the scheme:



Another method of oxidative degradation, a treatment with hydrogen peroxide in solution, was applied by Kagan and Sukhareva<sup>399</sup> to both sodium polybutadiene and to *Hevea* rubber. The oxidation was carried out in sealed ampoules at a fixed temperature, 43° C., and in the presence of glacial acetic acid. Both rubbers were in chloroform solution. The reaction was somewhat slower with the polybutadiene than with *Hevea* rubber (pale crêpe). In both cases the oxidation product was an

<sup>395</sup> K. Ziegler and K. Bähr, *Ann.*, **473**, 57 (1929); *Ber.*, **61**, 253 (1928).

<sup>396</sup> K. Ziegler, H. Grimm, and H. Willer, *Ann.*, **542**, 90 (1940).

<sup>397</sup> R. Pummerer, *Kautschuk*, **10**, 149 (1934); *Rubber Chem. Tech.*, **8**, 39 (1935).

<sup>398</sup> A. I. Ākubchik, V. M. Zhabina, and A. E. Mal'fseva, *Sintet. Kauchuk*, **4**, No. 6, 50 (1935).

<sup>399</sup> B. Kagan and N. Sukhareva, *Zhur. Resinovoĭ Prom.*, **11**, 46 (1934).

amorphous white powder; but the physicochemical behavior and the chemical composition of the two powders were different. The product obtained by the oxidation of *Hevea* is soluble in benzene, chloroform, acetone, and ethyl alcohol, and insoluble in ether; on heating it softens and decomposes at 70–80°. The product obtained from polybutadiene dissolves after swelling in alcohols, acetone, and pyridine, but is insoluble in benzene, anisole, and ether. It is soluble to only a limited extent in chloroform. It softens in a capillary at 70–80°; at 115–120° it becomes denser and transparent, but no fusion is observed. Elementary analysis, hydrogenation experiments, etc., show that the *Hevea* oxidation product is saturated and corresponds to the formula:  $C_{10}H_{15}(OH)O_2$ . The polybutadiene oxidation product is unsaturated (one double bond per unit) and corresponds to the general formula:  $C_{16}H_{26}(OH)_2O_2$ . None of the compounds contains any aldehyde groups.

## B. HYDROGENATION AND HYDRODEPOLYMERIZATION

The results obtained with the hydrogenation of the lower polymers prepared by sodium polycondensation have been given on page 151. They enabled Ziegler and coworkers<sup>396</sup> to determine the ratio of 1,4 and 1,2 additions as a function of temperature.

The hydrodepolymerization of high polymers (both of *Hevea* rubber and sodium polybutadiene) was investigated by Zelinskiĭ and Rapoport.<sup>400</sup>

The polymer was introduced into an autoclave in the presence of molybdenum sulfide as catalyst, and heated for several (2–3) hours to 400° C. under a hydrogen pressure of 150 atm. Small amounts of gaseous products (carbon dioxide, carbon monoxide, less than 0.1% of each) and of saturated hydrocarbons (3.0–3.8%) were found.

The main products of hydrodepolymerization are saturated and unsaturated derivatives of cyclohexane and free aromatic compounds. In other words, nearly all the products of hydrodepolymerization are cyclic compounds. These results are in agreement with the results previously reported by Zelinskiĭ and Kozlov<sup>401</sup> on the thermal decomposition of natural and synthetic rubber in the presence of aluminum chloride.

There too the results for natural and for synthetic rubber are pretty much alike. Both gave on cracking a gasoline-like fluid high in aromatics.

The results of Zelinskiĭ and Rapoport are in a perfect agreement with those obtained by Ipatieff and Schaad<sup>402</sup> on thermopolymerized polybutadiene. Instead of molybdenum sulfide, black nickel oxide was used as catalyst. The temperature was 250° C. Nearly 50% of the depolymerization

<sup>400</sup> N. D. Zelinskiĭ and I. B. Rapoport, *Bull. acad. sci. U.R.S.S., Ser. VII*, 1940, 681; *Rubber Chem. Tech.*, 15, 33 (1942).

<sup>401</sup> N. D. Zelinskiĭ and N. S. Kozlov, *Zhur. Priklad. Khim.*, 6, 36 (1933).

<sup>402</sup> V. N. Ipatieff and R. E. Schaad, *Ind. Eng. Chem., Ind. Ed.*, 32, 762 (1940).



product proved to be ethylcyclohexane, and about 12% corresponds to naphthenic hydrocarbons with two rings.

Zelinskii concludes from these experiments that the aromatic compounds present are "formed as a result of irreversible catalysis of the unsaturated derivatives of cyclohexene, which are the first and immediate products of the diene synthesis from both butadiene and isoprene" and that *Hevea* rubber is actually a polyterpene  $(C_5H_8)_x$ . Since, however, these conclusions are in absolute contradiction to what is known both on the polybutadiene formation from butadiene (Chapter III, *passim*) and on the structure of *Hevea* rubber as determined from x-ray diagrams,<sup>403</sup> we cannot adopt the views of this author and assume, until it is proved to the contrary, that the cyclic compounds found on dehydrogenative destruction are formed during the depolymerization process.

### C. SUMMARY

Although we have described the polymers in detail and have given their heats of formation, it seems useful to summarize all the results obtained in the form of a table (Table IV-3) in which, in addition to the chemical characteristics, we give also the heats of formation as determined by Lebedev and coworkers.<sup>404</sup>

## 5. Molecular Weight of Polymeric Materials. Experimental Methods

Several methods have been used for the determination of the molecular weights of high polymers. These can be divided into six groups, the first three of which are, for the time being, the only methods having a good theoretical foundation.

### A. THERMODYNAMIC METHODS

Of these, we are particularly concerned with measurements of osmotic pressure. Although the molecular weight of the high polymeric molecules is fairly high, methods have been developed recently which allow one to determine the osmotic pressure of solutions of such polymers with a fair degree of precision.<sup>405-408</sup>

A certain difficulty of interpretation arises, however, because the osmotic pressure,  $\pi$ , of a high polymeric solution is not a linear function of the concentration,  $c$ ,

<sup>403</sup> C. W. Bunn, *Proc. Roy. Soc. London*, **A180**, 82 (1942).

<sup>404</sup> S. V. Lebedev, G. G. Kobliński, M. A. Khokhlovkin, N. I. Kuřbina, and M. M. Gol'dman, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* **4**, 46 (1935).

<sup>405</sup> K. H. Meyer, E. Wolff, and C. G. Boissonnas, *Helv. Chim. Acta*, **23**, 430 (1940).

<sup>406</sup> G. Gee, *Trans. Faraday Soc.*, **36**, 1162 (1940).

<sup>407</sup> P. J. Flory, *J. Am. Chem. Soc.*, **65**, 372 (1943).

<sup>408</sup> R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).

but contains also a term of higher order in  $c$ . This difficulty has been overcome: both a theoretical treatment<sup>409-411</sup> and an abundance of experimental data have shown that, up to concentrations of at least 2 g. per 100 ml.,  $\pi/c$  is a virtually linear function of the concentration. The measured values  $[\pi/c]_c$  hence can be extrapolated in this way to infinite dilution, and the molecular weight,  $M$ , of the sample determined from

$$M = RT/[\pi/c]_{c=0} \quad (4.1)$$

where  $R$  is the gas constant and  $T$  the absolute temperature.

This method, particularly since it was made less time consuming (Fuoss and Mead),<sup>408</sup> is the least expensive method giving consistent and theoretically founded results.

Several other methods measuring osmotic pressure indirectly, such as isothermal distillation (Gee<sup>406</sup>) or cryoscopic measurements<sup>412, 413</sup> have been proposed; but they are too slow or too insensitive or give correct results only for relatively low molecular weight material (molecular weight below 10,000).

#### B. ULTRACENTRIFUGE METHODS

The molecular weight of a colloidal substance can be determined from the sedimentation constant,  $S$ , and diffusion constant,  $D$ , through the relation:

$$M = RT \cdot S/D \cdot (1 - v\rho) \quad (4.2)$$

where  $R$  is the gas constant,  $T$  the absolute temperature,  $v$  the specific volume of the solute, and  $\rho$  the density of the solvent.<sup>414</sup> The agreement between the molecular weights obtained by the ultracentrifuge and by measurements of osmotic pressure is fairly satisfactory.<sup>408</sup> The disadvantage of this method is the necessity of having an ultracentrifuge, a rather expensive and rare apparatus.

#### C. OPTICAL METHODS

An optical method, utilizing measurements of the scattering intensity as a function of the scattering angle, was proposed by Debye.<sup>415</sup> The intensity of the light

<sup>409</sup> P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

<sup>410</sup> M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941).

<sup>411</sup> M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 3 (1942).

<sup>412</sup> A. R. Kemp and H. Peters, *Ind. Eng. Chem., Ind. Ed.*, **33**, 1263 (1941).

<sup>413</sup> V. A. Komarov and N. P. Selivanova, *Sintet. Kauchuk*, **5**, No. 10, 7 (1936).

<sup>414</sup> For more detailed information, see J. L. Oncley, *Ann. N. Y. Acad. Sci.*, **41**, 121 (1941).

<sup>415</sup> P. Debye, *Am. Phys. Soc., Minutes of Fall Meeting, Chicago, Nov., 1943.*

scattering is related to the number of optically nonhomogeneous regions present in the solution, which is in turn proportional to the number of high-polymer molecules. This method has the advantage of becoming more and more sensitive as the molecular weight increases, *i. e.*, where the precision of the osmotic pressure measurements begins to drop.

#### D. FRACTIONAL PRECIPITATION

Schulz and Jirgensons<sup>416</sup> and Schulz<sup>417</sup> have suggested the use of precipitation curves to determine molecular weights. It is well known that polymeric molecules of the same composition but of different molecular weight (chain length) can be separated by adding to the solution increasing amounts of nonsolvent (see also page 248). Schulz relates this effect to the energy of interaction between the solvent and the rubber molecules, the interaction varying with the molecular weight.

By assuming this interaction to be known, it is possible to correlate the amount of precipitant necessary to precipitate a polymer of a given molecular weight to the molecular weight itself. However, Schulz makes the mistake of assuming that the distribution of the molecules between the two phases—solution and precipitate—depends on the energy of interaction rather than on the free energy of the polymer molecules in the two phases; so this method cannot be considered for the time being as justified by the theory.

#### E. VISCOSITY METHOD

Staudinger<sup>418</sup> found that the specific viscosity,  $\eta_{sp.}$ , of polymeric solutions increases with the molecular weight,  $\eta_{sp.}$  being defined as follows:

$$\eta_{sp.} = \frac{\eta_{soln.}}{\eta_{solv.}} - 1 = \eta_{rel.} - 1 \quad (4.3)$$

and claims<sup>419</sup> that:

$$\eta_{sp.}/c = K_s M \quad (4.4)$$

where  $c$  is the concentration (base moles in 100 ml. solvent), and  $K_s = 3 \times 10^{-4}$ . However, experience has proved that  $\eta_{sp.}/c$  is not independent of the concentration (see also page 255) and that, for higher values of  $\eta_{rel.}$ , it is more advisable to use instead of the specific viscosity the intrinsic viscosity  $[\eta]$  based on the Arrhenius equation.<sup>420, 421</sup>

<sup>416</sup> G. V. Schulz and B. Jirgensons, *Z. physik. Chem.*, **B46**, 105 (1940).

<sup>417</sup> G. V. Schulz, *Z. physik. Chem.*, **B46**, 137 (1940).

<sup>418</sup> H. Staudinger, *Ber.*, **59**, 3031 (1926).

<sup>419</sup> H. Staudinger and W. Heuer, *Ber.*, **63**, 222 (1930).

<sup>420</sup> S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

<sup>421</sup> H. Staudinger, *Ber.*, **63**, 921 (1930).

$$[\eta] = \frac{\ln \eta_{\text{rel.}}}{c} \quad (4.5)$$

In this case, equation (4.4) becomes

$$[\eta] = K_i M \quad (4.6)$$

For  $K_i$ , Staudinger claims the universal value of  $K_i = 3 \times 10^{-4}$  for all polymers in all solvents. Relation (4.6), although lacking any theoretical justification and confirmed only by measurements on material of very low molecular weight, is widely used by rubber scientists of all countries.

Several objections must, however, be raised to the Staudinger relation:

(1) The molecular weights calculated on the basis of this relation from viscosity data in different solvents give fairly different values. Thus, for the same polymer, Zhukov, Talmud, and Zil'berman<sup>422</sup> found values ranging between 10,000 and 90,000 when calculated from intrinsic viscosities measured in different solvents.

(2) The value of the Staudinger constant has been found in many cases to vary with the molecular weight, that is, the relation between the intrinsic viscosity and the molecular weight is not linear, in any case not for all high polymers. Flory<sup>407</sup> for polyisobutylene, Houwink<sup>423</sup> for a series of polyvinyl compounds, and Bartovics and Mark<sup>424</sup> for cellulose acetate have shown that the relation between intrinsic viscosity and molecular weight is best expressed by<sup>425</sup>:

$$[\eta] = KM^a \quad (4.7)$$

where  $a = 0.6-0.7$ . This relation is purely empirical; both  $K$  and  $a$  must be determined experimentally for each polymer and each solvent. For polyisobutylene, at least, it has been established that this relation can be used for all polymers of the same general composition but of different degrees of conversion.

#### F. METHOD OF INCOMPLETE VULCANIZATION

This method was proposed by Midgley, Henne, Shepard, and Renoll<sup>426</sup> and ap-

<sup>422</sup> I. I. Zhukov, S. L. Talmud, and V. A. Zil'berman, *Sintet. Kauchuk*, **4**, No. 6, 4 (1935).

<sup>423</sup> R. Houwink, *J. prakt. Chem.*, **157**, 15 (1940).

<sup>424</sup> A. Bartovics and H. Mark, *J. Am. Chem. Soc.*, **65**, 1901 (1943).

<sup>425</sup> A law of the form  $[\eta] = KM^{2/3}$  has been derived from theoretical consideration by W. Haller, *Kolloid-Z.*, **56**, 257 (1931). This paper has often been overlooked. Haller's derivation is discussed on page 255.

<sup>426</sup> T. Midgley, Jr., A. L. Henne, A. F. Shepard, and M. W. Renoll, *Rubber Chem. Tech.*, **7**, 518 (1934).

plied to sodium-polymerized polybutadiene by Komarov and Val'ter.<sup>427</sup> The polymer is compounded with tetramethylthiuram disulfide, vulcanized for one hour at 100° C., and then redissolved in benzene. A part of the vulcanizate remains undissolved. The rubber is then fractionated by addition of alcohol; and it is assumed that the first fraction contains one sulfur atom per chain, the second 1.5,

TABLE IV-4

MOLECULAR WEIGHT OF SODIUM POLYBUTADIENE OBTAINED BY THE METHOD OF INCOMPLETE VULCANIZATION

Sample No.	Fraction, g.	Sulfur content, %	I		II	
			Number of S atoms per chain	Mol. wt.	Number of S atoms per chain	Mol. wt.
1	1.44	0.26	1.0	12,300	2	24,500
2	3.42	0.36	1.5	13,300	3	26,500
3	17.20	0.50	2.0	12,700	4	25,500
4	3.35	1.45	6.0	13,100	12	26,100

the third 2, and so on. Determination of the sulfur content and of the weight of each fraction permits the determination of the average molecular weight of the chain. However, since the assumption that just one sulfur cross link per chain is formed is fairly unwarranted, the molecular weight obtained possibly ought to be multiplied by a factor of 2 or more. Table IV-4 gives the results of Komarov and Val'ter.

## 6. Average Molecular Weight and Molecular Weight Distribution

### A. AVERAGE MOLECULAR WEIGHT

If the molecular weight is determined on the polymer as a whole, the value obtained corresponds to the average molecular weight, either to the number average or to the weight average.<sup>428</sup> The *number* average molecular weight,  $\bar{M}_n$ , is defined by

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} \quad (4.8)$$

where  $n_i$  is the number of molecules having the molecular weight,  $M_i$ . The number average molecular weight is determined by osmotic pressure measurements or by measurement of the light scattering.

<sup>427</sup> V. A. Komarov and S. F. Val'ter, *Sintet. Kauchuk*, 5, No. 10, 11 (1936).

<sup>428</sup> For more details, consult H. Mark and R. Raff, *High Polymeric Reactions*. Interscience, New York, 1941, pp. 47 *et seq.*



The *weight* average molecular weight,  $\bar{M}_w$ , is defined by

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (4.9)$$

where  $w_i$  is the weight of the fraction with molecular weight  $M_i$ . It is determined in viscosity measurement if the Staudinger relation is assumed to hold.

It is clear, however, that the same average molecular weight can result from widely different molecular weight distributions, both from a very narrow one, where most of the molecules have the same molecular weight, and from a very broad one, in which the amount of material of low molecular weight is balanced by some of very high molecular weight. Other properties of the polymer ultimately may depend in a different way on the molecular weight of each chain than do the average molecular weights defined above. It is, therefore, important to know the actual molecular weight distribution. This is obtained by fractionating the polymer into a certain number of fractions of different molecular weights and determining the relative amount and molecular weight of each fraction. When the fraction is narrow, the number average molecular weight and the weight average molecular weight are nearly identical. But if the fraction is large and in particular if the determinations are carried out on an unfractionated polymer, the difference between  $\bar{M}_n$  and  $\bar{M}_w$  can be very appreciable.

## B. EXPERIMENTAL RESULTS ON MOLECULAR WEIGHT DISTRIBUTION

No data are available in the literature on the molecular weight distribution either of the thermopolymer or of the emulsion polymer. As far as the sodium polymerization is concerned, no systematic osmotic pressure data are available either, except for an indication of an average molecular weight of 40,000–60,000 for polymers of otherwise unknown characteristics.<sup>429</sup> However, substantial data exist on the viscosities and relative amounts of fractions of sodium-polymerized polybutadiene.<sup>430</sup> These are summarized in table IV-5, where  $\eta_{rel}$  is the relative viscosity of a 2% benzene solution and the plasticity of the samples is given in "Karrer units." From table IV-5 it may be seen that:

<sup>429</sup> V. A. Komarov, *unpublished report*, quoted in V. A. Komarov and S. F. Val'ter, *Sintet. Kauchuk*, 5, No. 10, 11 (1936).

<sup>430</sup> I. I. Zhukov, F. M. Simkhovich, S. L. Talmud, and V. P. Nikol'skaya, *Sintet. Kauchuk*, 4, No. 2, 6 (1935).

(a) The maximum of molecular weight distribution can be shifted over a wide range.

TABLE IV-5

RELATIVE VISCOSITIES OF 2% SOLUTIONS OF SODIUM POLYBUTADIENE FRACTIONS

Solution No.	P	$\eta_{rel.}$ (av.)	Per cent soluble	Fractions	
				$\eta_{rel.}$	Per cent of total
1	0.90	2.0	96.0	6.6	20
				2.4	40.0
				1.6	13.5
				1.2	12.5
				1.0	10.0
2	0.90	2.0	78.3	6.0	9.9
				2.1	55.2
				1.6	9.1
				1.2	4.1
3	0.87	2.2	97.9	7.0	22.2
				2.5	43.4
				1.7	8.8
				1.3	5.5
				1.2	8.0
4	0.87	2.5	96.0	1.0	10.0
				5.5	15.0
				2.9	35.0
				2.6	23.0
5	0.67	6.4	77.5	1.7	10.0
				1.1	13.0
				12.0	25.0
				6.7	35.0
				1.7	10.0
6	0.70	6.8	71.3	1.1	7.5
				20.0	20.8
				6.4	41.0
				1.6	9.5
7	0.55	8.4	95.0	14.6	6.0
				10.2	8.0
				7.6	32.0
				5.9	19.0
				4.4	12.0
				2.1	18.0
8	0.40	29.8	97.7	71.7	35.9
				57.5	7.5
				15.6	5.4
				13.8	32.3
				11.3	6.0
				4.3	6.6
9	0.30	35.3	67.8	...	4.0
				177.4	36.0
				39.3	24.3
				3.5	4.6
				2.3	2.4

(b) The polymer molecules have a fairly narrow molecular weight distribution.

(c) Material with a plasticity down to 0.40 and as high a relative viscosity as 29.8 can be prepared without any appreciable insoluble (gel) fraction (see also page 220).

(d) A very definite parallelism exists between the average intrinsic viscosities (or molecular weight) and the technologically important properties of plasticity. This relation is presented in a graphic form in figure IV-3.

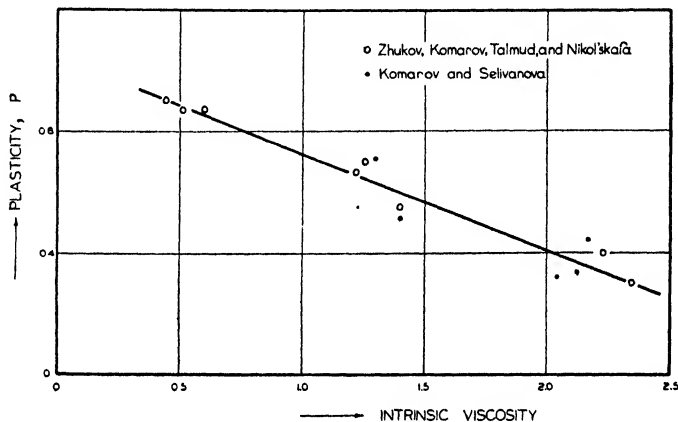


Fig. IV-3.—Relation between intrinsic viscosity and Karrer plasticity.<sup>418</sup>

The molecular weight distribution of unmilled *Hevea* rubber is not yet exactly known, but there are indications that the average molecular weight ranges from about 300,000 for low-grade rubber to about 700,000 for high-grade plantation *Hevea* rubber.<sup>406, 431</sup>

As already stated, no molecular weight distribution curves are published for emulsion-polymerized polybutadiene. However, Staudinger and Fischer<sup>431</sup> give as osmotic molecular weights for fractions of emulsion-polymerized butadiene values between 54,000 and 116,000 (for products with large amounts of modifier) and 227,000 to 440,000 (for a product with small amounts of modifier) for the sodium polymer. The corresponding values for the two fractions of German Buna 85 are 81,000 and 133,000; so it appears that the distribution in emulsion-polymerized butadiene is much broader than it is in the sodium-polymerized polybutadiene. This is undoubtedly related to the difference in the polymerization mechanisms.

<sup>431</sup> H. Staudinger and K. Fischer, *J. prakt. Chem.*, 157, 158 (1941).

Figure IV-4 gives the molecular weight distribution for emulsion-polymerized GR-S, based on ultracentrifuge data.<sup>432</sup> It can be assumed that

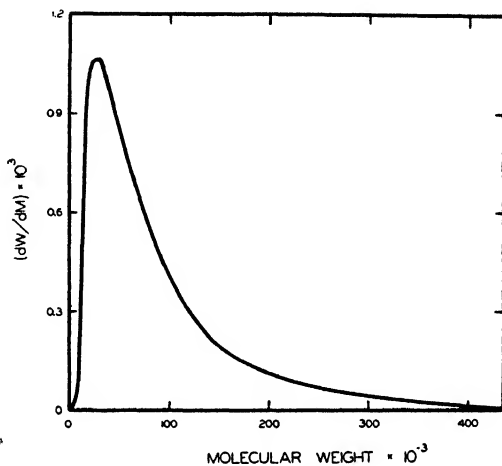


Fig. IV-4.—Molecular weight distribution of butadienestyrene polymer (Sebrell).<sup>432</sup>

the distribution curve for emulsion-polymerized polybutadiene is somewhat analogous.

## 7. Gel

The presence of insoluble gels in the polymer seems to affect to a certain extent various properties of the rubber, so that its amount is a characteristic property of the polymer. There is a definite difference between the so-called gel in natural rubber and the gel in synthetics. What is generally designated as gel in natural rubber is the chloroform-insoluble fraction. However, numerous experiments have shown that this fraction is completely soluble in benzene-butanol mixtures, that is, it is simply held together by van der Waals' forces of different strength than the sol fraction of the material. In the case of synthetic rubber gel, the situation is quite different. Such gels are completely insoluble in any solvent or mixture of solvents. Hence, it is to be assumed that they are held together by primary valence bonds. They can, however, be brought into solution<sup>433</sup> by heating them, in the presence of oxygen, in certain solvents (xylene,

<sup>432</sup> L. B. Sebrell, *Ind. Eng. Chem., Ind. Ed.*, **35**, 736 (1943).

<sup>433</sup> D. M. Sandomirskii and B. A. Dogadkin, *Kolloid. Zhur.*, **6**, 215 (1940).

toluene, ligroin, decalin) for about 100 hours at 80–140° C. No dissolution takes place if oxygen is replaced by pure nitrogen, so that the dissolution is undoubtedly due to a chemical reaction between polybutadiene and oxygen (oxidative scission, see page 225). The dissolution is accelerated by addition of fatty acids or salts of fatty acids.

The gels do not dissolve even in presence of oxygen if the solvents listed above are replaced by benzene, carbon tetrachloride, piperidine, chlorobenzene, bromobenzene, or dimethylaniline. However, once dissolved in, say, toluene, the gel can be redissolved also in these solvents if heated to 100° C. These gel solutions are said to be less transparent than the sol solution. The density of "solubilized" gel was  $d_{20}^{20} = 0.907$ , and the refractive index,  $n_D^{20} = 1.5196$ .

Two kinds of information can be obtained about these gels: their relative amount and the number of cross links per unit volume. The amount of gel is given by solubility measurements, while the number of cross links can be deduced from their maximal swelling,<sup>434</sup> through the relation:

$$M_c = \rho V \frac{\varphi^{1/2}}{\ln(1 - \varphi) + \varphi + \frac{\Delta\bar{H}}{RT}} \quad (4.10)$$

where  $M_c$  is the molecular weight of rubber between cross links,  $\Delta\bar{H}$  the heat of mixing,  $T$  the absolute temperature,  $R$  the gas constant,  $V$  the volume of the inbibing liquid,  $\rho$  the density of the rubber, and  $\varphi$  the volume fraction of the rubber that can be calculated from the maximum swelling,  $Q$  (see page 244) through the relation:

$$\varphi = 1/(Q + 1) \quad (4.11)$$

The amount of gel in sodium-polymerized butadiene depends on the sodium-butadiene ratio and the impurities present. It varies, according to Zhukov and coworkers, from 2.1 to 32.2%. It should be emphasized that rubbers of as high a relative viscosity as 29.8 (plasticity, 0.4) can be prepared without any appreciable amount of gel (2.3% for sample 7 in table IV-5). With higher average molecular weights (sample 9) the amount of gel sometimes becomes appreciable, although Zhukov, Talmud, and Zil'berman<sup>422</sup> report about a polymer of as low a plasticity as 0.26 (Karrer units) which was 95% soluble.

The only data available in the literature concerning the swelling of gel refer to a completely insoluble polymer of plasticity 0.11, which shows a maximum swelling coefficient of  $Q = 15.4$  (in toluene).<sup>435</sup> Using the

<sup>434</sup> P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).

<sup>435</sup> I. I. Zhukov and F. M. Simkhovich, *Kolloid. Zhur.*, **1**, 11 (1935).

formula of Flory and Rehner (Eq. 4.10) and assuming that, for a first approximation, the heat of mixing can be neglected, one can calculate that the molecular weight between cross links is about 16,000, which is equivalent to saying that one cross link occurs once for each 300 butadiene groups. For comparison, it may be mentioned that, from the data of Whitby, Evans, and Pasternak<sup>436</sup> on vulcanized *Hevea* gum stock, one deduces a molecular weight between cross links equal to 3000, that is, one cross link for 55 butadiene groups.

## 8. Plasticity

While from the point of view of the scientist the polymer is completely described by the characteristics listed on page 199, for technological purposes it is important to be able, in addition, to determine the "processing characteristics" of the rubber. The "processing" of rubber comprises two basic steps: (a) the compounding of the crude elastomer with vulcanizing agents (sulfur, accelerators) and with other substances (reinforcing and extending fillers, softeners, antioxidants, etc.) which so modify its properties as to produce satisfactory processing characteristics in the uncured state, as well as required ultimate physical qualities after vulcanization; and (b) the molding or shaping of the stock into the desired form and appearance, either by itself or in combination with other structural materials (like textiles or metals).

The most widely used processing operations are: milling, calendering, and extruding. Milling is a kneading operation. On a two-roll mill or in an internal mixer, rubber is subjected to severe shearing. At the same time, compounding ingredients are gradually added and dispersed therein. Calendering can be defined as a process of plastic (compressive) deformation of a rubber compound under the action of heat and mechanical force on the part of parallel calender rolls followed first by a relaxation period during which the stock is temporarily restricted from shrinking ("kicking back") through adhesion to the roll surface and then by a cooling period. The extruding operation ("tubing") can be defined as the process of forcing the preheated and mechanically worked compound under pressure through a shaped orifice plate. The forces involved in this operation include compression, shear (at a very high rate), and also extension (due to the tendency of elastoviscous materials to extrude at a nonuniform rate through various districts of the orifice).

<sup>436</sup> G. S. Whitby, A. B. A. Evans, and D. S. Pasternak, *Trans. Faraday Soc.*, **38**, 7, 269 (1942).

This brief outline of the processing steps indicates why technologists have taken an intense interest in the elastoplastic properties of rubberlike polymers. It also makes it fairly obvious that no simple individual test can evaluate completely all the characteristics that combine in the term "processability" of an elastomer or of a rubber compound.

Several apparatus have been devised for laboratory determinations of these properties, the most widely used being the parallel-plate plastometer of Williams in its various modifications, *e. g.*, the Goodrich (or Karrer) plastometer,<sup>437</sup> the shearing plastometer (viscometer) of Mooney,<sup>438</sup> and Dillon's form of Marzetti's extrusion plastometer.<sup>439</sup> Since the processing behavior of the rubber depends on several factors and each one of the plastometers is designed to test one or several of these factors, the measurements made on one of them can hardly be correlated with the measurements made on another. The Russian synthetic rubber industry has adopted for standard measurements the parallel-plate plastometer.

The results obtained with the parallel-plate plastometer can be expressed in different ways. The treatment given by Karrer is used in order to present results of the Russian rubber industry. According to Karrer, the parallel-plate plastometer allows one to determine two different properties: the "susceptibility" or "softness" ( $s$ ) to and the "retentivity" ( $R$ ) of deformation.<sup>440,441</sup> The two results are combined through the equation,  $P = sR$ , to give the plasticity,  $P$ . The measurement is made in the following way: A cylindrical sample of standard dimensions (height  $h_0$ ) at a given temperature (70° C. is usual in U.S.S.R.) is placed under a given load and the deformation (height of the compressed sample,  $h_1$ ) determined after a certain time (3 min.). Then the load is suddenly removed and the recovery of the sample (height  $h_2$ ) attained 3 min. after the removal of the load is measured at room temperature. The change in height during the compression is expressed by  $(h_0 - h_1)$ , and the more or less permanent deformation by  $(h_0 - h_2)$ .

The "softness," expressed in terms of change in height, is:

$$s = f(t, F) \frac{h_0 - h_1}{(h_0 + h_1)/2} = K \frac{h_0 - h_1}{h_0 + h_1} \quad (4.12)$$

<sup>437</sup> E. Karrer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 158 (1929). E. Karrer, J. M. Davies and E. O. Dieterich, *ibid.* **2**, 96 (1930).

<sup>438</sup> M. Mooney, *Ind. Eng. Chem., Anal. Ed.*, **6**, 147 (1934).

<sup>439</sup> J. H. Dillon, *J. Applied Phys.*, **4**, 225 (1933), **7**, 73 (1936). See also H. A. Schultz and R. C. Bryant, *J. Applied Phys.*, **15**, 360 (1944).

<sup>440</sup> E. Karrer, *Ind. Eng. Chem., Ind. Ed.*, **21**, 770 (1929).

<sup>441</sup> A. A. Ivanov, *Kauchuk i Rezina*, **2**, No. 6, 25 (1938).

if as a first approximation  $(h_0 + h_1)/2$  is taken as the average height during deformation. If load  $F$  and time  $t$  are constant and the nature of materials tested is closely related, variations in  $K$  may be neglected, so that  $s$  may be taken as:

$$s = \frac{h_0 - h_1}{h_0 + h_1} \quad (4.13a)$$

Retentivity is defined as the ratio of the amount of deformation retained to the amount of deformation given:

$$R = \frac{h_0 - h_2}{h_0 - h_1} \quad (4.13b)$$

Plasticity,  $P$ , then is:

$$P = sR = \frac{h_0 - h_2}{h_0 + h_1} \quad (4.14)$$

As already stated the two coefficients,  $s$  and  $R$ , are more significant separately than their combination to  $P$  (Ivanov<sup>411</sup>).

The plasticity of sodium polybutadiene depends on the ratio of sodium to butadiene, on the dispersion of sodium, and on the percentage of modifiers of diluting gases.

The Russian synthetic rubber factories produce a variety of polymers—as a concession to the consuming industry—the plasticity of S.K. ranging from  $P = 0.25$  to  $P = 0.65$ .

The Mooney "viscometer"<sup>412</sup> measures the resistance of rubber to a shearing force. A sample of rubber is sheared between the surfaces of a rotating disk and the walls of a stationary chamber surrounding the disk, and the torque is measured. In order to prevent slippage, the rubber is kept under a confining pressure (of 400–800 p.s.i.) and the surfaces of rotor and stator are roughened. The rotor is driven at a constant speed (2 r.p.m.) and the torque is measured by the deflection of a spring-loaded floating shaft, interposed between the synchronous a.c. motor and the worm gear and vertical spindle turning the rotor. The stator chamber is electrically heated (mostly to 100° C.) and shearing "viscosity" readings are taken at thixotropic equilibrium (and after the air has been worked out of the sample), *i. e.*, usually after 4 minutes running time, following a warm-up period of one minute.

A discussion of methods of evaluating processing behavior of rubber would not be complete without a mention of the "extrusion index" method<sup>413</sup> in which the external appearance of a laboratory-extruded profile, incorporating the elements of a square corner, a radius, and a lip is graded qualitatively.

A method<sup>414</sup> also gaining increasing popularity is the measurement of the free

<sup>411a</sup> B. S. Garvey, Jr., M. H. Whitlock, and J. A. Freese, Jr., *Ind. Eng. Chem., Ind. Ed.*, **34**, 1309 (1942).

<sup>411b</sup> A. E. Juve, *Symposium on the Application of Synthetic Rubbers*. A.S.T.M., Philadelphia, 1944, p. 50.



shrinkage of a freshly milled fixed volume of rubber on a laboratory mill under controlled conditions of time, temperature, and mill opening.

### C. EFFECTS OF CHEMICAL AND PHYSICAL AGENTS ON THE SOLID POLYMER\*

Relatively little is known about the chemistry of polybutadiene except its reaction with oxygen, which is of course technologically the most important since Cotton<sup>442</sup> and Busse<sup>443</sup> demonstrated that the mastication and plastication of rubber are to a large extent conditioned by reactions of rubber with oxygen. On the other hand, the temperature and mechanical treatment of the rubber during plastication cannot be neglected. We have found it preferable to treat the problem of resistance of polybutadiene toward the chemical and physical agents together.

#### 1. Resistance to Acids and Bases

The resistance of sodium-polymerized polybutadiene toward the common acids and bases has been investigated by Vergiles<sup>444</sup> who used in his investigations a polymer with a plasticity of 0.4 (Karrer), an ash content of

TABLE IV-6  
RESISTANCE OF VULCANIZATE TO ACIDS AND BASES

Sulfuric acid		Nitric acid, room temp.	Hydrochloric acid, room temperature	Potassium hydroxide, room temp.
Room temperature	Higher temperature			
Decreasing resistance ↓	Sodium poly- butadiene	Neoprene	Sodium poly- butadiene	All three equally re- sistant
	Neoprene	<i>Hevea</i>	<i>Hevea</i>	
	<i>Hevea</i>	Sodium poly- butadiene <i>Hevea</i>	Neoprene	

0.34%, and a basicity of 0.067%. Vergiles found that dilute (25% by volume) sulfuric acid scarcely affected the raw polymer (a weight decrease of 0.25% was observed); 50% sulfuric and nitric acids had no influence on the weight or properties of the polymer, as is the case also with *Hevea*.

\* The author wishes to thank Dr. A. V. Tobolsky for numerous discussions and suggestions concerning this section.

<sup>442</sup> F. H. Cotton, *Trans. Inst. Rubber Ind.*, **6**, 487 (1931).

<sup>443</sup> W. F. Busse, *Ind. Eng. Chem., Ind. Ed.*, **24**, 140 (1932).

<sup>444</sup> F. Vergiles, *Zhur. Resinovol Prom.*, **11**, 423 (1934).

In much the same way as with *Hevea*, concentrated sulfuric and nitric acids produce a certain small weight increase and a hardening of the polymer. A weight increase is also observed with 50% hydrochloric acid and with concentrated sodium hydroxide (30 g. per 100 ml.).

As far as the resistance of vulcanizate is concerned, the results of Vergiles can be summarized in table IV-6 in which the different elastomers are given in the order of their decreasing resistance.

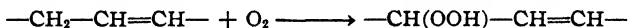
Carbon dioxide is adsorbed by a fresh polymer fairly fast at first—1.5 ml. carbon dioxide per g. polymer in 1 hour at room temperature—but after this no further absorption is observed.<sup>445</sup>

## 2. Halogenation

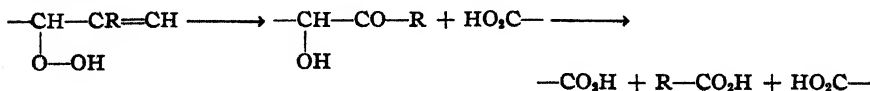
Solid butadiene polymer can be chlorinated with liquid chlorine. Thin threads of the polymer are slowly drawn through the liquid chlorine and then subjected to a treatment with ultraviolet light.<sup>446</sup>

## 3. Reactions of Polyolefins with Oxygen. Theoretical Considerations

The reaction of polyolefins with oxygen was very carefully investigated by Farmer and coworkers.<sup>447</sup> They have shown that the first step of the reaction is an absorption of oxygen by the polyolefin and formation of hydroperoxide groups on the methylenic carbon atom in the alpha position:



In the case of polybutadiene  $-\text{C}^\alpha\text{H}_2-\text{C}^\beta\text{H}=\text{C}^\gamma\text{H}-\text{C}^\delta\text{H}_2-$ , where  $\text{C}^\alpha$  and  $\text{C}^\delta$  are identical, either can be the seat of the hydroperoxide group. In the case of polyisoprene,  $-\text{C}^\alpha\text{H}_2-\text{C}^\beta(\text{CH}_3)=\text{C}^\gamma\text{H}-\text{C}^\delta\text{H}_2-$ , the alpha position is somewhat preferred. These hydroperoxides are highly unstable and are capable of several reactions, the most important from the practical point of view being: (a) the "scission" reactions, for instance, through

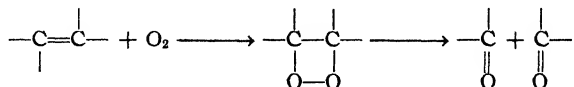


<sup>445</sup> I. I. Zhukov, V. A. Komarov, and G. Sibirakova, *Kolloid. Zhur.*, **1**, 9 (1935).

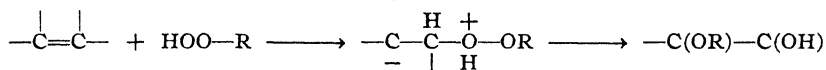
<sup>446</sup> E. Gebauer-Fuelnegg, U. S. Pat. 2,072,255, issued March 2, 1937 (Marbo Patents, Inc.).

<sup>447</sup> E. H. Farmer and A. Sundralingam, *J. Chem. Soc.*, 1942, 121. E. H. Farmer and D. A. Sutton, *ibid.*, 139. E. H. Farmer, G. F. Bloomfield, A. Sundralingam, and D. A. Sutton, *Trans. Faraday Soc.*, **38**, 348 (1942). E. H. Farmer, *ibid.*, 340.

or sometimes through the formation and immediate decomposition of a cyclic peroxide,



and (b) the "cross linking" or "polymerization" reaction:



In the "scission" reaction, a large molecule is divided into two smaller ones; in the cross-linking reaction, the two molecules are tied together as a step to gel formation. These two modes of reaction of a decomposing peroxide have different rates, depending on the substituents and so on. We must also consider that *Hevea* has all its double bonds in the main chain, so that every breaking of a double bond considerably decreases the molecular weight of the chain, while polybutadiene, particularly sodium-polymerized polybutadiene, has a large number of double bonds in the vinyl side chains (1,2 additions). While the scission of this double bond does not change the molecular weight effectively, the cross-linking reaction on this vinyl side group contributes as much to the gel formation as the cross linking occurring on a double bond of the main chain.<sup>448</sup> We may therefore expect that the cross-linking reaction, when compared with the scission reaction, will be more important for polybutadiene than *Hevea*. This assumption proves to be essentially correct: in the case of natural rubber the scission reaction predominates; in the case of polybutadiene the cross-linking reaction is the more predominant. In other words, while *Hevea* rubber, when left at a somewhat elevated temperature in the presence of oxygen, becomes softer and softer, polybutadiene rubber under the same conditions becomes hard and brittle.

However, certain authors believe that the hardening reaction which occurs in polybutadiene is due to cyclization processes occurring in the absence of oxygen.

Two remarks must be made before we consider the oxidation of polybutadiene in more detail. First, attention must be called to the small amount of oxygen necessary to produce degradation: indeed, one molecule of oxygen can cut into two parts a molecule of rubber of molecular weight 100,000, and so decrease its average weight to 50,000—in other words, 32 g.

<sup>448</sup> B. Dogadkin, quoted from V. Margaritov, *Acta Physicochim. U.R.S.S.*, 9, 917 (1938).

oxygen added to 100 kg. rubber of molecular weight 100,000 can decrease its average degree of polymerization by a factor of two. Second, in order to decrease the rate of oxidation reactions, antioxidants or stabilizers are added to the rubber. Their addition is somewhat less necessary in the case of *Hevea* rubber, because natural rubber contains some natural antioxidants; but deprived of these natural antioxidants, polyisoprene is oxidized even faster than polybutadiene. Since the amount of oxygen reacting is very small, the necessary and useful concentration of antioxidants is also small. Most antioxidants like Agerite act as inhibitors for both secondary reactions, probably by reacting with the hydroperoxide.

#### 4. The Oxidation of Sodium Polybutadiene\*

As distinct from the very large amount of published literature on the oxidation of natural rubber, only a few papers deal with the oxidation of raw polybutadiene.

##### A. OXIDATION OF THE PURE POLYMER

The oxidation of raw polybutadiene in the absence of antioxidant was investigated by Lebedev and coworkers<sup>449</sup> and by Zhukov, Komarov, and Sibirĭakova.<sup>450</sup> Both papers are concerned with the gravimetric method. Lebedev *et al.* found that washed polymer (sodium-free) gained 1.9% in weight upon storage for two months, whereby the sample hardened progressively from the surface inward, while Zhukov *et al.* found, in very good agreement with Lebedev, that the polymer, carefully purified by repeated precipitation with alcohol from benzene solutions, absorbs 1-3% oxygen within 10-20 days. They also observed a sharp change in the properties: The polymer becomes hard and brittle, assumes a slight yellow coloring, and no longer swells or dissolves, but crumbles in benzene into small pieces, in other words, becomes highly cross linked, recalling through its properties ebonite rather than rubber. Liquid polymers were found to oxidize faster than the elastic samples,<sup>451</sup> perhaps because the diffusion of oxygen is made easier, but they never became as hard as the polymers which are solid from the beginning.

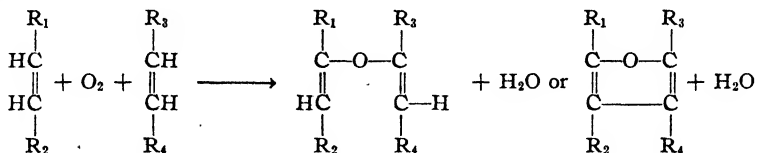
\* We thank Dr. A. V. Tobolsky for numerous discussions and suggestions concerning this paragraph.

<sup>449</sup> S. V. Lebedev, G. G. Koblĭanskiĭ *et al.*, *Zhizn' i Trudy*, Leningrad, 1938.

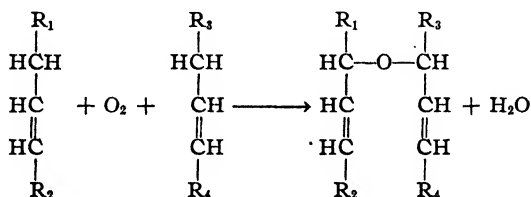
<sup>450</sup> I. I. Zhukov, V. A. Komarov, and G. Sibirĭakova, *Sintet. Kauchuk*, 4, No. 3, 4 (1935).

<sup>451</sup> L. S. Kofman and A. M. Perminov, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 84 (1935).

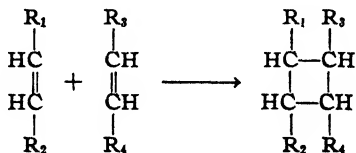
Dogadkin, Sandomirskii, and Sharkevich<sup>376</sup> observed that this "gelation" or cross-linking process is accelerated by temperature and requires only 30 hours at 150° C. It is accompanied by a formation of water. Dogadkin suggested that the chemical process taking place may be:



or more likely in the light of the work of Farmer *et al.*:



In the absence of oxygen, in pure nitrogen, the cross-linking process is very much slower, but is accelerated by addition of diazoaminobenzene, the polymerization catalyst (300 hours at 150° C.). No water is eliminated; according to Dogadkin, the gelation is due in this case to a cyclization by opening of the double bonds, a reaction requiring a higher activation energy than the cross linking through an oxygen bridge:



In the presence of certain compounds (*p*-diazoaminobenzene, nitrobenzene, aniline, dimethylaniline, phenol) and oxygen, the cross-linking reaction is replaced by the scission reaction.

#### B. OXIDATION IN THE PRESENCE OF ANTIOXIDANTS

In this case, the rate of oxygen consumption is greatly decreased. Thus, for example, Volzhinskii and Loginova,<sup>452</sup> using the method of Kemp,<sup>453</sup>

<sup>452</sup> I. A. Volzhinskii and L. I. Loginova, *Kauchuk i Resina*, 4, No. 4/5, 41 (1940).

<sup>453</sup> A. R. Kemp, W. S. Bishop, and P. A. Lasselle, *Ind. Eng. Chem., Ind. Ed.*, 23, 1444 (1931).

established that a sodium polybutadiene polymer of plasticity 0.3, not purified from any of its admixtures, and containing antioxidants, when kept for 280 hours in a finely subdivided (solid) state in an atmosphere of pure oxygen at room temperature as well as at 100° C., did not absorb oxygen to any measurable degree. The polymer remained soft and elastic and did not lose its valuable properties. This observation is in agreement with the findings of Lur'e<sup>454</sup> that the sodium-polymerized butadiene, once washed free from sodium and mixed with the antioxidants, can be stored for at least one year.

The antioxidant most widely used in the U.S.S.R. is aldol- $\alpha$ - or phenyl- $\beta$ -naphthylamine (Agerite).

#### C. OXIDATION IN THE PRESENCE OF METAL SALTS

There exists an unexplained contradiction between the findings of Volzhinskiĭ and Loginova<sup>452</sup> and Bobrova<sup>455</sup> as to the question of the catalytic oxidative action of polyvalent metal salts. Bobrova observed no detrimental effect of manganese or other heavy metal salts (soluble and insoluble in polybutadiene) upon the oxidation resistance of sodium polybutadiene. Volzhinskiĭ and Loginova claim to have observed such a detrimental effect: "Sodium polybutadiene,  $P = 0.34$  (Karrer), compounded on the mill with oleates of copper, manganese, and cobalt, reacts with oxygen very energetically. The rubber disaggregates and loses all its basic properties. It becomes a brittle, crumbly substance not capable of being milled." Elementary analysis gives 10–15% oxygen. General experience points, however, to the fact that polyvalent metal salts are much less detrimental in polybutadiene than in natural rubber.

#### D. EFFECT OF TEMPERATURE

The main effect of high temperatures, as long as they do not exceed 200° C., is an acceleration of the oxidation process. This is true even in an inert gas atmosphere or *in vacuo*, since the hydroperoxides in the rubber chains are numerous enough to support, to a certain extent, the oxidation reaction without any fresh oxygen supply.

If one wanted to avoid the oxidation reaction, he would be obliged not only to work in an inert atmosphere but also to avoid any contact between the synthetic rubber and air during the entire process of polymerization, as well as any use of peroxide catalysts.

<sup>454</sup> M. A. Lur'e, *Sintet. Kauchuk*, 1, No. 3, 21 (1932).

<sup>455</sup> A. Bobrova, *Kauchuk i Rezina*, 1, No. 3, 34 (1937).

When rubberlike substances are heated above 200° C., one observes, above a given temperature, a blow-hole formation,<sup>456</sup> corresponding to a decomposition of the hydrocarbon (Table IV-7). The temperature of the blow-hole formation of polybutadiene polymer lies at 220° C.<sup>457</sup> in agreement with what can be expected from the data in this table. When heated to this temperature, polybutadiene decomposes, giving three different residues: a liquid, tarlike mass; a hard, porous layer (probably due to cross linking); and a soft, elastic, sticky, and gummy substance.

TABLE IV-7  
BLOW-HOLE FORMATION OF RUBBERLIKE SUBSTANCES

Polymer	Temperature of formation, °C.	
	Pure gum stock	Tread stock
<i>Hevea</i>	198	198
Buna S	254	233
Buna NM	248	244
Buna NX	248	233
Neoprene GN	244	233

The effect of temperature on the rate of oxidative deterioration and the character of this deterioration of sodium polybutadiene tread stocks when compared with natural rubber were investigated by Andreev and Belen'kil<sup>458</sup> and Lebedev, Subbotin, and Bugakov.<sup>459</sup> These last authors measured as a function of time the tensile strength, the maximum elongation, and the residual elongation for *Hevea* and for sodium polybutadiene treads (washed and unwashed), in air as well as in pure nitrogen, at three different temperatures—70, 100, and 150° C. A typical curve for the tensile strength is presented in figure IV-5, for 100° C. The tensile strength of *Hevea* in air drops to zero in 144 hours, while in pure nitrogen the tensile strength first decreases slightly and then remains constant. The tensile strength of polybutadiene remains practically unchanged, even increasing slightly. The maximum elongation first decreases sharply in all the samples. After a certain time it falls to zero for *Hevea* in air, whereas in the

<sup>456</sup> I. B. Prettyman, *Ind. Eng. Chem., Ind. Ed.*, **34**, 1294 (1942).

<sup>457</sup> E. N. Poloskin, S. I. Apevalkin, and L. V. Gotovkina, *Zhur. Rezinovoĭ Prom.*, **12**, 829 (1935).

<sup>458</sup> V. Andreev and I. Belen'kil, *Zhur. Rezinovoĭ Prom.*, **10**, 218 (1933).

<sup>459</sup> S. V. Lebedev, S. A. Subbotin, and G. I. Bugakov, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* **4**, 72 (1935), reprinted in *Zhizn' i Trudy*, Leningrad, 1938, p. 746.

other cases (*Hevea* in nitrogen and polybutadiene in air and nitrogen) the maximum elongation decreases slowly, without reaching zero at the end of the experiment. At 150° all the processes go faster; in particular, the maximum elongation of polybutadiene in air drops sharply to zero.<sup>460</sup> Sodium polybutadiene heated in air at this temperature becomes hard and brittle (cross-linking reaction), starting on the surface and progressing inward. The sample heated in nitrogen shows no visible deterioration. The experiments carried out at 70° exhibit the same trends, although the oxidation reactions are much slower.

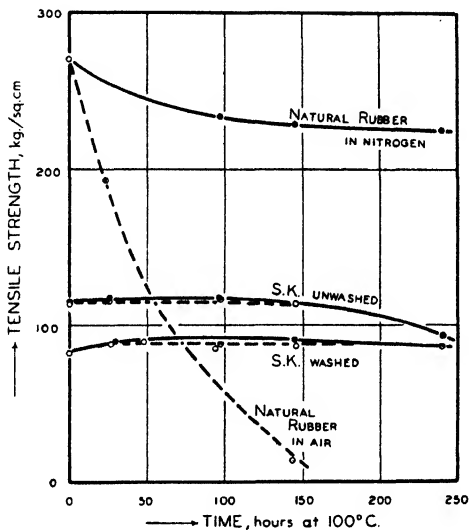


Fig. IV-5.—Loss of tensile strength of natural rubber and S.K. compounds after heating in nitrogen (solid line) and in air (broken line).<sup>469</sup>

Lebedev *et al.* also investigated the behavior in air of a sodium polybutadiene sample vulcanized with a very low amount (0.5%) of sulfur. They observed a tensile strength increase at 70° C., a time-independent tensile strength at 100°, and a decrease of the tensile strength at 150°. The maximum elongation always decreased with time. From their experiments, Lebedev and his coworkers drew the following conclusions:

(1) Changes in the physical properties of *Hevea* and polybutadiene treads on heating are different.

<sup>460</sup> This difference in the rates for *Hevea* and polybutadiene appears also in the stress-strain relaxation experiments described by A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon in *Abstracts of the Chicago Meeting of the Am. Phys. Soc.*, November, 1943.



(2) Although sodium polybutadiene treads conserve their tensile strength better, they easily exhibit a decrease in maximum elongation (and a consequent deterioration of their elastic properties).

(3) The temperature at which sodium polybutadiene shows a decrease in tensile strength lies higher than the corresponding temperature for *Hevea*, i. e., the resistance toward oxidation of stock protected with antioxidant is higher than that of natural rubber.

(4) A decrease of the sulfur content of sodium polybutadiene improves its stability toward oxidation.

### 5. Plastication and Milling

As has already been stated, plastication and milling comprise mainly an oxidative degradation (depolymerization) of rubber. The effect of working consists essentially in presenting to the action of oxygen "fresh" rubber

TABLE IV-8

EFFECT OF MILLING ON PLASTICITY AND MECHANICAL PROPERTIES OF ROD POLYMER CONTAINING ANTIOXIDANT

Property	Before milling	Milling time	
		10 minutes	1 hour
Plasticity (Karrer)	0.567	0.552	0.540
Tensile strength, p.s.i. <sup>a</sup>	1925	1890	1970
Ultimate elongation at break, % <sup>a</sup>	531	525	539
Relative residual elongation, <sup>a</sup> % of elongation at break	35	35	36

<sup>a</sup> Optimal cure; standard carbon black compound.

surfaces, and the effect of heating, in accelerating the reaction. The plastication process can be followed by means of two laboratory methods, by measurements of the plasticity or of the viscosity of rubber solution, which in turn is a way of estimating the average molecular weight of the rubber.

From what was previously said about the difference of the predominant secondary oxidation processes in *Hevea* and polybutadiene (scission in the case of natural rubber, cross linking in the case of butadiene), one can immediately predict that the effect of milling on the two polymers will be different. While rubber can be plasticized to a very high extent, even "milled dead," and its molecular weight brought down to a fraction of its initial value, the plasticity of butadiene will not be greatly affected by the milling, yet can be decreased if no antioxidant has been added.

While the molecular weight of a good smoked sheet rubber is, as already stated, about 600,000, that of milled rubber is about 140,000<sup>466</sup> and that of "dead" rubber even below 50,000.

The molecular weight of polybutadiene (viscosity in solution) will also remain nearly constant.

These are the effects observed by a number of investigators.<sup>451, 461-464</sup> Typical results for the variation of plasticity with milling time are given in table IV-8,<sup>468</sup> while the effect of milling on viscosity is shown in figure IV-6.<sup>451</sup>

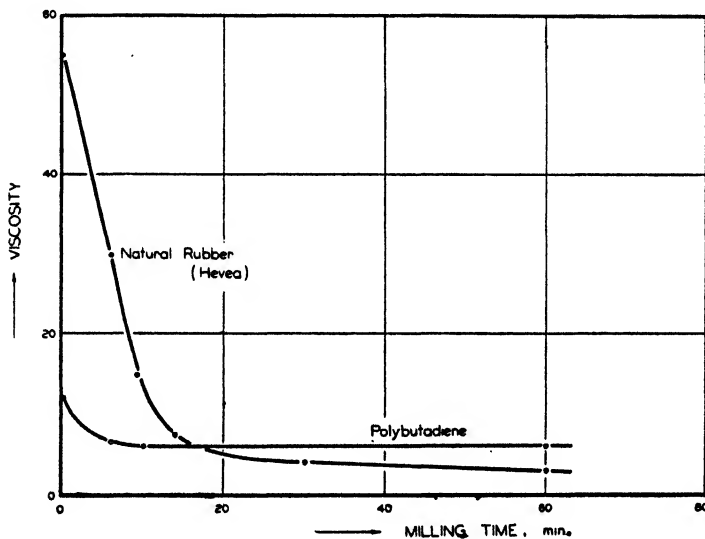


Fig. IV-6.—Effect of milling time on the viscosity of *Hevea* and polybutadiene solutions (viscosity in arbitrary units).<sup>451</sup>

Although, roughly speaking, our prediction is thus confirmed, and the usual processing operations like vacuum kneading, refining, and milling (over time periods customary in processing crude natural rubber) are unable to change significantly the mechanical properties of polybutadiene or to rectify any deviation in the process of polymerization, the conclusion is, in

<sup>451</sup> S. V. Lebedev, G. G. Kobljanskii, and S. A. Subbotin, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 1, 33 (1933).

<sup>462</sup> A. Ermolaev and I. Telkov, *Zhur. Resinovoĭ Prom.,* 8, 147 (1932).

<sup>463</sup> M. M. Malzenberg, *Kauchuk i Rezina,* 4, No. 7, 20 (1940).

<sup>464</sup> H. Hagen, *Kautschuk,* 14, 203 (1938).

this form, nonetheless too summary. The Karrer plasticity is a composite magnitude, containing two factors, "softness" and "retentivity," and it is possible that the relative constancy of  $P$  is due to a compensation of these two terms. Furthermore, a more detailed investigation shows that the polymers prepared by different methods (emulsion, rod, rodless) show some small individual differences.

#### A. VARIATION OF PLASTICITY COMPONENTS

By measuring softness and retentivity separately, Augert and Kalinin<sup>465</sup> showed that such increase in plasticity  $P$  as can be measured occurs mainly through reduction of "retentivity" (while Hagen<sup>464</sup> has shown that, for the heat softening of Buna S, the factor mainly affected is softness).

In the same way, if instead of a parallel-plate plastometer an extrusion-type plastometer (Marzetti) is used, an increase in plasticity on milling can be observed.<sup>466</sup>

On the other hand, while *Hevea* rubber after a comparatively short time, e. g., 1 hr., is "milled dead" and shows on further milling no increase of plasticity, the change in the plasticity of polybutadiene, small as it is, is increased by more prolonged milling. Thus Smykov<sup>467</sup> found, on a laboratory scale, that if a "rodless" polymer ( $P = 0.25$ ,  $h_2 = 3.13$ ) is plasticized in a Banbury, the maximum plasticity is reached after four hours, at which time the softness is twice that of the initial softness and the recovery is reduced.

#### B. EFFECT OF POLYMERIZATION TECHNIQUE

As has been mentioned, certain small differences in the behavior of differently polymerized polymers can be detected. Maizenberg<sup>463</sup> observed that the plasticity of emulsion-polymerized polybutadiene decreased on milling to a larger extent than that of sodium-polymerized samples. While the rodless polymer shows a slight but continuous increase in plasticity (see above), the rod polymer becomes, on the contrary, less plastic. This is due to the mechanical breaking up and dispersion of harder (overpolymerized or oxidized) regions that are likely to occur in the rod polymer, e. g., Z. B. Ginzburg *et al.* report that repeated refining of the rod polymer reduced the amount of tendons (overpolymerized strands) in a rod polymer from an average of 1.85 to 0.38%.

<sup>465</sup> Quoted from A. A. Ivanov, *Kauchuk i Rezina*, 2, No. 6, 26 (1938).

<sup>466</sup> P. S. Raĭdetskii, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* 4, 131 (1935).

<sup>467</sup> N. N. Smykov, *Kauchuk i Rezina*, 7, No. 4, 128 (1939).

## C. EFFECT OF MILLING TEMPERATURE

The effect of milling temperature is about the same for *Hevea* and polybutadiene: plastication is somewhat slowed down at higher temperatures. But in addition, the milling of butadiene on hot mills leads to the formation of cracks in the sheets (due to surface hardening) which eventually tear; so the milling of polybutadiene must be carried out at lower temperatures (25–45° C.).<sup>462, 468</sup>

## D. EFFECT OF MILLING GAP

The smaller the distance between the mill rollers, the more the plasticity is lowered under otherwise equal conditions, but the effect is not very significant. Thus, Ermolaev and Telkov<sup>462</sup> found that, after identical milling times, the plasticity of the sample (in Williams units) decreased from 5.64 to 4.56 if the distance between the rollers was 5.6 mm., and to 4.18 if the distance was reduced to 1.8 mm.

## E. EFFECT OF MILLING ON THE PHYSICO-CHEMICAL PROPERTIES OF POLYBUTADIENE

Some more information about the effect of milling on polybutadiene can be obtained from a study of the variation of the physicochemical properties of polymer on milling. This investigation was carried out by Zhukov and coworkers<sup>468</sup> on rodless polymers of plasticity  $P = 0.20$ – $0.30$ , of various initial solubility (35–80% insoluble), and on a completely soluble rod polymer of plasticity 0.25 (Karrer).

The rod polymer contained antioxidant. After three hours of milling at 15° C., the intrinsic viscosity of benzene solutions dropped from  $[\eta] = 1.01$  to  $[\eta] = 0.79$ . If the milling was carried out at 60°, the drop in the intrinsic viscosity was much less, from  $[\eta] = 1.05$  to  $[\eta] = 1.01$ .

With rodless polymers, the experiments have been carried out without any antioxidants; with antioxidant added during the milling; and with antioxidant added during the polymerization.

As can be seen from figure IV-7, if no antioxidant is added, the relative viscosity of benzene solutions drops continuously from about 2.0 (for a 0.25% solution) to 1.04–1.00, while the amount of the insoluble material increases from 68 to 96%. The two processes, the scission (decrease of the molecular weight) and the cross linking (formation of insoluble gel) are both very pronounced. At the same time as the amount of insoluble material increases, its "tightness" increases also—in other words, the degree

<sup>468</sup> I. I. Zhukov, V. A. Komarov, E. I. Gribova, and N. L. Selivanova, *Sintet. Kauchuk*, 5, No. 4, 4 (1936).

of cross linking of the gel increases, as can be seen from the decrease in swelling. The maximum imbibition drops from  $Q \sim 15$  to  $Q \sim 9$ , indicating that, while at the start we have one cross link for about every 330 butadiene units, after the milling we have a cross link for about every 160 butadiene units (see page 220).

If the antioxidant is introduced during milling, the picture is about the same so far as the decrease of average molecular weight is concerned, al-

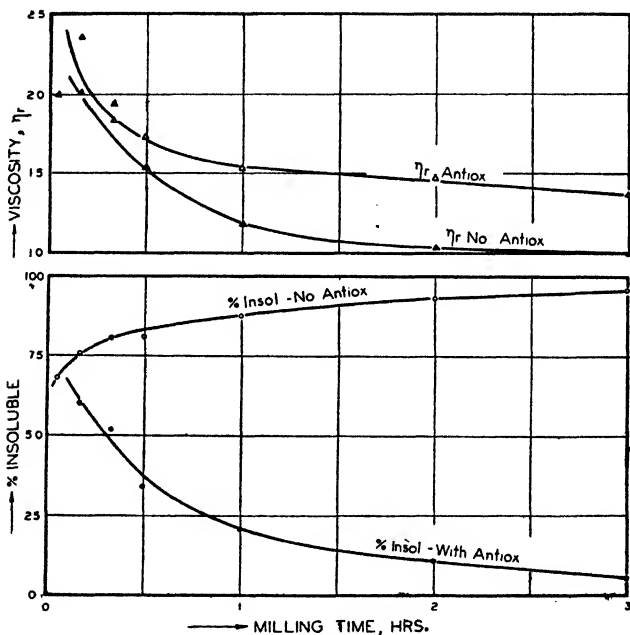


Fig. IV-7.—Effect of milling on solubility and viscosity.<sup>468</sup>

though the drop is not so pronounced (Fig. IV-8); but, in this case, the amount of insoluble material *decreases* on milling, from 60 to 6% after three hours. If the antioxidant had been introduced during polymerization, the decrease in molecular weight would have been much smaller, from 250,000 to 135,000, and the amount of insoluble material increase only slight, from 85 to 93%.

In order to determine if any surface-active oxidation products of low molecular weight are formed during the milling process, Zhukov *et al.* measured the surface tension of benzene solution against water as a func-

tion of milling time. Since no variation in surface tension could be detected, it can be stated that no appreciable amounts of such products are formed.

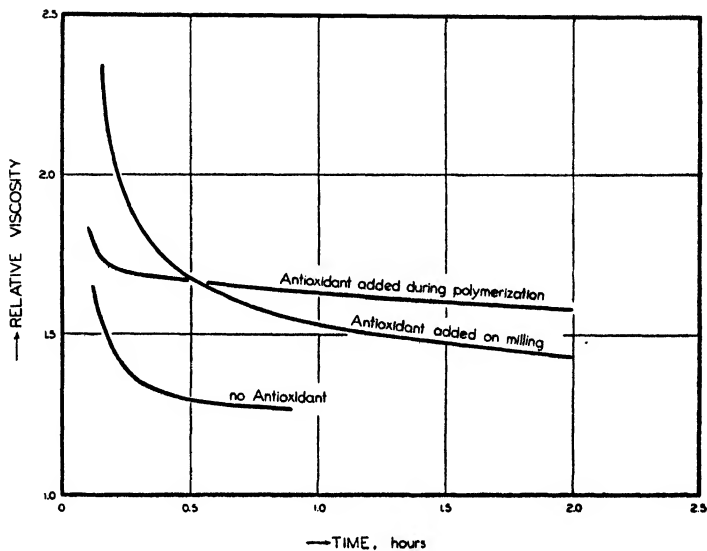


Fig. IV-8.—Relative viscosity of an 0.25% benzene solution of polybutadiene vs. time of milling under different conditions.<sup>468</sup>

#### F. RECOVERY AFTER MILLING

For the time being, no theory can be put forward to explain recovery after milling. Zhukov and coworkers found that, if the polymer is allowed to stand after milling, the relative viscosity increases again, as long as the milling time does not exceed a certain limit. However, it never reaches its initial value. No recovery in viscosity could be observed on a sample milled for three hours.

On the other hand, the amount of insoluble material in samples containing antioxidant decreases with recovery time. Ermolaev and Telkov<sup>462</sup> observed that, when milled polybutadiene is allowed to stand at 25° C. for 72 hours, the plasticized polymers show on the surface a tacky, brilliant film. The plasticity remains unchanged. The tensile strength of the vulcanizate is not affected by the "rest" time, and elongation is somewhat increased, from 740 to 905%—hence allowing a "rest" time for recovery is not useful for polybutadiene.

## 6. Heat Treatment

Since milling cannot affect the softness of polybutadiene polymer, other methods must be devised to bring about the softening of polymers of this type. The most widely used are those for heat softening, either in conjunction with oxidation or in conjunction with a solvent treatment.

### A. OXIDATIVE THERMO-SOFTENING

The oxidative thermosoftening of emulsion polymers is adequately described by Hagen<sup>469, 470</sup> for Buna S. The polymer containing a certain amount of antioxidant (Agerite) is heated for a certain length of time (about 30 min.) to 140–150° C. in a double-jacketed vulcanizer under oxygen or air pressure and under continuous agitation.<sup>471</sup> Experiments show that the main effect of this treatment is to increase softness by a factor as large as 10, while recovery decreases only by a factor of 2. If the process is continued too long, the effect reverses: the polymer hardens again and its recovery goes up. Parallel with this, the insoluble (prior to this treatment) or partly soluble polymer becomes completely soluble; the viscosity of the solution decreases to a minimum, which is reached at about the same time as the maximum softness; the viscosity then increases (cross linking); and the polymer soon again becomes insoluble. Experiments on the influence of temperature on softening for the same heating time (30 min.) show that softening is much more pronounced at 150° than at 115°, but that nothing is gained in using still higher temperatures because the hardening period then begins earlier and the time of maximum softness (minimum hardness) is very sharply defined.

Springer<sup>472</sup> has investigated the kinetics of thermosoftening of Buna S, assuming a superposition of the two processes mentioned above: the scission reaction which decreases the intrinsic viscosity of the polymer and its elastic modulus and increases its plasticity without affecting the chemical structure very much (the iodine number remains constant); and the cyclization reaction (cross linking) which hardens the rubber. In the first stages of thermosoftening, the first reaction is predominant, and in the later stages, the second. Oxygen plays an important part in both. Springer found that the "scission" reaction can be adequately described by the equation:<sup>472</sup>

$$\ln D_0/D = kt^a \quad (4.15)$$

<sup>469</sup> H. Hagen, *Kautschuk*, **14**, 203 (1938).

<sup>470</sup> H. Hagen, *Rubber Chem. Tech.*, **16**, 866 (1943).

<sup>471</sup> See also French Pat. 835,448, issued Dec. 21, 1938 (I. G. Farbenindustrie).

<sup>472</sup> A. Springer, *Kautschuk*, **16**, 72 (1940).

where  $k$  is the rate constant,  $a$  a specific constant,  $t$  the time, and  $D_0$  the initial hardness (Defo units, Continental deformation test, a variation of the Williams plastometer), and  $D$  the Defo hardness, after time  $t$ . The temperature coefficient for the first reaction is 2.2 for 10° C., corresponding to an activation energy of about 24 kcal. per mole, and that for the second reaction is 1.1 to 1.2. The pressure coefficient for the scission reaction is 1.16.

Hagen points out that the process can be greatly accelerated and probably carried out at a lower temperature if certain catalysts accelerating the scission reaction are used. These are not specified; but from the wording of the Gumlich patent<sup>473</sup> it may be implied that these are hydrazine<sup>473-475</sup> derivatives (see page 265).

The softening method apparently used by the Russian industry is described by Poloskin, Apevalkin, and Gotovkina.<sup>476</sup> It comprises heating raw polybutadiene either in the presence of "Eskol," a solvent consisting of polymerized residues of butadiene rectification (in other words, a by-product of the Lebedev process) or in the presence of the products of thermal decomposition of the polybutadiene.

If "Eskol" is used, the rubber is heated *in vacuo* at 90° C. for 3-4 hours. The product of this treatment is said to resemble natural rubber greatly and to have a higher tensile strength than the untreated polybutadiene, whereas the oxidative softening decreases the tensile strength somewhat.<sup>469, 470</sup> If the products of thermal decomposition of polybutadiene are used (boiling point, 220-230° C.) the raw polymer is heated for 5 hours at 140°. The treated polymer is a soft, elastic, sticky, and gummy substance, soluble in benzene and benzine, with the formation of cement.

## B. HEAT HARDENING

The tendency of polybutadiene to cross link in the presence of oxygen can be also used to harden polymers which are too soft.<sup>477</sup> Polymers of plasticity  $P = 0.75$  (Karrer) are treated with water vapor (4-4.5 atm.) in the presence of aldol- $\alpha$ -naphthylamine for one to two hours at 125-165° C. and then dried *in vacuo*. The plasticity of the product decreases to 0.60-

<sup>473</sup> W. Gumlich, U. S. Pat. 2,230,894, issued Feb. 4, 1941 (hydrazones prepared from mono-substituted hydrazines).

<sup>474</sup> I. Williams and C. C. Smith, U. S. Pat. 2,132,505, issued Aug. 15, 1935 (du Pont).

<sup>475</sup> W. F. Busse, U. S. Pat. 2,136,373, issued Oct. 24, 1935 (Goodrich) (hydrazine derivatives).

<sup>476</sup> E. N. Poloskin, S. I. Apevalkin, and L. V. Gotovkina, *Zhur. Resinovoĭ Prom.*, **12**, 829 (1935).

<sup>477</sup> M. Farberov and F. Merzlikin, *Zhur. Resinovoĭ Prom.*, **10**, 123 (1933).



0.68 (Karrer); the tensile strength increases; and the adhesion to metal, deleterious to the milling, is lessened.

### C. HEAT TREATMENT IN THE PRESENCE OF CHEMICALLY ACTIVE GASES

Heat treatment of sodium polybutadiene in the presence of chemically active gases was investigated by Poloskin, Apevalkin, and Gotovkina<sup>476</sup> (ammonia) and by Osipovskii<sup>477</sup> (ammonia, hydrogen sulfide, and sulfuric dioxide). It was found that the effect of these gases on the properties of the polymer can be observed even at 100° C. after 40–48 hours, a temperature at which heating in inactive gases has no effect whatever. In all three cases a sharp decrease was observed in solubility, as well as in plasticity. But, while the samples treated by ammonia and hydrogen sulfide at 100° and 150° showed a deterioration of mechanical properties (tensile strength, maximum elongation, and residual elongation) the samples treated by sulfuric dioxide exhibited a certain increase in the tensile strength of the treads, provided the temperature did not exceed 100° and the treatment period, 24 hours. Treatment at a higher temperature, for example, 150°, or extended over more than 24 hours resulted in a sharp drop in mechanical characteristics. Treatment with sulfuric dioxide increased the curing time.

### D. PROPERTIES OF SOLUTIONS AND CEMENTS

Like natural rubber, polybutadiene is completely miscible with a large number of organic solvents forming highly viscous solutions and cements. However, as will be seen later, the viscosity, and particularly the structural viscosity, of these solutions is less than those of *Hevea* rubber solutions, and the cements are characterized by an absence of tackiness, making them fairly unsuitable for agglutination purposes. Like natural rubber, polybutadiene can be fractionally precipitated from solutions by addition of nonsolvents. It can also be degraded by the effect of chemical and physical agents (oxygen, light, heat). In this section, we shall first give a theoretical picture of rubber molecules in solutions and then try to explain the experimental results in terms of this picture.

#### 1. Theoretical Concepts

##### A. THERMODYNAMICS OF RUBBER SOLUTIONS

As suggested by Weber<sup>478</sup> and Pickles<sup>479</sup> and shown by Staudinger,<sup>480</sup> the rubber molecules can be represented as nonrigid threads which, if left to

<sup>478</sup> C. O. Weber, *The Chemistry of India Rubber*. Griffin, London, 1909.

<sup>479</sup> S. S. Pickles, *J. Chem. Soc.*, 97, 1088 (1910).

<sup>480</sup> H. Staudinger, *Die hochmolekularen organischen Verbindungen*. Springer, Berlin, 1932.

themselves, have a tendency to assume the most probable configurations. It may easily be seen that the stretched configuration which can be realized in only one way is highly improbable, while the most probable forms are coiled configurations, which make full use of the "free rotation" around single bonds and hence can be realized in a large number of ways. We thus have to expect rubber molecules in solution, in the absence of any external force, to assume a "coiled" structure.

The freedom of rotation around the single bonds is in reality limited by potential barriers. The effect these barriers have on the statistical theory of rubber elasticity is discussed by Bresler and Frenkel.<sup>481</sup>

The thermodynamic behavior of any solution can be predicted if we know the partial molal free energies of the components. Since the partial molal free energy  $\Delta\bar{F}$  is defined as:

$$\Delta\bar{F} = \Delta\bar{H} - T\Delta\bar{S} \quad (4.16)$$

where  $\Delta\bar{H}$  is the partial molal heat of mixing and  $\Delta\bar{S}$  is the partial molal free entropy, the problem reduces to that of determining, theoretically or experimentally,  $\Delta\bar{H}$  and  $\Delta\bar{S}$ .

The heat of mixing depends on the interaction between the molecules of the solvent and segments of the rubber molecules that are of the same size as the solvent molecules. Hence, it can be assumed that the Scatchard-Hildebrand rule will apply to rubber solutions in nonpolar solvent in about the same way as to any other solution or mixture of nonpolar compounds.<sup>482</sup> According to Hildebrand,<sup>483</sup> the partial molal heats of mixing are given by:

$$\Delta\bar{H}_1 = V_2\varphi_1^2(\sqrt{E_1/V_1} - \sqrt{E_2/V_2})^2 \quad (4.17a)$$

and

$$\Delta\bar{H}_2 = V_1\varphi_2^2(\sqrt{E_1/V_1} - \sqrt{E_2/V_2})^2 \quad (4.17b)$$

where  $V_1$  and  $V_2$  are the molecular volumes of the two components,  $\varphi_1$  and  $\varphi_2$  ( $= 1 - \varphi_1$ ) are the volume fractions, and  $E_1$  and  $E_2$  are the internal energies of vaporization that can be calculated from the approximate relation:

$$E = \lambda - RT \quad (4.18)$$

where  $\lambda$  is the total heat of vaporization.

<sup>481</sup> S. E. Bresler and J. Frenkel, *Acta Physicochim. U.R.S.S.*, **11**, 485 (1939).

<sup>482</sup> G. Gee, *Trans. Faraday Soc.*, **38**, 419 (1942).

<sup>483</sup> J. H. Hildebrand, *Solubility*. Reinhold, New York, 1936, p. 73.

While the long-chain character of rubber molecules is of no importance for the heat term, it is essential for the entropy term because, in addition to the usual entropy of mixing, the possibility of different configurations of the molecule in the solution is to be considered. This was derived independently by Flory,<sup>484</sup> Huggins,<sup>485</sup> and Miller.<sup>486</sup> Their results are in good agreement; but since Huggins derived his theory for the most general case, we shall use his equations here.

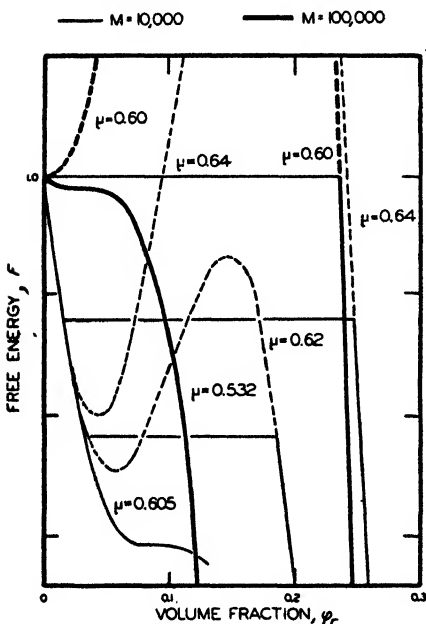


Fig. IV-9.—Free energy  $F$  vs. volume fraction of rubber,  $\phi_r$ , for different values of parameter,  $\mu$  for polymers of different molecular weight ( $M$ ).<sup>488</sup>

$V_r/V_0 = M/\rho_r V_0$  (where  $\rho_r$  = density of rubber). The corresponding partial molal free energies are:

$$\Delta \bar{F}_r = RT \ln \phi_r - RT(m-1)(1-\phi_r) + RTm\mu(1-\phi_r)^2 \quad (4.21)$$

$$\Delta \bar{F}_0 = RT \ln (1-\phi_r) + RT(1-1/m)\phi_r + RT\mu\phi_r^2 \quad (4.22)$$

<sup>484</sup> P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).

<sup>485</sup> M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

<sup>486</sup> A. R. Miller, *Proc. Cambridge Phil. Soc.*, **39**, 54 (1943); *Rubber Chem. Tech.*, **16**, 805 (1943).

<sup>487</sup> J. Frenkel, *Acta Physicochim. U.R.S.S.*, **9**, 235 (1938).

An attempt to apply these general ideas to the properties of rubber solutions and to the question of swelling was made earlier by Frenkel.<sup>487</sup>

As a result of rather long calculations, the partial molal entropy of the rubber becomes:

$$\Delta \bar{S}_r = R[\ln \phi_r - (m-1)(1-\phi_r) + m \cdot 1/\gamma \cdot (1-\phi_r)^2] \quad (4.19)$$

and that of the solvent:

$$\Delta \bar{S}_0 = R[\ln (1-\phi_r) + (1-1/m)\phi_r + 1/\gamma \cdot \phi_r^2] \quad (4.20)$$

where  $\phi_r$  is the volume fraction of rubber,  $\gamma$  is a constant (the "coordination number"), and  $m =$

The corresponding

where  $\mu$  is, for a given temperature, a constant characteristic of the rubber-solvent system.

$$\mu = 1/\gamma + \frac{V_0}{RT} (\alpha_0 - \alpha_r)^2 \quad (4.23)$$

where  $\alpha = \sqrt{E/V}$  as in equations (4.17a) and (4.17b).

The solubility of rubber in a solvent is determined by the shape of the curve obtained when  $\Delta\bar{F}$  is plotted as a function of  $\varphi_r$ . As can be seen from figure IV-9,<sup>488</sup> so long as  $\mu$  is  $< 0.5$  the free energy slope is always negative—that is, the two components are miscible in any proportion. For  $\mu = 0.532$ , the curves corresponding to  $m = 1000$  show an inflection point, and for  $\mu > 0.532$  they have a form analogous to that of van der Waals' isotherms below the critical point. In other words, the system decomposes into two phases, one corresponding to a solution of rubber (with limited solubility) and the other, to a swollen rubber (solution of the solvent in the rubber, "limited" swelling). It also can be seen from the same figure that the critical value of  $\mu$  is higher for smaller molecules ( $m = 100$ ) than it is for the larger ones.

Huggins<sup>488</sup> has shown that, for *Hevea* rubber,  $1/\gamma$  is of the order of 0.3, while Gee<sup>482</sup> determined for the same polymer that  $\alpha = \sqrt{E/V} = 8.15$ . If the corresponding values were determined for polybutadiene, it would be possible to predict *a priori* the "good" solvents and the dependence of the thresholds of precipitation for the different fractions of polybutadiene on the solvents, temperature, and precipitants used.

We understand by "good" solvents those whose mixtures with rubber are characterized by as small values as possible of  $\mu$ . They are to be distinguished from the "ideal" solvents, for which the second and the third terms of the equations just compensate each other, so that the partial free energy of rubber reduces to the entropy term of "ideal" mixing. "Ideal" solvents are generally "poor" solvents."

## B. KINETICS OF DISSOLUTION

When one observes the process of dissolution of sol rubber, it is observed that two processes are involved, which proceed with different rates but overlap each other to a certain extent. First one observes a fairly rapid volume increase of the sample (swelling) and then a slower volume decrease, which asymptotically leads to complete disappearance of the sample. Romashev<sup>489</sup> has given an adequate mathematical description of this com-

<sup>488</sup> M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).

<sup>489</sup> G. I. Romashev, *Kolloid. Zhur.*, **2**, 443 (1936).

posite process. If the process were a pure swelling process,  $Q_m$ ,<sup>490</sup> the maximum imbibition and  $Q_t$ , the imbibition at time  $t$ , the change in  $Q_t$ ,  $dQ_t$ , would be given by:

$$dQ_t = k_s(Q_m - Q_t)dt \quad (4.24)$$

and the swelling rate,  $k_s$ :

$$k_s = \frac{1}{t} \ln \frac{Q_m - Q_0}{Q_t - Q_0} \quad (4.25)$$

This formula must apply to the swelling of rubber gels (see page 220). In the case of the sols, a simultaneous dissolution process takes place, so that  $Q_t$  is not as large as it would be in the case of the pure swelling.

$$Q_t = M_t q_t \quad (4.26)$$

where  $M_t$  is the undissolved fraction and  $q_t$  is the specific volume of the rubber, which is in turn a function of the swelling, so that:

$$\frac{dQ}{dt} = M \frac{dq_t}{dt} + q_t \frac{dM}{dt} \quad (4.27a)$$

and

$$dq_t = k_d(q_m - q_t)dt \quad (4.27b)$$

for an infinite amount of solvent. The rate of dissolution,  $k_d$ , is given by:

$$-\frac{dM}{dt} = k_d M_t \quad (4.28)$$

Combining equations (4.27), (4.25), and (4.28), we obtain:

$$Q_t = Q_m e^{-k_d t} - (Q_m - Q_0) e^{-(k_s + k_d)t} \quad (4.29)$$

an equation which represents fairly accurately the experimental results.

## 2. Experimental Results

### A. SOLUBILITY AND SWELLING

Polybutadiene is soluble in the same solvents as natural rubber, *i. e.*, in all hydrocarbons (except the very lowest ones), chlorinated hydrocarbons (including chloroform and carbon tetrachloride), carbon disulfide, and ether. It would be more correct to state that, with all these solvents, polybutadiene and *Hevea* rubber are *miscible* in all proportions. Like

<sup>490</sup>  $Q$  is generally defined as the number of ml. of solvent absorbed per ml. rubber.

polyisoprene, polybutadiene is insoluble in water, alcohols, and lower ketones. We can therefore deduce that its alpha value (see page 243) is not very significantly different from that for natural rubber. We can predict, on the basis of the theory of Flory and Rehner,<sup>491</sup> that the swelling power of different solvents will be about the same for *Hevea* rubber and for polybutadiene. We can thus predict that polybutadiene vulcanizate will be no more resistant to gasoline and oil than are the vulcanizates of natural rubber. This was found by Faĭnberg, Trankovskaja and Bogomolova,<sup>492</sup> who observed that the resistance of polybutadiene treads to aliphatic solvents is somewhat superior to that of vulcanized natural rubber; its resistance to aromatics is possibly slightly inferior. With rising plasticity of the uncured polymer, and with a constant sulfur content, its solvents resistance in the vulcanized state decreases.

In other words, in terms of the Flory-Rehner theory, the number of cross links formed by the same amount of sulfur is less for the polymer of low molecular weight than for that of high molecular weight.

If the number of cross links is increased (by addition of carbon black, by slight overcure, or by increased sulfur content<sup>493</sup>), the absolute value of maximum imbibition  $Q_m$  is decreased.

## B. RATE OF SWELLING

The rate of swelling of a completely insoluble polymer of plasticity  $P = 0.11$  was determined by Zhukov and Simkhovich<sup>494</sup> using equation (4.25). They found that the maximal swelling corresponded to  $Q_m \sim 15.4$  and that the rate constant was  $k_s = 0.0027 \text{ min.}^{-1}$

## C. RATE OF SOLUTION

The rate of solution depends both on the polymer<sup>495</sup> and on the solvent.<sup>496</sup> The dependence of this rate on the solvent was extensively investigated by Zhukov and coworkers, who used in their experiments the soluble fraction of a sodium butadiene polymer.

<sup>491</sup> P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 512 (1943).

<sup>492</sup> B. A. Faĭnberg, N. I. Trankovskaja, and A. I. Bogomolova, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* **4**, 109 (1935).

<sup>493</sup> I. I. Zhukov and F. M. Simkhovich, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* **4**, 148 (1935).

<sup>494</sup> I. I. Zhukov and F. M. Simkhovich, *Kolloid. Zhur.*, **1**, 11 (1935).

<sup>495</sup> V. Molodenskiĭ and N. Mikhallov, *Zhur. Resinovoĭ Prom.*, **11**, 343 (1934).

<sup>496</sup> I. I. Zhukov, S. L. Talmud, and V. A. Zil'berman, *Sintet. Kauchuk*, **4**, No. 6, 4 (1935).

The polymer, prepared in the laboratory (bottle), had a plasticity of 0.26 (Karrer scale) and was 95% soluble. The experiment was carried out in the dark under an atmosphere of pure nitrogen. The volume of the undissolved polymer was measured as a function of time in a modified Lottermoser<sup>497</sup> apparatus. In this method, a specimen is enclosed between a mercury seal and a permeable membrane. The solvent is poured on the membrane and the level of mercury lowered so that the solvent comes in contact with the polymer. After a given time, the mercury level is brought up, the solvent expelled from the space below the membrane, and the volume of the sample determined.

Figure IV-10 shows a few examples of the volume *vs.* time curves determined by these authors. Table IV-9 gives (for 16 solvents out of 31 measured) the time elapsing before the sample again reaches its initial

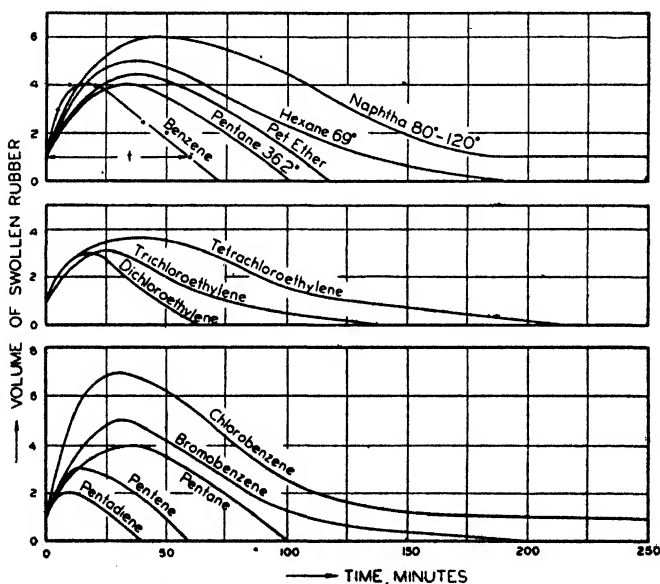


Fig. IV-10.—Rate of dissolution of sol polybutadiene in various solvents.<sup>498</sup>

volume. This time is chosen in preference to the time necessary for complete solution because of the asymptotic character of the solution branch of the curve. Table IV-10 contains the values for maximum imbibition (ml. of solvent absorbed per ml. of rubber) for eight solvents which failed to dissolve the polymer and hence led to a limited swelling:

<sup>497</sup> A. Lottermoser and H. Radestock, *Z. angew. Chem.*, 40, 1506 (1927).

No definite relation between the chemical structure of the solvent and its rate of solution can be established, although it may be stated roughly that the unsaturated and aromatic hydrocarbons dissolve sodium butadiene faster than do the saturated aliphatics. Nor can there be established a definite relation between the amount of swelling and the rate of solution, although here also we may say that the faster the solution the less the swelling.

TABLE IV-9  
EFFECT OF SOLVENTS ON SOLUTION TIME

Solvent	$t_s$ , min.	Solvent	$t_s$ , min.
1,3-Pentadiene	30	Toluene	80
Dichloroethane	40	Pentane	90
Cyclohexane	50	Carbon tetrachloride	110
Carbon disulfide	50	Cyclohexane	120
Vinyl acetate	60	Hexane	130
Ethyl ether	60	Chloroform	160
Xylene	60	Decalin	270
Benzene	60	Chlorobenzene	450

TABLE IV-10  
MAXIMUM IMBIBITION OF POLYMER NONSOLVENTS

Solvent	$Q$ , ml. solvent per ml. polymer
Methanol.....	0
Benzyl alcohol.....	0
Aniline.....	0
Acetone.....	0
Amyl alcohol.....	2
Nitrobenzene.....	2
Methylaniline.....	2.5
Phenyldiazine.....	3

Zhukov and Simkhovich<sup>494</sup> found that, for samples of different plasticity and solubility, the maximum swelling varied from 66 to 2200%, the lower values corresponding to the soluble polymers in general and to polymers of high plasticity value in particular. They deduced from their observations that the values of maximum swelling for different soluble polymers are in reverse relation to the plasticity or in direct relation to the molecular weight. In the light of Romashev's theory, this would mean that the rate of swelling is not strongly influenced by the molecular weight (or the length) of the molecular chains, while the rate of solution decreases when the chain length increases.

The experiments of Zhukov and coworkers were all performed on



sodium-polymerized polybutadiene. Dogadkin and Vinogradova<sup>498</sup> made very similar observations on emulsion-polymerized polybutadiene.

### 3. Precipitation and Fractionation of Polybutadiene from Solutions

Zhukov, Simkhovich, Talmud, and Nikol'skaĭa<sup>499</sup> have very carefully investigated the process of precipitation of polybutadiene from benzene solution. They found that ethyl alcohol can be added to the solution to about 20% in volume without inducing any precipitation. At a concentration between 20 and 30% of ethyl alcohol, depending somewhat on the

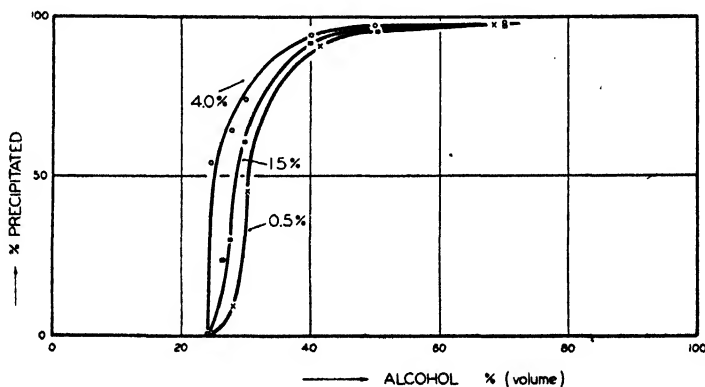


Fig. IV-11.—Precipitation curves from polybutadiene solutions of different concentrations.<sup>499</sup>

concentration of polybutadiene, the solution suddenly becomes cloudy (precipitation threshold) and polybutadiene begins to precipitate. Most of the polymer is precipitated in a very narrow range of ethyl alcohol concentrations, but a certain amount remains unprecipitated even when a large excess of alcohol is added. This substance corresponds to a material of very low molecular weight.

The fractionation of the polymer is then carried out in the following way: Alcohol is added to the solution until a cloudiness is observed; the solution is allowed to stand in the dark and in an inert atmosphere for several hours until all the insoluble fraction precipitates; the solution is carefully decanted from the precipitant; more alcohol is added; and the procedure is repeated as often as necessary to pre-

<sup>498</sup> B. Dogadkin and M. Vinogradova, *Kolloid. Zhur.*, 3, 129 (1937).

<sup>499</sup> I. I. Zhukov, F. M. Simkhovich, S. L. Talmud, and V. P. Nikol'skaĭa, *Sintet. Kauchuk*, 4, No. 2, 6 (1935).

precipitate all but the lowest molecular weight material, which is recovered by evaporating the solution.

The amount of precipitated material (in per cent of the total) as a function of the amount of alcohol added is called the precipitation curve. Its shape is related to that for the molecular weight distribution of the polymer.<sup>500</sup> The precipitation curve naturally depends on the concentration of rubber in the solution: the higher the concentration, the less solvent necessary to precipitate the polymer of the same molecular weight. The shape of such precipitation curves and the effect of concentration are shown

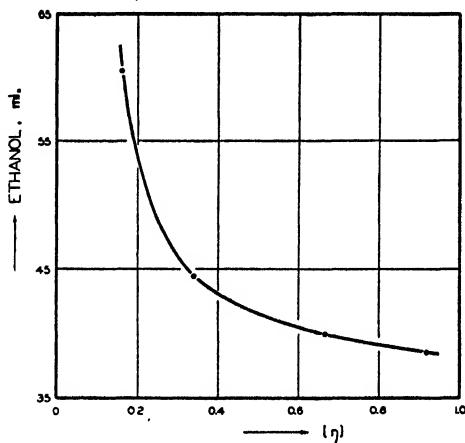


Fig. IV-12.—Relation between the intrinsic viscosity of a fraction in benzene solution and amount of precipitant required.<sup>501</sup>

in figure IV-11 as taken from Zhukov *et al.* The relation between the intrinsic viscosity of the fraction in benzene solution and the number of milliliters of alcohol necessary to precipitate it at room temperature from 100 milliliters of a 0.25% solution are given in figure IV-12, recalculated by the author from the data of Komarov and Selivanova.<sup>501</sup>

Since the molecular weight distribution of the polymer (pp. 211 *et. seq.*) is determined from viscosity and osmotic pressure measurements on fractions obtained by precipitation fractionation, it is important to know whether degradation of rubber takes place on precipitation. Zhukov and coworkers have precipitated and redissolved the same fraction several times and

<sup>500</sup> G. V. Schulz and B. Jirgensons, *Z. physik. Chem.*, **B46**, 105 (1940).

<sup>501</sup> V. A. Komarov and N. P. Selivanova, *Sintet. Kauchuk*, **5**, No. 10, 7 (1936).

found always the same, or very close values, for the intrinsic viscosity of the fraction. It can therefore be concluded that no degradation of the polymer takes place during the fractionation.

TABLE IV-11  
THRESHOLD OF PRECIPITATION FOR DIFFERENT PRECIPITANTS

Precipitant	Threshold, ml. per 100 ml. solution
Methanol.....	24.5
Ethanol.....	31.0
<i>n</i> -Propanol.....	69.0
<i>n</i> -Butanol.....	91.0
Acetone.....	112.5
Benzyl alcohol.....	62.0

Other methods that can be used for fractionation of the polymer are the successive extraction method and the progressive cooling method; but since these have never been used for the fractionation of polybutadiene we do not intend to discuss them in detail. For more information see, for instance, Kemp and Peters.<sup>502</sup>

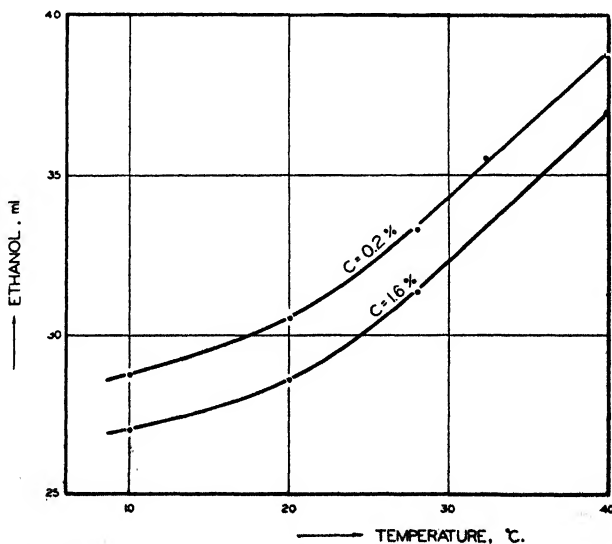


Fig. IV-13.—Precipitation threshold as a function of temperature.<sup>501</sup>

For a given polymer, Komarov and Selivanova<sup>501</sup> found that the amounts of different precipitants in table IV-11, when added to 100 ml. of a 0.25% benzene solution, just produced precipitation.

<sup>502</sup> A. R. Kemp and H. Peters, *Ind. Eng. Chem., Ind. Ed.*, **33**, 1263 (1941).

If we now add to the same solution equal amounts (50–60%) of alcohols of increasing chain length (methanol through hexanol), we must expect that the higher alcohols will precipitate only the polymer of high molecular weight, while the lower alcohols will, in addition, precipitate a sizable portion of lower molecular weight substances. Hence, the intrinsic viscosity of the precipitate precipitated with hexanol will be higher than that precipitated with methanol. This was actually observed by Margaritov and Serebrîanikova.<sup>503</sup>

TABLE IV-12  
RELATION BETWEEN PLASTICITY AND THE PRECIPITATION THRESHOLD

Sample No.	Plasticity	Intrinsic viscosity	Precipitation threshold <sup>a</sup>
1	0.33	2.12	30.5
2	0.33	2.03	32.5
3	0.44	2.17	32.0
4	0.51	1.40	33.5
5	0.51	1.40	31.5
6	0.70	1.29	33.5

<sup>a</sup> Ml. ethanol added to 100 ml. of a 0.25% polybutadiene solution in benzene in order to induce precipitation.

The effect of temperature on the precipitation threshold is shown in figure IV-13.<sup>501</sup> The amount of ethanol (in ml.) to be added to 100 ml. of a 0.25% benzene solution in order to induce precipitation is plotted against the temperature.

No definite connection could be established for the relation of precipitation threshold to plasticity of sample, as can be seen from the table IV-12.<sup>501</sup>

#### 4. Some Theoretical Aspects of the Viscosity of Rubber Solutions

##### A. VISCOSITY OF COLLOIDAL SOLUTIONS

Einstein<sup>504</sup> derived, in 1906, a formula for the viscosity of a colloidal solution,  $\eta_{soln.}$ , relating the viscosity increase over that of the pure solvent to the size and number of colloidal particles, which were assumed to be large (compared with the molecules of the solvent), spherical, and rigid. If

$$\eta_{rel.} = \eta_{soln.}/\eta_{solv.} \quad (4.30a)$$

and

$$\eta_{sp.} = \eta_{rel.} - 1 \quad (4.30b)$$

<sup>503</sup> V. B. Margaritov and L. S. Serebrîanikova, *Kolloid. Zhur.*, **6**, 283 (1940).

<sup>504</sup> A. Einstein, *Ann. Physik*, **19**, 289 (1906); **34**, 591 (1911).

then according to Einstein:<sup>505</sup>

$$\eta_{sp.} = 2.5nv + 7.8(nv)^2 + \dots \quad (4.31)$$

where  $n$  is the number of molecules in a unit volume of solvent and  $v$  the volume occupied by each molecule. Since  $n = aN/M$ , where  $N$  is the Avogadro number,  $M$  the molecular weight of the solute, and  $a$  the amount of solute in grams, the equation can be also written:

$$\eta_{sp.} = 2.5(a/V)(N/M)v \quad (4.32)$$

where  $V$  is the volume of the solution. Now  $a/V$  is the concentration,  $c$ , so that equation (4.32) can be written:

$$\eta_{sp.} = 2.5 c(N/M)v \quad (4.33a)$$

or

$$\eta_{sp.} = 2.5\varphi \cdot c/100 \quad (4.33b)$$

where  $c$  is the concentration in grams per 100 ml. and  $\varphi$  is the volume of 1 gram of solute.

Kuhn<sup>506</sup> calculated  $\eta_{sp.}$  for the case of rod-shaped molecules and found

$$\eta_{sp.} = \left[ 2.5 + \frac{1}{6} \left( \frac{l}{d} \right)^2 \right] \cdot \frac{\varphi c}{100} \quad (4.34)$$

where  $l$  is the length and  $d$  the cross section of the molecule. In the most general way, Sakurada<sup>507</sup> writes:

$$\eta_{sp.} = a\varphi \cdot c/100 \quad (4.35)$$

where  $a$  is a constant depending on the shape of the molecule.

## B. SOLVATION

Einstein's formula was verified for a certain number of colloidal solutions of rigid particles,<sup>508</sup> but when applied to rubberlike molecules the calculated values of  $\eta_{sp.}$  are much smaller than those observed. This is due to the fact that the individual rubber molecules are "solvated," or "swollen," entrapping a fairly large amount of solvent so that their effective volume is

<sup>505</sup> Einstein has given only the first term of this relation. The second term has been calculated by E. Guth, *Kolloid Zhur.*, **74**, 147 (1936), and E. Guth and R. Simha, *ibid.*, **266**.

<sup>506</sup> W. Kuhn, *Z. physik. Chem.*, **A161**, 7 (1932).

<sup>507</sup> I. Sakurada, *Kolloid-Z.*, **64**, 195 (1933).

<sup>508</sup> See, for example, M. Bancelin, *Compt. rend.*, **152**, 1382 (1911).

many times their intrinsic volume. By "solvation" we understand in this case something absolutely different from the "surface solvation" of ions, for instance, although the surface solvation of rubber may exist, according to certain authors.<sup>509</sup>

As emphasized by Flory,<sup>510</sup> the solvation of rubber molecules is due to the fact that the rubber molecule, although threadlike, does not stay in the stretched form once left to itself, but coils up. In so doing the rubber molecule entraps various amounts of solvent molecules, the amount entrapped being largely determined by the heat of interaction with the solvent. "When the heat of mixing of polymer and solvent is (strongly) positive, *i. e.*, in a poor solvent, the polymer molecules should tend to prefer more compact configurations, where intramolecular contacts are more numerous. . . . Therefore, the low intrinsic viscosity in poor solvents very probably reflects changes in average configuration of polymer molecules, dependent upon the solvent medium."<sup>510</sup>

We may thus expect that the specific viscosity will be different in different solvents. Several semiempirical formulas have been proposed in order to determine experimentally the amount of solvation, the most current among them being those derived by Fikentscher and Mark<sup>511</sup> and Fikentscher.<sup>512</sup> Neither formula is based on the picture indicated above. Fikentscher and Mark assume that the polymer molecule is a thread of a length dependent on the molecular weight, that is, surrounded by the solvent in such a way as to become a rotational ellipsoid. The viscosity depends, then, on  $M^2$ , where  $M$  is the molecular weight of the polymer, a conclusion which is not in agreement with the experimental evidence (see pages 214 and 254). Fikentscher and Mark arrive at the equation:

$$\eta_{sp.} = \frac{2.5\varphi c}{100 - \varphi c} \quad (4.36)$$

Somewhat later, Fikentscher proposed another equation which, although without any theoretical foundation, represents the experimental data fairly well:

$$\log \eta_{rel.} = \left( \frac{aK^2}{1 + bKc} + K \right) c \quad (4.37)$$

where  $a$  ( $= 75$ ) and  $b$  ( $= 1.5$ ) are universal constants,  $c$  is the concentration in g. per 100 ml., and  $K$  (called by Fikentscher "Eigen viscosity") is a value

<sup>509</sup> V. B. Margaritov, *Acta Physicochim. U.R.S.S.*, **7**, 707 (1937).

<sup>510</sup> P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

<sup>511</sup> H. Fikentscher and H. Mark, *Kolloid-Z.*, **49**, 135 (1929).

<sup>512</sup> H. Fikentscher, *Cellulosechem.*, **13**, 58 (1932).

characteristic for the given polymer and depending on the solvation. Sakurada<sup>507</sup> gives:

$$f = 92K \quad (4.38)$$

### C. DEPENDENCE ON MOLECULAR WEIGHT

As we have seen, the Fikentscher-Mark formula leads to the proportionality of the specific viscosity with  $M^2$ . Earlier, Staudinger,<sup>518</sup> extrapolating his results obtained on paraffins containing 20–36 methyl groups, postulated that  $\eta_{sp}$  was proportional to the first power of the molecular weight. The experimental work on fractionated samples leads to a law of the form:

$$[\eta] = KM^a \quad (4.39)$$

where  $a \sim 2/3$  (see page 214).

Several attempts have been made to calculate the intrinsic viscosity *a priori* from the mere consideration of the "coil" model described below. The results are dependent on the hypothesis made on the distribution of atoms in the coil and the mechanism of viscosity. Since it is beyond the scope of this book to give the detailed calculations, we shall confine ourselves to an indication of the principles underlying these theories and the results as far as the dependence of the viscosity on molecular weight is concerned.

Hulburt, Harman, Tobolsky, and Eyring<sup>514</sup> assume that the swollen coil behaves like a rigid sphere, the entrapped liquid moving together with the polymer molecule. In this case, the Einstein law applies with the condition that the intrinsic volume of the molecular chain is replaced by the volume it occupies in the solution. For a chain kinked at random, the volume is proportional to  $M^{3/2}$ , so the specific viscosity ought to be proportional to  $M^{1/2}$ . An analogous picture was proposed earlier by Kuhn.<sup>515</sup>

Huggins<sup>516</sup> considers that the liquid inside the coil is not imboilized, but flows, exerting a torque on the segments of the polymer molecule that are on its way, as assumed by Kuhn for diatomic molecules. With this picture, and assuming the segments to be distributed as they are in a randomly "kinked" chain,<sup>516, 517</sup> Huggins finds that the specific viscosity is proportional to the molecular weight itself, as in the Staudinger relation.

<sup>513</sup> H. Staudinger, *Kolloid-Z.*, **51**, 71 (1930). See also *Die hochmolekularen organischen Verbindungen*, Springer, Berlin, 1932.

<sup>514</sup> H. M. Hulburt, R. A. Harman, A. V. Tobolsky, and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943) (p. 417 *et seq.*).

<sup>515</sup> W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934).

<sup>516</sup> M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).

<sup>517</sup> H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

Haller,<sup>518</sup> using the same picture as Kuhn and Huggins, but assuming that the segments are homogeneously distributed in the space the molecule occupies, like gas atoms, found that the specific viscosity is proportional to  $M^{2/3}$ , a result which best represents the observations. It is, however, not impossible that, with certain slight modifications, other theories would lead to the same result.

#### D. DEPENDENCE ON CONCENTRATION. STRUCTURAL VISCOSITY

Two concentration regions are to be distinguished: the domain of low concentrations, in which the molecules of rubber in solution are not touching and for which the Hagen-Poiseuille law is strictly valid; and the region of higher concentration, at which the interaction between the solute molecules can no longer be neglected, the Hagen-Poiseuille law is no longer valid, and the structural viscosity becomes predominant.

(1) In the region of low concentrations, if the Einstein law in its primitive form were valid, one could expect that:<sup>519</sup>

$$\eta_{sp.}/c = \text{const.} \quad (4.40)$$

However, the experimental results and the extension of the Einstein theory by Guth *et al.*<sup>505</sup> have shown that the relation expressed in equation (4.40) is not true. Hence, Staudinger and Heuer<sup>520</sup> suggested the use of a characteristic value,  $(\eta_{sp.}/c)_{c \rightarrow 0}$ , and the extrapolation of the experimental results through the relation:

$$\left(\log \frac{\eta_{sp.}}{c}\right)_{c \rightarrow 0} = \left[\log \left(\frac{\eta_{sp.}}{c}\right)_c\right] - ac \quad (4.41)$$

where  $a$  was presumed to depend on the polymer only. As can easily be seen  $(\eta_{sp.}/c)_{c \rightarrow 0}$  is identical with the "intrinsic viscosity,"  $[\eta]$  first introduced by Arrhenius<sup>521</sup> and Duclaux and Wollman<sup>522</sup> (see also Staudinger and Heuer<sup>520</sup>). The intrinsic viscosity is defined by:

$$[\eta] = \frac{\ln \eta_{rel.}}{c} \quad (4.42)$$

$[\eta]$  is easier to determine than  $(\eta_{sp.}/c)_{c \rightarrow 0}$  because it does not require any extrapolation to infinite dilution provided  $\eta_{rel.}$  is  $< 1.3$ .

<sup>518</sup> W. Haller, *Kolloid-Z.*, **56**, 257 (1931).

<sup>519</sup> H. Staudinger and H. F. Bondy, *Ann.*, **468**, 21 (1929).

<sup>520</sup> H. Staudinger and W. Heuer, *Z. physik. Chem.*, **A171**, 129 (1934).

<sup>521</sup> S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

<sup>522</sup> J. Duclaux and E. Wollman, *Compt. rend.*, **158**, 1580 (1911); *Bull. Soc. Chim.*, **27**, 417 (1920).



(2) When rubber molecules start touching each other, the solution can no longer be expected to obey the Hagen-Poiseuille law:

$$V = \frac{\pi \Delta p}{8\eta l} tr^4 \quad (4.43)$$

where  $V$  is the amount of liquid of viscosity  $\eta$  flowing in a time  $t$  through a capillary of length  $l$  and radius  $r$  under a pressure difference,  $\Delta p$ , because the movement of molecules of the solute is no longer independent. This deviation from Poiseuille's law can be expected and is observed with many colloids; but it is characteristic for rubber solution that the concentrations at which these deviations are observed are particularly low. So, for the smoked sheet,  $\overline{\text{Tsvetkov}}$  and Petrova<sup>523</sup> observed a dependence of viscosity on the flow rate for concentrations as low as  $c = 0.25$  g. per 100 ml. This concentration is not very different from the one we would calculate from a formula derived by Hulburt, Harman, Tobolsky, and Eyring<sup>514</sup> for the concentration at which coils of randomly kinked, threadlike molecules completely fill the volume of solution, if we assume the average molecular weight of *Hevea* rubber to be 800,000.

$$c = \frac{m^{3/2}}{5.18\gamma^{3/2}M^{1/2}} = 0.53 \quad (4.44)$$

where  $m$  is the average molar weight of each carbon atom plus its attached side group (17 in the case of *Hevea*) and  $\gamma$  is the number of carbon atoms per free orientable segment (about 2 for *Hevea*). The agreement is highly satisfactory, particularly in view of the fact that formula (4.44) gives the upper limit for the appearance of the structural viscosity.

#### E. DEPENDENCE OF VISCOSITY ON TEMPERATURE

Two formulas have been proposed to describe the temperature dependence of viscosity, the first:

$$\log \frac{1}{\eta_{\text{rel.}}} = \frac{A}{T} + B \quad (4.45)$$

an empirical relationship found by Dunn<sup>524</sup>; and the second, a relationship derived by Ewell and Eyring<sup>525</sup> on the basis of the absolute reaction rate theory and which is fairly analogous:

$$\log \eta = \log AT^2 + \frac{Q}{2.3RT} \quad (4.46)$$

<sup>523</sup> V.  $\overline{\text{Tsvetkov}}$  and A. Petrova, *J. Tech. Phys. U.S.S.R.*, **12**, 423 (1942).

<sup>524</sup> J. S. Dunn, *Trans. Faraday Soc.*, **22**, 401 (1926). See also W. F. Busse and E. Karrer, *Kolloid-Z.*, **65**, 211 (1933).

<sup>525</sup> R. H. Ewell and H. Eyring, *J. Chem. Phys.*, **5**, 726 (1937).

where  $A$  and  $s$  are constants, and  $Q$  a heat term. While in the formula of Dunn the logarithm of the fluidity is a linear function of  $1/T$ , in the formula of Ewell and Eyring it is the logarithm of the viscosity itself. A more detailed theory of the temperature dependence of the viscosity of high polymer solutions has been given by Powell and Eyring.<sup>526</sup>

## 5. Experimental Results on the Viscosity of Polybutadiene Solutions

### A. DEPENDENCE ON CONCENTRATION IN THE LOW CONCENTRATION REGION

The variation of  $\eta_{sp.}$  with concentration in the range in which  $\eta_{rel.}$  is  $< 1.3$  (where according to Staudinger  $\eta_{sp.}$  is independent of the concentration) was observed by Zhukov, Komarov, and Gribova<sup>527</sup> for benzene solutions of polybutadiene of different plasticity, for Neoprene and for sodium-polymerized isoprene.

TABLE IV-13  
DEPENDENCE OF VISCOSITY OF POLYBUTADIENE-BENZENE SOLUTIONS  
ON CONCENTRATION

Concentration, g./100 ml.	$\eta_{rel.}$	$\eta_{sp.}/c$	$[\eta]^a$
0.23	1.12	0.52	0.50
0.413	1.34	0.82	0.68
0.675	1.72	1.07	0.80
0.98	2.08	1.10	0.75
1.80	4.16	1.76	0.79
2.92	10.8	3.37	0.81
3.69	20.8	5.38	0.83

<sup>a</sup> The slight increase of  $[\eta]$  with concentration is not necessarily a general rule. Philip-poff<sup>530</sup> found for sodium polybutadiene solutions in tetrachloroethane a decrease of  $[\eta]$  with increasing concentration.

Talmud and Sheremet'ev<sup>528</sup> have checked extrapolation formula (4.41) on fractionated sodium-polymerized polybutadiene and have found that the constant  $a$  is not independent of the molecular weight of the fraction but increases with molecular weight.

Table IV-13<sup>529</sup> gives the dependence of  $\eta_{rel.}$ ,  $\eta_{sp.}/c$ , and  $[\eta]$  on concentration for a sodium polybutadiene polymer solution in benzene. We see that

<sup>526</sup> R. E. Powell and H. Eyring, in *Advances in Colloid Science*, Vol. I. Interscience, New York, 1942, p. 183.

<sup>527</sup> I. I. Zhukov, V. A. Komarov, and E. I. Gribova, *Sintet. Kauchuk*, 5, No. 2, 9 (1936); *Kolloid. Zhur.*, 2, 113 (1936).

<sup>528</sup> S. L. Talmud and V. Sheremet'ev, *Kauchuk i Rezina*, 1, No. 4, 6 (1937).

<sup>529</sup> I. I. Zhukov, V. A. Komarov, and V. N. Sokovkina, *Sintet. Kauchuk*, 4, No. 2, 16 (1935); *Kolloid. Zhur.*, 1, 5 (1935).

$[\eta]$  is really independent of the concentration and can be considered as characterizing the polymer-solvent couple. Since, as already stated:

$$(\eta_{sp.}/c)_{c \rightarrow 0} \equiv [\eta]$$

it is preferable to use  $[\eta]$  instead of  $(\eta_{sp.})_{c \rightarrow 0}$  in the molecular weight-viscosity relations discussed above (page 214).

#### B. DEPENDENCE ON MOLECULAR WEIGHT OF THE POLYMER

The experimental results concerning this point have already been discussed on pages 214 *et seq.*

#### C. DEPENDENCE ON TEMPERATURE

In figures IV-14 and IV-15, the dependence of  $[\eta]$  on temperature is given for polybutadiene solutions<sup>529</sup> according to relationships (4.45) and

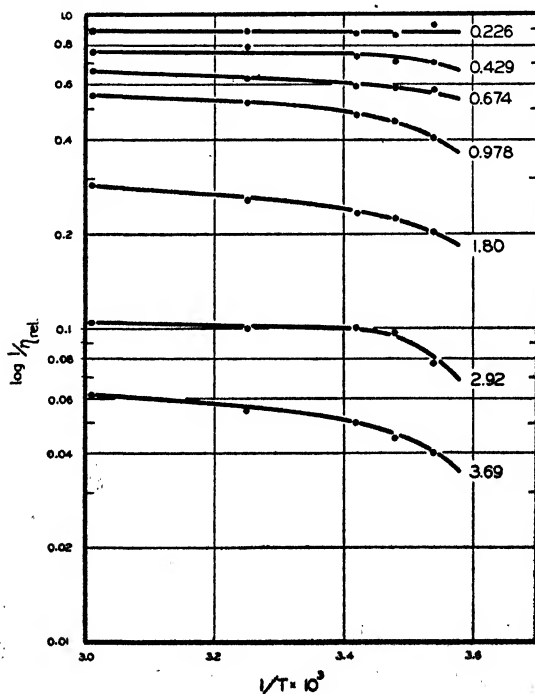


Fig. IV-14.—Dependence of relative viscosity of polybutadiene solutions on temperature (Dunn).<sup>524</sup>

<sup>529</sup> W. Philippoff, *Kautschuk*, 13, 149 (1937).

(4.46). Figure IV-14 corresponds to the theory of Dunn and we can see that this theory holds in a satisfactory way for dilute solutions, while in figure IV-15, corresponding to the theory of Ewell and Eyring, the experimental points are much closer to the theoretical straight-line relationship at high concentrations than at low concentrations. The experimental data are not precise enough to warrant the more detailed calculations required

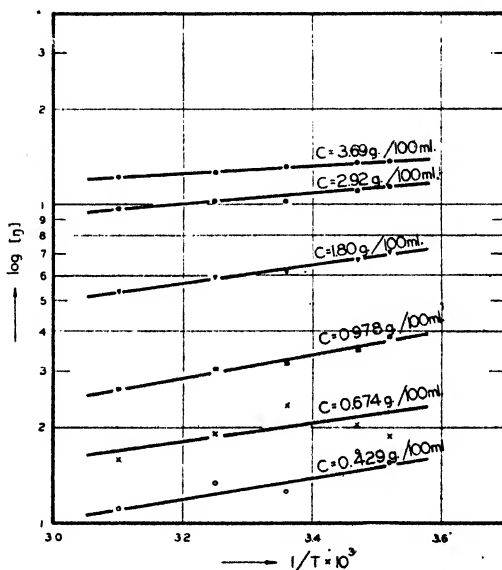


Fig. IV-15.—Variation of the intrinsic viscosity of polybutadiene solutions with temperature (Ewell and Eyring).<sup>525</sup>

by the theory of Powell and Eyring. Some data on the temperature dependence of the viscosity of the polybutadiene solution can also be found in a paper by Staudinger and Fischer,<sup>530a</sup> who found  $[\eta]$  practically independent of temperature between 20° and 60°C.

For emulsion-polymerized polybutadiene, Dogadkin and Vinogradova<sup>498</sup> found that  $\eta_{rel.}$  was independent of temperature between 25° and 60°C.

#### D. SOLVATION AND EFFECT OF SOLVENTS

Zhukov, Komarov, and Sokovnina<sup>529</sup> have calculated from their data on the viscosity of polybutadiene-benzene solutions of different concentra-

<sup>530a</sup> H. Staudinger and K. Fischer, *J. prakt. Chem.*, **157**, 158 (1941).

tion the solvation, " $f$ ," that is, the number of milliliters of solvent "immobilized" by one milliliter of polybutadiene. Their results are given in table IV-14. The values in the third column are calculated on the basis of the formula of Mark and Fikentscher (Eq. 4.36), and the values listed in the fourth column, on the basis of the formula of Fikentscher (Eq. 4.37).

TABLE IV-14  
SOLVATION OF SODIUM-POLYMERIZED POLYBUTADIENE IN BENZENE

Concentration, g./100 ml.	$\eta_{rel.}$	$f$ , calculated from	
		Eq. (4.36)	Eq. (4.37)
0.226	1.12	21.3	20.0
0.429	1.34	31.7	27.3
0.674	1.72	43	32.0
0.978	2.08	44.2	29.1
1.80	4.16	70	31.6
2.92	10.8	124.5	32.6
3.685	20.8	214.5	33.1

With this latter formula, the agreement is definitely better,  $f$  being practically independent of  $c$ , while, when calculated from equation (4.36),  $f$  increases with the concentration, an absolutely impossible trend. As is to be expected, the two formulas give a fairly close agreement for highly dilute solutions.

TABLE IV-15  
SPECIFIC VISCOSITY AND VOLUME SOLVATION OF POLYBUTADIENE  
IN DIFFERENT SOLVENTS

Solvent	$\eta_{sp.}$	$f$ , ml./g.	Solvent	$\eta_{sp.}$	$f$ , ml./g.
Chlorobenzene	0.16	21.8	Decalin	0.59	77.0
Ethyl ether	0.165	22.1	Cyclohexene	0.65	...
Hexane	0.23	51.1	Xylene	0.69	107.0
Pentane	0.25	58.2	Dichlorethylene	0.71	70.0
Piperylene	0.38	79.5	Chloroform	0.76	62.3
Toluene	0.44	69.2	Cyclohexane	1.08	153
Carbon disulfide	0.45	48.3	Carbon tetrachloride	1.38	89.1
Benzene	0.51	77.9			

Although, in his first papers, Staudinger assumed that specific viscosity is independent of the solvent, he soon found this not to be the case. The specific viscosity varied from solvent to solvent, and Staudinger and Heuer,<sup>520</sup> Staudinger and Schneiders,<sup>531</sup> Gee<sup>532</sup> and several others soon made

<sup>520</sup> H. Staudinger and J. Schneiders, *Ann.*, 541, 151 (1939).

<sup>532</sup> G. Gee, *Trans. Faraday Soc.*, 36, 1171 (1940).

the observation that the intrinsic viscosity is highest for the good solvents and the lowest for the poor ones. That the viscosity of polybutadiene solutions is also a function of the solvent was shown by Zhukov, Talmud, and Zil'berman.<sup>496</sup> Table IV-15 gives their data on the specific viscosities of solutions (0.25 g. per 100 ml.) of a polymer of plasticity 0.26 (Karrer) in different solvents, together with the values of  $f$ , the solvation number calculated from the equation of Mark and Fikentscher (Eq. 4.36). We see that specific viscosity depends strongly on the solvent; it varies between chlorobenzene and carbon tetrachloride by a factor as large as 9.

If we now add to a good solvent a small amount of a poor solvent (precipitant), the intrinsic viscosity of the solution decreases long before the point of initial precipitation is reached.<sup>533</sup> Table IV-16 shows the variation of intrinsic viscosity as function of ethanol (ml.) added to 10 ml. of a 0.2% solution of the polymer.

TABLE IV-16

EFFECT OF ADDITION OF A NONSOLVENT ON THE VISCOSITY OF POLYBUTADIENE SOLUTIONS

Ethanol added, ml.	[ $\eta$ ]	
	Benzene solution	Ethyl ether solution
0	0.306	0.175
0.2	0.272	0.164
0.5	0.262	0.169
1.0	0.240	0.143
2.0	0.195	0.095

This effect of precipitants on the viscosity of polymer solutions is well known in the case of *Hevea* rubber.<sup>534</sup> Although, generally speaking, the intrinsic viscosity is highest in the "best" solvents, it should be emphasized that the values of  $f$  in table IV-15 are not exactly in the same order as the swelling power of the solvents. Particularly, cyclohexane was never described as being a better swelling agent than the aromatics.

Another way of evaluating the relative "size" of dissolved rubber molecules is based on measurement of the intensity of light scattering.<sup>535</sup> For particles of the size of rubber molecules, the intensity of scattering,  $I$ , is,

<sup>533</sup> V. A. Komarov and E. I. Gribova, *Sintet. Kauchuk*, **5**, No. 11, 9 (1936).

<sup>534</sup> W. F. Busse in C. C. Davis and J. T. Blake, *Chemistry and Technology of Rubber*. Reinhold, New York, 1937, pp. 203 and 219.

<sup>535</sup> V. B. Margaritov and B. M. Kovarskaja, *Acta Physicochim. U.R.S.S.*, **8**, 279 (1938).

at first approximation, proportional to the volume—or a function of the volume,  $f(v)$ —of the scattering particles and to the difference of the squares of the refractive indices of the solute ( $n_1$ ) and of the solvent ( $n_2$ ):

$$I = K(n_1^2 - n_2^2) \cdot f(v) \quad (4.47)$$

The refractive index,  $n$ , for sodium polybutadiene is  $n_D^{20} = 1.518$  (page 200). In table IV-17 the data of Margaritov and Kovarskaia are given, corrected by us for the difference in the refractive indices.  $I$  represents the intensity of scattering of light in arbitrary units for a 0.25% solution,  $f$  the solvation number, and  $\eta_{sp}$  the specific viscosity for the same concentration (from Table IV-15). We see that this method also gives "molecule sizes" varying with the solvent in the same way as the values calculated from the viscosity.

TABLE IV-17  
RELATIVE SIZES OF "SWOLLEN" RUBBER MOLECULES CALCULATED FROM LIGHT SCATTERING

Solvent	$I$	$n_1^2$	$2.32 - n_2^2$	$K \cdot f(v)$	$\eta_{sp}$	$f$
Hexane	44.5	1.89	0.43	103	0.23	51.1
Octane	59.5	1.96	0.37	160	...	...
Nonane	48.0	1.98	0.34	141	...	...
Toluene	20.0	2.25	0.07	286	0.44	69.2
Benzene	21.5	2.26	0.06	358	0.51	77.9
Trichloroethylene	51.5	2.18	0.14	368	...	...
Dichloroethylene	...	...	...	...	0.71	70.0

## 6. Structural Viscosity

The effect of pressure difference,  $\Delta p$ , on the rate of flow of polybutadiene solution was investigated by Zhukov, Komarov, and Sokovnina,<sup>529</sup> who found that their data obtained on low solutions of sodium-polymerized polybutadiene can be represented by the Ostwald relation:<sup>536</sup>

$$W = kp^n \quad (4.48)$$

where  $W$  is the amount of solution flowing through a capillary in a unit of time,  $p$  is the pressure difference, and  $k$  and  $n$  are constants depending on the solution and the capillary. Dogadkin and Vinogradova<sup>498</sup> obtained analogous results with emulsion-polymerized polybutadiene.

Since the structural viscosity is due to the interaction of rubber molecules, the average molecular weight of polybutadiene is lower than that of *Hevea*, and the weight of each carbon link is higher (because of 1,2 addi-

<sup>536</sup> W. Ostwald, *Kolloid-Z.*, **36**, 99, 157, 248 (1925); **47**, 176 (1929).

tions), it is to be expected that the structural viscosity will appear in higher concentration in polybutadiene solutions than in those of *Hevea*. Using equation (4.44), we can calculate as an upper limit ( $M = 100,000$ ;  $m = 27$ ) as  $c_i = 3$  g. per 100 ml. against 0.5 g. per 100 ml. for *Hevea*. Tsvetkov and Petrova<sup>523</sup> observed no deviation from the Hagen-Poiseuille law in carbon tetrachloride solutions containing 1% polybutadiene and having a definite deviation at 1.5% (see Fig. IV-16). For *Hevea* the corresponding values are 0.188% and 0.25%. Kheraskova and Krūkova<sup>527</sup> observed no deviations from Poiseuille's law in 10% solutions of a polymer of plasticity  $P = 0.5$ , while in *Hevea* rubber a marked deviation was observed in solutions of 0.3 g. per 100 ml.

A different approach to the problem of structural viscosity is taken by Margaritov,<sup>528, 529</sup> who relates it to surface solvation. Margaritov has measured the "apparent fluidity,"  $\varphi = dW/dp$ , for the part of  $W = f(p)$  curves which is linear in  $p$ , as a function of concentration  $c$  and of temperature  $T$ . He found that the variation of  $\varphi$  with temperature is largest for the lowest concentration, and that for *Hevea* solutions in solvents this "apparent fluidity" extrapolates to zero for a certain temperature (independent of the concentration) which is higher than the freezing temperature of the liquid, in other words—several degrees before the solvent freezes the solution becomes a gel. This is the case for *Hevea* solutions in hexane, heptane, trichloroethylene, ethylbenzene, *p*-cymene, and mesitylene. Margaritov

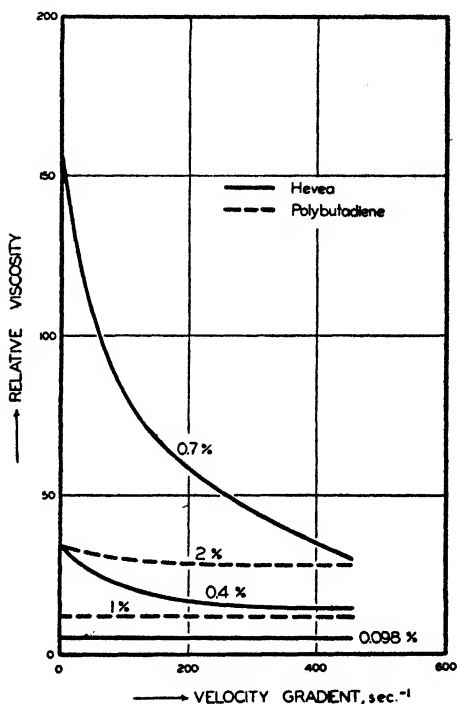


Fig. IV-16.—Relative viscosity of polybutadiene and *Hevea* solutions as a function of velocity gradient.<sup>523</sup>

<sup>527</sup> E. Kheraskova and A. S. Krūkova, *Kauchuk i Rezina*, 1, No. 1, 10 (1937).

<sup>528</sup> V. B. Margaritov, *Acta Physicochim. U.R.S.S.*, 7, 707 (1937).

<sup>529</sup> V. B. Margaritov and I. Epel'baum, *Kolloid. Zhur.*, 6, 311 (1940).



also investigated sodium-polymerized polybutadiene dissolved in hexane and found that the solutions do not gel above the melting point of the solvent, although, like *Hevea* solutions, the  $\varphi T$  curves extrapolate to the same temperature for all the concentrations between  $c = 0.56$  and  $c = 2.25$ .

At this point it is worth noting that the temperature coefficient of the apparent fluidity,  $d\varphi/dT$ , is very sensitive to additions of minute amounts of "surface-active" substances like fatty acids; so the addition of  $2.5 \times 10^{-5}$  mole per liter lauric acid to a 0.1% hexane solution of polybutadiene decreases  $d\varphi/dT$  from  $0.18 \times 10^{-4}$  to  $0.11 \times 10^{-4}$ , while further addition leads again to higher values of  $d\varphi/dT$ . The temperature of gelation remains unaffected. Since at such low concentrations of fatty acids one cannot expect any appreciable change in the solvent properties, Margaritov concludes that surface solvation of swollen molecules plays an important part in the mechanism of the structural viscosity.

In a later paper, Margaritov and Serebrĭanikova<sup>540</sup> found that certain surface-active nitrogen compounds (*p*-aminoazobenzene, chrysoidine, "brown typhophore") decrease the yield value,  $\theta$ , characteristic for the structural viscosity of sodium polybutadiene solution in toluene, while others (*e. g.*, heptylamine, nitraniline red) increase  $\theta$ .

The yield value,  $\theta$ , was introduced by Bingham in order to describe the behavior of liquids exhibiting a non-Newtonian flow. Their behavior is described by:

$$\tau = \theta + \eta(du/ds) \quad (4.49)$$

where  $\tau$  is the shearing stress,  $\theta$  the elastic deformation prior to flow,  $\eta$  the "viscosity," and  $du/ds$  the velocity gradient.

In much the same way, the viscosity of polybutadiene solutions is greatly decreased when they are heated to 160° C. in the presence of azo dyes, *e. g.*, "brown typhophore," particularly if the heating is extended to 180 minutes. This effect of the azo compounds is strongly dependent on their concentration. For instance, in the case of *p*-aminoazobenzene, the yield value is first enhanced and then decreased. The authors explain their observations as being due to the variation of surface solvation, but it seems possible to us that they are due to a chemical scission by certain nitro compounds (see page 281). This explanation can be substantiated by the observations of the same authors<sup>541</sup> on the effect of the heating of polybutadiene in the presence of *p*-nitrosodimethylaniline on its solubility and on the molecular weight distribution: a polymer containing, initially, 58.7% gel and 2.1% of highly soluble material contained, after heating in the presence of 0.44% *p*-nitrosodimethyl-

<sup>540</sup> V. B. Margaritov and L. K. Serebrĭanikova, *Acta Physicochim. U.R.S.S.*, **7**, 707 (1937).

<sup>541</sup> V. B. Margaritov and L. K. Serebrĭanikova, *Acta Physicochim. U.R.S.S.*, **9**, 963 (1938).

aniline, 67.5% gel and 20.6% highly soluble material. When heated with 0.88% of the azo compound, the amount of gel dropped to 16.4% and that of low molecular weight material increased to 62%.

These observations of Margaritov and Serebrñanikova seem to be closely related to the observations of Williams<sup>542</sup> and Williams and Smith<sup>543</sup> on the peptizing effect of phenylhydrazine and of piperidine and its derivatives (as well as of certain other

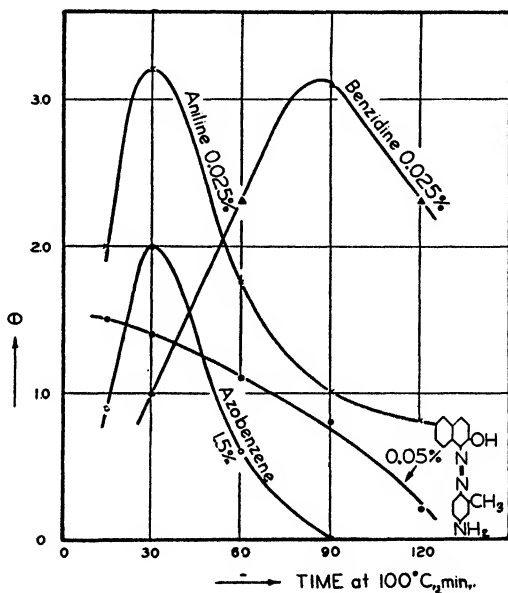


Fig. IV-17.—Effect of heating different substances on the yield point of polybutadiene solutions.

vulcanization accelerators) on *Hevea* sols and gels. Williams found that phenylhydrazine cannot be recovered, nor can the rubber be brought back to its original state. This also indicates that we are dealing rather with a chemical reaction than with a purely physical effect of desolvation or of variation of surface solvation.

Figure IV-17 shows the effect of heating 2% solutions of polybutadiene in toluene at 100° C. in the presence of certain nitro compounds on the yield value of such solutions (data of Margaritov<sup>544</sup>). A definite optimal concentration of addition agent, as well as an optimal time and tem-

<sup>542</sup> I. Williams, *Ind. Eng. Chem., Ind. Ed.*, **26**, 1191 (1934).

<sup>543</sup> I. Williams and C. C. Smith, *Ind. Eng. Chem., Ind. Ed.*, **27**, 1317 (1935).

<sup>544</sup> V. B. Margaritov, *Kauchuk i Rezina*, **1**, No. 3, 9, and No. 5, 3 (1937); **2**, No. 8/9, 23 (1938).

perature of treatment, was found to exist for the maximal yield value. Thus, for example, Margolina<sup>545</sup> found for phenylhydrazine that the structural viscosity reached a maximum ( $\theta = 16$ ) with 2% phenylhydrazine (weight per cent of the weight of rubber) after heating for 2.5 hours at 110° C. (Phenylhydrazine was milled into the rubber prior to dissolving it in benzene.)

An analogous effect of azo dyes on the viscous properties of solutions could also be observed with Neoprene.<sup>546</sup>

### 7. Surface Tension

Only little consideration has been given so far to the theory of the surface tension ( $\sigma$ ) of high polymer solutions. It is, however, not impossible for liquid polymers, as was shown by Eirich and Simha,<sup>547</sup> that a connection exists between viscosity and the surface tension.

The main points of the argument of Eirich and Simha follow: According to Ewell and Eyring<sup>525</sup> the temperature dependence of viscosity is given by the relation:

$$\log \eta = \log AT^s + \frac{Q}{2.3RT} \quad (4.50)$$

If the heat of activation,  $E_{\text{vis.}}^\ddagger$ , of the viscous flow is defined as:

$$E_{\text{vis.}}^\ddagger = R \frac{\ln \eta}{d(1/T)} = Q - sRT \quad (4.51)$$

then Ewell and Eyring could show that:

$$E_{\text{vis.}}^\ddagger = E_{\text{vap.}}/n \quad (4.52)$$

where  $E_{\text{vap.}}$  is the internal energy of vaporization (see page 241) and  $n$  is a number between 3 and 4. On the other hand, the internal energy of vaporization can be calculated from the surface energy  $\sigma V_m^{2/3}$ :

$$E_{\text{vap.}} = F \left[ \sigma V_m^{2/3} - T \frac{d(\sigma V_m^{2/3})}{dT} \right] \quad (4.53)$$

where  $V_m$  is the molar volume.

$F$ , the Stefan factor, is temperature dependent; but the experimental results show that, in the temperature interval of 20–150° C., the variations are small and 2.5 <

<sup>545</sup> I. Margolina, *Kauchuk i Rezina*, 1, No. 10, 26 (1937).

<sup>546</sup> V. B. Margaritov, *Kauchuk i Rezina*, 1, No. 5, 3 (1937).

<sup>547</sup> F. Eirich and R. Simha, *J. Chem. Phys.*, 7, 116 (1939).

$F < 3.5$ . We can, hence, in a very rough approximation, cancel  $F$  against  $n$  and say that the activation energy of the viscous flow is (up to a factor of 0.7–1.0) equal to the molecular surface energy, and that therefore:

$$\eta = Ae \left( \frac{\sigma V_m^{2/3}}{m} - T \frac{d\sigma V_m^{2/3}}{dT} \right) / RT \quad (4.54)$$

From the experimental point of view, Krotova<sup>548</sup> made a comparative investigation of the surface tension of xylene solutions of natural rubber (pale crêpe) and of 'rodless' polybutadiene. Her results are reproduced in figure IV-18. In conformity with previous investigators,<sup>549, 550</sup> she found

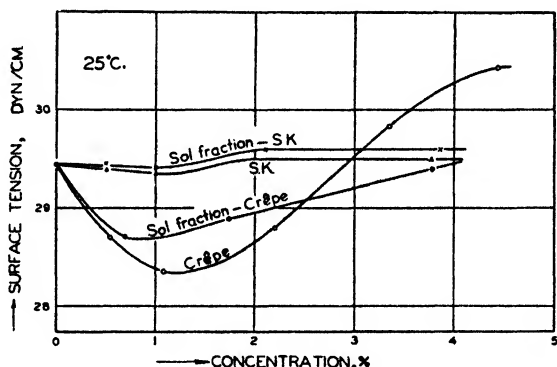


Fig. IV-18.—Surface tension as a function of concentration.<sup>548</sup>

that purified and fractionated pale crêpe at small concentrations (up to 0.7%) lowers the interfacial tension at the xylene–air boundary, while at larger concentrations natural rubber is ineffective. The polybutadiene, in contradistinction, has practically no effect upon surface tension at any concentration. The general character of the graphs for the purified fractionated materials is the same as for the unpurified ones.

An x-ray study<sup>548</sup> of a thin film of solution on a gelatin surface gave, for natural rubber, a diagram which could be interpreted as revealing a certain orientation of its molecules at the surface. No such orientation could be detected in films of polybutadiene solutions.

<sup>548</sup> N. A. Krotova, *Kauchuk i Rezina*, 4, No. 8, 28 (1940).

<sup>549</sup> B. Dogadkin and G. Panchenkov, *Kautschuk*, 7, 198, 217 (1931).

<sup>550</sup> K. Shimada, *Rubber Chem. Tech.*, 8, 69 (1935).

### 8. Shape of Rubber Molecules in Solution. Flow Birefringence

The question may arise as to the actual shape of the "coiled" molecule in solution. While it is often assumed that this shape can be approximated by a sphere, Kuhn<sup>551</sup> deduces from statistical calculations that this approximation is probably too rough. At any given moment the "swollen molecule" can be better approximated by a "bean," the length axis of the bean corresponding to the direction between the two ends of the molecular chain. Under certain conditions the ratio of the axes for the "most probable configuration" was found to be 6:2.3:1. It is recalled that the "most probable configuration" is the configuration which can be realized in the largest number of ways. It is only one of a large number of possible configurations, so that the above axes ratio has only a purely indicative character.

Some experimental evidence on the shape of rubber molecules in solutions can be obtained from streaming birefringence. Boeder<sup>552</sup> and Kuhn<sup>553</sup> have shown that the streaming birefringence observed in solutions of high polymers can be due to the orientation of nonspherical molecules, to a deformation of the spherical molecules by the flow itself, or, more generally, to a combination of both. The two limiting cases can be distinguished experimentally: In the case of the pure deformation birefringence, the extinction angle,  $\alpha$ , is equal to  $45^\circ$  independently of the gradient of velocity; in the case of orientation birefringence,  $\alpha$  is a function of  $a = g/D$ , where  $g$  is the gradient of the flow rate and  $D$  is the diffusion coefficient, depending on the size and shape of the "swollen" rubber molecules.

The experiments of  $\overline{\text{T}}\text{Svetkov}$  and Petrova<sup>554</sup> on the birefringence of solutions of milled and unmilled smoked sheet, "rodless" polybutadiene, butadiene-styrene, Buna S, and Buna N have shown that, in most cases, the birefringence is due, either completely or at least predominantly, to the orientation. The exceptions are: the unmilled Buna N; and, at low values of  $g$ , the sodium polybutadiene polymer. At higher rates of flow, sodium polybutadiene shows, however, the orientation birefringence. By comparing the experimental results with the theoretical curves, values of the diffusion coefficient,  $D$ , can be determined. Once  $D$  is known, one can determine the force of resistance  $F$  opposing the rotation of the particle:

$$F = kT/\eta D \quad (4.55)$$

<sup>551</sup> W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934).

<sup>552</sup> P. Boeder, *Z. Physik*, **75**, 258 (1932).

<sup>553</sup> W. Kuhn, *Z. physik. Chem.*, **A161**, 1, 427 (1932); *Kolloid-Z.*, **62**, 269 (1933).

<sup>554</sup> V. N.  $\overline{\text{T}}\text{Svetkov}$  and A. Petrova, *J. Tech. Phys. U.S.S.R.*, **12**, 423 (1942).

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\eta$  is the viscosity of the solvent.  $F$  is the larger the more prolate the molecule.  $\overline{\text{TS}}$ vetkov and Petrova found that  $F$  was 6 for unmilled smoked sheet, 1 for milled smoked sheet, 0.1 to 0.2 for the various synthetics. This difference in the  $F$  values can, however, be due at least in part to the difference in the molecular weights, since these workers unfortunately did not use fractionated samples of comparable molecular weight.

The same authors have also measured  $\Delta n$ , the difference in the refractive indices for the ordinary and the extraordinary ray. According to the theory:

$$\Delta n = M_0 c_0 \eta g \quad (4.56)$$

where  $c_0$  is the concentration (g. per 100 ml. of solvent),  $\eta$  is the viscosity,  $g$  is the gradient of velocity, and  $M_0$  is the so-called Maxwell constant. It can be shown, on the other hand, that:

$$\Delta n \sim c_0 \Delta \epsilon g \eta F \quad (4.57)$$

where  $\Delta \epsilon$  measures the optical anisotropy. A combination of equations (4.55) and (4.56) shows that:

$$M_0 \sim \Delta \epsilon F \quad (4.58)$$

Hence,  $M_0$  depends on two factors,  $\Delta \epsilon$  and  $F$ , and the interpretation of the results is rather difficult. However, it can be said that both  $\Delta \epsilon$  and  $F$  are the larger the less spherical the molecule—in other words, for molecules of about equal molecular weight, the “swollen” molecule closest to the sphere will have the lowest  $M_0$ .

TABLE IV-18  
FORCE OF RESISTANCE AND MAXWELL CONSTANT FOR VARIOUS POLYMERS

Polymer	Pretreatment	Solvent	$F \times 10^4$	$M_0 \times 10^{12}$
Polystyrene Smoked sheet	...	Carbon tetrachloride	0.5	19
	Unmilled	Carbon tetrachloride	6	5
Butadiene-styrene	Milled	Carbon tetrachloride	1	1.6
	Milled (1941)	Carbon tetrachloride	0.2	1.6
	Milled (1942)	Carbon tetrachloride	0.1	2.9
Buna S	Milled (1941)	Tetralin	0.17	3.2
	Milled (1942)	Tetralin	0.17	4.9
Buna N	Unmilled	Benzene	...	6.7
	Milled (1942)	Benzene	0.1	5.4
Sodium polybutadiene “Rodless”	Plasticity 0.24	Carbon tetrachloride	...	0.52
	Plasticity 0.41	Carbon tetrachloride	...	0.61

Comparison of the data of  $\overline{\text{TS}}$ vetkov and Petrova for polystyrene and *Hevea* rubber makes it appear that the effect of the molecular weight on  $M_0$  is only secondary, and that the conclusions which can be drawn for molecules of the same molecular

weight hold even when the molecular weights of the molecules compared are far from being identical.

Table IV-18 contains the values of  $F$  and  $M_0$  determined by  $\bar{T}$ Svetkov and Petrova for several polymers. ( $F$  is calculated according to Boeder's theory of pure orientation.  $M_0$  decreased with increasing concentration, even at concentrations at which no structural viscosity could be observed. Always, the highest measured value of  $M_0$  is tabulated.)

We can see from table IV-18 that, among the synthetic elastomers, sodium-polymerized polybutadiene has the smallest value of  $M_0$ , and Buna N the highest. According to the above consideration, then, the swollen polybutadiene molecule is the closest to a sphere, and the Buna N molecule is the least spherical.

### 9. Tackiness of Polybutadiene Cements

Among all the properties of rubber cements, their "tackiness" or, more exactly, their agglutination power, is the least well known both theoretically and empirically. As a matter of fact, no explanation of its presence or of its absence based on molecular structure has yet been advanced and

TABLE IV-19  
ENERGY OF PLY SEPARATION FOR MIXTURES OF POLYBUTADIENE AND *Hevea*

Compound No.	Composition		Ply separation, g./cm. <sup>a</sup>	
	Smoked sheet, %	Polybutadiene, %	Uncured	Cured
1	100	0	353	1563
2	90	10	269	1235
3	70	30	287	...
4	50	50	153	851
5	30	70	106	354
6	0	100	73	85

<sup>a</sup> The cement was spread on sheeting, doubled and rolled.

no standard testing procedure has been developed, as, for instance, for plasticity, tensile strength, etc. This lack of information is mainly due to the fact that natural rubber cements have a very high agglutinating power, so that explaining or measuring it, or even the idea of creating it, never became a problem. With the appearance of synthetic rubbers, however, "tackiness" became one of the major problems, for all the polybutadiene-based polymers give cements characterized by a more or less complete absence of "tack" and by a low agglutination power, as may be seen from the

results of Panova and Serebrîakova<sup>555</sup> (Table IV-19) on the separation of plies cemented with solutions of mixtures of natural rubber and polybutadiene in different proportions.

Two ways were open to the Russian synthetic rubber industry: either to rely on the more or less problematic importation of certain quantities of natural rubber for the cements; or to create "tacky" solutions of polybutadiene. It seems that this second possibility was not neglected and several attempts were made, none of them very successful.

#### A. MCBAIN'S THEORY OF AGGLUTINATION

The only theoretical lead existing in the domain of agglutination was developed by McBain and coworkers<sup>556-558</sup> for protein adhesives. According to this theory, the agglutinating power of a cement is determined by three factors:

(a) *the adhesion*, determining the strength of the bond between the layer of cement and the material to be cemented;

(b) *the cohesion*, the inherent mechanical strength of the cement film proper; and

(c) *the autohesion*, the strength of the bond between two contacting layers of the same cement.

McBain and coworkers<sup>556</sup> found that glues having the highest agglutinating power are those containing strongly polar groups ( $-\text{OH}$ ,  $-\text{CO}-$ ,  $-\text{NH}-$ , etc.). Hence, one might have thought the good "tack" of natural rubber to be due to protein admixtures rather than to polyisoprene itself. However, experiments have shown that cements of excellent quality could be prepared from polyisoprene purified by several precipitations, so this explanation had to be abandoned.

If all three properties, *i. e.*, cohesion, adhesion, and autohesion, are equal to or greater than the tensile strength of the materials cemented together, the break will occur in the bulk materials and not along the cemented surface. The site of break then depends on which of the three factors has the lowest tensile resistance: If adhesion is weaker than cohesion, the

<sup>555</sup> A. Panova and V. Serebrîakova, *Zhur. Rezinovoĭ Prom.*, **12**, 360 (1935).

<sup>556</sup> J. W. McBain and J. Alexander, in J. Alexander, *Colloid Chemistry*. Vol. III, Chem. Catalog Co., New York, 1931, p. 9.

<sup>557</sup> J. W. McBain and D. J. Hopkins, *J. Phys. Chem.*, **29**, 188 (1925); **30**, 114 (1926).

<sup>558</sup> J. W. McBain and W. B. Lee, *J. Phys. Chem.*, **31**, 1674 (1927); *ibid.*, **32**, 1178 (1928); *Proc. Roy Soc. London*, **A103**, 606 (1927); *J. Soc. Chem. Ind.*, **46**, 321 (1927); *Ind. Eng. Chem., Ind. Ed.*, **19**, 1005 (1927).



cement will separate from the material; if cohesion or the autohesion is weaker than adhesion, the break will occur in the cement film proper.

#### B. ADHESION, COHESION, AND AUTOHESION OF POLYBUTADIENE

In order to determine which of the three factors considered in the McBain theory is responsible for the low agglutination power of polybutadiene, Zhukov and Talmud<sup>559</sup> attempted to measure each one separately.

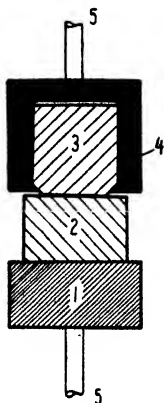


Fig. IV-19.— Attachment to tensile tester for measurement of adhesion and cohesion.<sup>559</sup>

These workers used a small attachment to the tensile tester represented in figure IV-19. The attachment consisted of: two universal joints, 5; a brass clamp, 4, holding a cylinder slug of material to be tested, 3, with an optically ground bottom surface of 1 sq. cm. (test area); and a piece of ebonite, 1, to which a piece of rubber, 2 (test piece of the same shape as used for the parallel-plate plastometer) was attached.

Adhesion was effected by introduction of about 0.02 ml. of benzene to the surface between 2 and 3. Tests were taken at varying time intervals after effecting the bond.

In the case of autohesion, where the test piece was the raw polymer itself, flat surfaces were prepared in the following way: The sample was pasted with benzene on an optically ground glass surface and then torn off. With some experience, perfectly glassy surfaces could be obtained. These surfaces were exposed to air for 24 hours, then pressed together (with 0.02 ml. benzene between the two surfaces) and the autohesion determined 24 hours later.

For cohesion tests, the rubber sample was fixed between two wooden disks.

The results of Zhukov and Talmud are presented in the tables IV-20 to IV-21. As may be seen from table IV-20, there is no marked difference between the strength of adhesion of polybutadiene and of smoked sheet. In both cases the adhesion increased upon compounding. Table IV-21 shows that, in polybutadiene, the cohesion forces are fairly low, of the same order as those of adhesion, and that both decrease with increasing plasticity. This was also observed by Maslovskii and Popova.<sup>560</sup>

Table IV-22 definitely demonstrates that the factors responsible for the low agglutination power of polybutadiene cements are cohesion and, even more so, autohesion. While cohesion can be increased by compounding, autohesion is not influenced at all by the presence of carbon black.

<sup>559</sup> I. I. Zhukov and S. L. Talmud, *Zhur. Resinovoĭ Prom.*, 12, 1005 (1935); *Kolloid Zhur.*, 1, 20 (1935).

TABLE IV-20  
ADHESION OF VARIOUS UNCURED RUBBERS TO DIFFERENT MATERIALS  
EXPRESSED IN GRAMS PER SQUARE CENTIMETER

Surface	Sodium polybutadiene ( $P = 0.330-0.374$ )		Smoked sheet		Neoprene (Sovprene),
	Raw polymer	Standard carbon black mix	Raw polymer	Standard carbon black mix <sup>b</sup>	
Quartz	1387	2920	1303	3030	3140
Steel	1319	3400	1736	.....	.....
Copper	1571	3970	1549	.....	.....
Aluminum	1309	2925	1559	.....	.....
Platinum	1464	3210	1926	.....	.....
Graphite	a	a	3160	.....	.....
Wood	a	a	3256	.....	.....
Ebonite	a	a	3990	.....	.....

<sup>a</sup> Could not be measured because adhesion is stronger than cohesion (tensile strength), which is about 1750 g. per sq. cm. for the raw polymer and 3000 g. per sq. cm. for the carbon black mix. This last figure is dubious; the recalculation to 1 sq. cm. is not quite justified because of the excessive stretch of the samples being tested.

<sup>b</sup> The tensile of uncured smoked sheet-carbon black mix was about 15,000 g. per sq. cm.

TABLE IV-21  
ADHESION TO QUARTZ AND COHESION FOR POLYBUTADIENE SAMPLES  
OF DIFFERENT PLASTICITY

Plasticity	Adhesion, g./sq. cm.	Cohesion, g./sq. cm.
0.330	1425	1898
0.374	1387	1762
0.461	1117	1447
0.505	1022	...
0.650	907	...
0.872	400 <sup>a</sup>	407 <sup>b</sup>

<sup>a</sup> Could not be measured: the tensile strength of the rubber (cohesion) is of the same order as the adhesion.

<sup>b</sup> On actual area attained.

TABLE IV-22  
COHESION AND AUTOHESION OF UNCURED SODIUM POLYBUTADIENE AND SMOKED SHEET  
EXPRESSED IN GRAMS PER SQUARE CENTIMETER

Factor	Sodium Polybutadiene ( $P = 0.374$ )		Smoked sheet	
	Raw	Carbon black compound	Raw	Carbon black compound
Cohesion	1762	3030	4925	5812
Autohesion	1130	1250	3983	3180

The good adhesive and poor cohesive properties of polybutadiene may explain the apparently greater tendency of synthetic rubbers to adhere to steel rolls of mills, as compared with natural rubber.

## C. PLY SEPARATION. EFFECT OF TEMPERATURE AND PRESSURE

Zhukov and Talmud<sup>559</sup> have also investigated the total agglutinating power of polybutadiene and *Hevea* cements by the method of the ply separation of rubberized fabrics. Strips 1 cm. wide were coated with polybutadiene and *Hevea* cements and ply-separated on a dynamometer. The authors concluded from their experiments that the agglutination of "doubled" fabrics is mostly a function of the cohesive strength of the binding layer.

Krotova<sup>548</sup> observed that the resistance to ply separation of surfaces cemented with polybutadiene and those cemented with *Hevea* rubber solution is in both cases sensitive to temperature. At low temperatures, a "freezing" of the cement layer film takes place; its cohesive strength increases while its adhesive power remains substantially unaltered.

The footwear industry is the one possibly most concerned with the problem of ply adhesion in multicomponent rubber articles. In this connection data published by Prikloniskaia<sup>559a</sup> may be of interest. The effect was studied of various operating conditions on the adhesion (before and after cure) of synthetic shoe stocks made with rodless polybutadiene of plasticity  $P = 0.38$ . Of all the conditions investigated (type of cement, pressure and time employed in consolidating the parts, temperature of compound, and its plasticity and storage history) the consolidating pressure had the greatest effect. Thus, without any consolidating pressure virtually no adhesion at all was observed. At a constant pressing time of 15 seconds, it was found that, at a pressure of 20 kg. per sq. cm., the adhesion of the upper stock to sole stock was (cured or uncured) almost double that measured at 5 kg. per sq. cm. If the consolidating pressure was increased to 40 kg. per sq. cm., tearing through the unvulcanized stock took precedence over ply separation. The bond between identical stocks was found to be slightly stronger, compared with heterogeneous compounds. Increasing the time of pressure application beyond 5 sec. had little effect on the quality of the bond obtained. It is, however, suggested that benefits may be derived from applying the pressure at a high rate.

## D. IMPROVEMENT OF AGGLUTINATION POWER

\* Varying attempts have been made toward improving the agglutination power of polybutadiene cements.

• The first method investigated comprised the addition of neutral sub-

<sup>559a</sup> N. Prikloniskaia, *Kauchuk i Resina*, 1, No. 5, 43 (1937).

stances like unsaturated high-boiling substances, some of them by-products of the Lebedev process.<sup>561</sup> Along the same lines is the investigation of the influence of solvents. Here, the results on "tackiness" of solutions are contradictory: While Maslovskii and Popova<sup>560</sup> could detect no influence of the solvent, Talmud and Aleksandrova<sup>561</sup> claimed that certain differences in the cementing power were observed when dissolving polybutadiene in different solvents. Marked increases in resistance to ply separation (3 to 4 times) were observed also when the surfaces were freshened up with "Polymer" solvent, a by-product of the petroleum cracking industry, instead of benzene.

Another method consisted of an incomplete prevulcanization of the cement compound, a process which increases the cohesion and the viscosity of solutions. At the same time, tackifiers like rosin, tar, etc., were added.<sup>562</sup> (Addition of tar without prevulcanization had no effect.<sup>563</sup>) Prevulcanization can also be replaced by addition of ultra-accelerators which allow a rapid cure below 100° C.<sup>564</sup>

Working in the same direction of increasing tack through an increase of the molecular weight of the polymer, Borisoglebskii and Voloschenko<sup>565</sup> observed a certain improvement in the cementing power of polybutadiene cements, if these were exposed to a silent electric discharge in an atmosphere of hydrogen (oxygen-free and dry). The resistance to ply separation after this treatment rose some 20%. No improvement was observed when oxygen was present.

These authors used 13–18,000 kv.<sub>max.</sub> at 50 mm. Hg pressure of hydrogen and extended their experiments over 4 to 4.5 hours. For more details about this "voltization" or "electrification" of polybutadiene solutions, see page 283.

Finally, Margolina<sup>566</sup> obtained favorable results by introducing into the cements nitro compounds which at certain concentrations increase its structural viscosity, *e. g.*, phenylhydrazine (see page 266).

In the opposite direction—the depolymerization of the polybutadiene,

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<sup>560</sup> V. A. Maslovskii and T. N. Popova, *Kozhevenno-Obuvnaia Prom.*, **16**, No. 9, 28 (1937).

<sup>561</sup> S. L. Talmud and V. Aleksandrova, *Zhur. Rezinovoi Prom.*, **12**, 1014 (1935).

<sup>562</sup> A. I. Gorina, *Kauchuk i Resina*, **8**, 37 (1940).

<sup>563</sup> V. A. Maslovskii and T. N. Popova, *Kozhevenno-Obuvnaia Prom.*, **16**, No. 6, 59 (1937).

<sup>564</sup> E. Fabritsiev, G. Bulko, and E. Pakhomova, *Zhur. Rezinovoi Prom.*, **13**, 886 (1936).

<sup>565</sup> P. V. Borisoglebskii and N. Voloschenko, *Kauchuk i Resina*, **6**, No. 3, 9 (1938).

<sup>566</sup> I. Margolina, *Kauchuk i Resina*, **1**, No. 10, 26 (1937).

Fabritsiev and Buiko<sup>567, 568</sup> have reported successful experiments on increasing the "building tack" by addition of *p*-nitrosodimethylaniline to the sodium polybutadiene, coupled with a heat treatment: 10% *p*-nitrosodimethylaniline was milled into the polymer, together with about 5% vaseline oil, and the mixture held at 100° C. for 1–2 hours. The adhesive power was increased by 25–135%. The drawbacks of such a method are the toxicity and the high accelerating power of *p*-nitrosodimethylaniline. We think that it is not impossible that, on depolymerization, *polar* fragments of this compound are built into the polybutadiene molecule, thus increasing the agglutination power (see page 271). In one of the S.K. plants,<sup>569</sup> the polymer is subjected to a heat treatment (3 hours at 90° C. under 600 mm. Hg pressure) in the presence of a polymerized, hydrocarbon-spent liquor. This treatment is said almost to double the agglutination power.

## E. EFFECT OF CHEMICAL AND PHYSICAL AGENTS ON POLYBUTADIENE IN SOLUTION

### 1. Halogenation and Peroxidation

The bromination of polybutadiene in chloroform solution was carried out by Kobljanskiĭ, Gorin, and Krasnobaeva.<sup>569a</sup> Bromine can be added in various proportions. The formula of the completely brominated product corresponds most closely to  $(C_4H_6Br_2)_n$ .

The reactions of polybutadiene with ozone (ozonolysis) and with hydrogen peroxide have already been described (see page 206).

### 2. Oxidation

The oxidation of polybutadiene in solution was fairly carefully investigated, mainly by viscosity measurements. Various factors (temperature, concentration, amount of oxygen) have been systematically varied; the influence of light was observed, as well as the effect of the addition of anti-oxidant. In most cases, oxidation leads to a degradation (depolymerization) of polybutadiene, although the cross-linking reaction (formation of the gel) was also observed in certain cases. Since the results of these investigations are fairly important, we shall consider them more closely.

<sup>567</sup> E. Fabritsiev and G. Buiko, *Zhur. Rezinovoi Prom.*, **13**, 141 (1936).

<sup>568</sup> English Patent 352,080, issued July 30, 1931 (Dunlop Rubber Co. Ltd., London).

<sup>569</sup> Quoted from E. Fabritsiev, *Novosti Tekhniki*, **1936**, No. 3, 35.

<sup>569a</sup> G. G. Kobljanskiĭ, Ū. A. Gorin, and P. N. Krasnobaeva, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka Litera "B,"* **4**, 91 (1935).

## A. AT ROOM TEMPERATURE

Figure IV-20 reproduces the results of Zhukov, Komarov, and Sibirâkova<sup>570</sup> on the degradation of polybutadiene at room temperature under different conditions as a function of time. It may be seen immediately that the rate of degradation is determined by two factors: the amount of oxygen present; and the presence or absence of light, this last factor apparently predominating. However, we must take into consideration that the amount of oxygen necessary to produce degradation is very small, and that

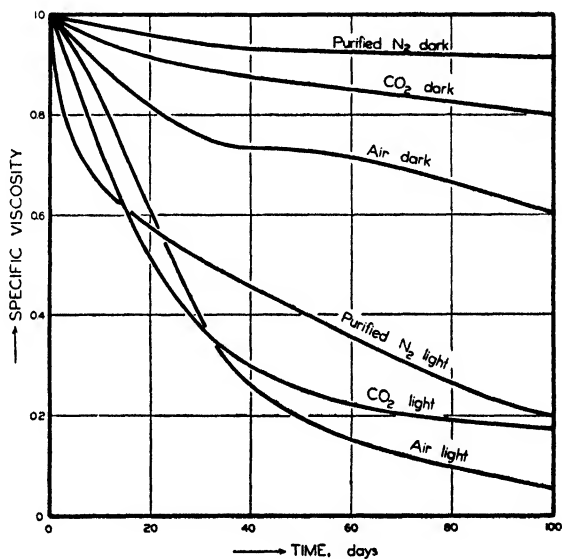


Fig. IV-20.—Degradation at room temperature of sodium polybutadiene solution stored under various gases in light and in the dark.<sup>571</sup>

carbon dioxide and nitrogen always contain minute amounts of oxygen and cannot be considered as oxygen-free unless extensive precautions are taken to purify them. Much the same is true in the vacuum experiments to be discussed later; the amount of oxygen physically adsorbed or chemically bound to the polymer as peroxide can be responsible, at least to a certain extent, for the degradation observed.

These experiments of Zhukov *et al.* were carried out in a sealed viscometer of special construction which allows the determination of viscosity without bringing

<sup>570</sup> I. I. Zhukov, V. A. Komarov, and G. A. Sibirâkova, *Kolloid. Zhur.*, 1, 9 (1935).

the solution into contact with air. For emulsion polybutadiene, Dogadkin and Vinogradova<sup>571</sup> found that, on storage in light in the presence of oxygen, the viscosity decreases; on storage in the dark and in pure nitrogen it increases.

### B. EFFECT OF TEMPERATURE

In determining the effect of temperature, Zhukov, Komarov, Val'ter, and Gribova<sup>572</sup> measured the surface tension at the solution-water interface and the viscosity of benzene solutions of purified polybutadiene after they had been heated in the presence of air for 48 hours at different temperatures: 100°, 115°, 130°, and 150° C.

All the experiments were carried out in sealed test tubes, in duplicate. A carefully purified "wire" polymer and dried benzene were used. The surface tension was measured at the solution-water interface. Solutions of two different concentrations were used.

Their results are presented in table IV-23. We see that the degree of rubber degradation after 48 hours increases very much with temperature; this degradation is indicated by the sharp decrease of intrinsic viscosity as well as by the decrease of surface tension, indicating the formation of oxides of low molecular weight. As long as the kinetics of the process are not established, it is impossible to deduce from these values any indications as to the heat of activation.

TABLE IV-23

EFFECT OF TEMPERATURE ON VISCOSITY AND SURFACE TENSION ( $\sigma$ ) OF SODIUM POLYBUTADIENE SOLUTIONS HEATED IN PRESENCE OF AIR FOR 48 HOURS

Temp., ° C.	Concentration, 0.088 g./100 ml.			Concentration, 0.440 g./100 ml.		
	$\eta_{rel.}$	$[\eta]$	$\sigma$	$\eta_{rel.}$	$[\eta]$	$\sigma$
Control	1.18	1.925	41.4	2.33	1.925	42.8
100	1.16	1.73	41.3	2.11	1.702	42.2
115	1.085	0.97	31.0	1.34	0.67	33.0
130	1.03	0.37	29.2	1.13	0.28	31.5
150	1.005	0.079	23.3	1.105	0.23	20.0

### C. RATE OF THE DEGRADATION REACTION

The only data published so far on the rate of the oxidation reaction of polybutadiene in solution have been determined at 150° C.<sup>573</sup> Further-

<sup>571</sup> B. Dogadkin and M. Vinogradova, *Kolloid Zhur.*, **3**, 129 (1937).

<sup>572</sup> I. I. Zhukov, V. A. Komarov, L. F. Val'ter, and E. I. Gribova, *Sintet. Kauchuk*, **5**, No. 2, 1 (1936).

<sup>573</sup> H. Staudinger, *Proc. Rubber Tech. Conf. London*, 1938, 283.

more, the first point measured already corresponded to a fair amount of degradation: the intrinsic viscosity had fallen from 1.93 to 0.81 for the more dilute solution. It is thus impossible for the time being to establish the reaction mechanism even tentatively. It is interesting to note that the intrinsic viscosity decreases very rapidly in the first 48 hours and that afterwards it increases slightly. It is hard to say if the increase, or at least the leveling off, of the intrinsic viscosity is due to the formation of cross links or an exhaustion of the oxygen, or if it lies within the limits of error which necessarily are fairly high when  $\eta_{rel.}$  becomes of the order of 1.05. Table IV-24 gives the results of Zhukov and coworkers.

TABLE IV-24

DEGRADATION OF POLYBUTADIENE IN BENZENE SOLUTIONS AT 150° C.,  
IN THE PRESENCE OF AIR, AS A FUNCTION OF TIME

Time, hours	Concentration, 0.088 g./100 ml.		Concentration, 0.440 g./100 ml.	
	$[\eta]$	$\sigma$	$[\eta]$	$\sigma$
0	1.925	41.4	1.925	42.8
5	0.81	32.0	0.60	29.0
24	0.42	18.2	0.36	25.3
48	0.08	21.2	0.23	20.0
78	0.21	27.6	0.25	22.3
96	0.16	21.0	0.32	21.5

#### D. EFFECT OF POLYBUTADIENE CONCENTRATION

The effect of the concentration of polybutadiene is not very pronounced.<sup>573</sup> However, the decrease of intrinsic viscosity after heating the solutions for 14 hours at 150° C. is less the higher the concentration. The highest concentration used by Zhukov and coworkers is not very different from the concentration at which the structural viscosity makes its appearance.

#### E. EFFECT OF OXYGEN CONCENTRATION

A lowering of the oxygen concentration, *i. e.*, by evacuation or a replacement of the air by nitrogen, greatly decreases degradation. For instance, the intrinsic viscosity of a polybutadiene solution (0.44 g. per 100 ml.) in benzene when heated for 24 hours at 130° C., decreases from  $[\eta] = 2.00$  to  $[\eta] = 0.42$  in air, to  $[\eta] = 0.57$  in nitrogen and to  $[\eta] = 1.47$  *in vacuo*. This definitely proves that the degradation process is due to an oxidative scission. The viscosity decrease in nitrogen and vacuum may be due to the difficulty of eliminating the oxygen dissolved in the solvent and adsorbed in the rubber (see page 229). However, Dogadkin, Sandomirskij, and



Sharkevich<sup>574</sup> found that 6% solution of the emulsion polymer in toluene, if heated at 105° C. in nitrogen, first shows a slow decrease of viscosity, then an increase. After 250 hours, the solution gels. The gelation process can be accelerated by addition of diazoaminobenzene (polymerization catalyst), thereby reducing the heating time to 100 hours.

#### F. EFFECT OF ANTIOXIDANTS

This conception of degradation as an oxidative scission finds further confirmation in the effect of an addition of antioxidants. To 100 ml. of a polybutadiene solution ( $c = 0.44$  g. per 100 ml.) 0.01 g. antioxidant was

TABLE IV-25  
EFFECT OF ANTIOXIDANTS ON DEGRADATION OF POLYBUTADIENE IN SOLUTIONS

Antioxidant	Initial values		After 24 hours at 130° C.	
	$[\eta]$	$\sigma$	$[\eta]$	$\sigma$
Control	2.00	33.4	0.44	14.4
VGB <sup>a</sup>	1.96	34.1	1.80	29.6
Phenyl- $\beta$ -naphthyl-amine (air)	1.96	34.6	1.80	32.1
Phenyl- $\beta$ -naphthyl-amine (N <sub>2</sub> )	1.96	33.9	1.85	28.9
Nonox	1.96	40.3	1.69	29.6
Aldol- $\alpha$ -naphthyl-amine (air)	1.98	33.7	1.85	29.3
Aldol- $\alpha$ -naphthyl-amine (vacuum)	1.98	32.8	1.88	29.2

<sup>a</sup>A ketone amine.

TABLE IV-26  
EFFECT OF THE CONCENTRATION OF ANTIOXIDANT ON POLYBUTADIENE DEGRADATION

Antioxidant, concentration in per cent of wt. of rubber	Initial values		After 24 hours at 130° C.	
	$[\eta]$	$\sigma$	$[\eta]$	$\sigma$
0.0156	1.93	34.6	0.63	24.3
0.0625	1.93	34.6	1.75	26.8
0.125	1.93	34.6	1.85	30.0
0.250	1.93	34.6	1.88	34.0

added, the mixture sealed in a test tube and heated at 130° C. for 24 hours. As can be seen from table IV-25 all the antioxidants investigated are about equally effective in preventing a decrease of viscosity and of surface tension.

<sup>574</sup>B. A. Dogadkin, D. M. Sandomirskii, and P. Sharkevich, *Kolloid. Zhur.*, **6**, 199 (1940).

The decrease of  $[\eta]$  and of  $\sigma$  is somewhat smaller in nitrogen than in air. Results analogous to those in the table have been found for other commercial antioxidants.

The amount of antioxidant added is important only up to a certain limit, after which the addition of further amounts has only a slight effect on the degradation reaction, as can be seen from the experimental data reproduced in table IV-26. (The experimental conditions are the same as above.)

#### G. EFFECT OF SOLVENTS AND OF SCISSION CATALYSTS

Zhukov and coworkers have also investigated the effect of the solvents on the amount of degradation of polybutadiene in 24 hours at 130° C. As may be seen from table IV-27, the ratio of  $[\eta]$  to  $[\eta]_0$  has different values in different solvents. These differences can be due to a variety of reasons:

(1) As stated on page 214, the molecular weight of the rubber, which is primarily affected by the scission reaction, is related to intrinsic viscosity by the equation:

$$[\eta] = KM^a \quad (4.59)$$

Since the values of  $a$  can be different for various solvents, different values of  $[\eta]/[\eta]_0$  can correspond to the same value of  $M/M_0$ .

TABLE IV-27  
EFFECT OF SOLVENTS ON THE DEGRADATION OF POLYBUTADIENE IN SOLUTION  
IN 24 HOURS AT 130° C.

Solvent	$[\eta]_0$	$[\eta]$	$[\eta]/[\eta]_0$
Chloroform	1.19	0.14	0.12
Carbon tetrachloride	1.26	0.16	0.12
Chlorobenzene	1.38	0.21	0.15
Benzene	2.07	0.35	0.17
Cyclohexane	3.03	0.62	0.20
Dichloroethylene	1.11	0.30	0.27
Xylene	2.29	0.63	0.27
<i>d</i> -Pinene	1.87	0.70	0.38
Cymene	2.24	0.99	0.44
<i>l</i> -Pinene	1.73	1.03	0.59

(2) The solubility of oxygen in the different solvents can vary appreciably.

(3) The most probable explanation is, however, that certain solvents can act as catalyst or even take an active part in the degradation reaction. That such compounds exist has been emphasized in the discussion of heat softening and of the effect of certain nitro compounds on structural viscosity.

Figure IV-21 shows the accelerating effect of an azo dye of the chrysoidine type on the degradation of polybutadiene in toluene solution.<sup>575</sup> We see that, after an inhibition period, the fluidity of the solution containing the dye increases steeply (sharp decrease of viscosity) while the fluidity of the pure sol is scarcely changed.

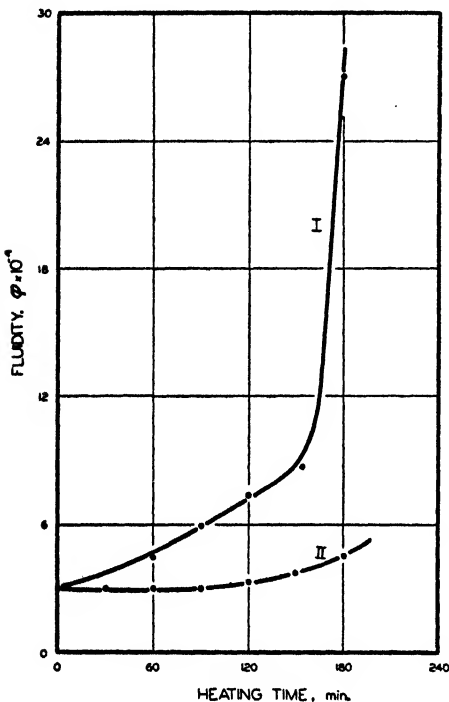


Fig. IV-21.—Fluidity of polybutadiene solution as a function of heating time.<sup>575</sup> I—solution with azo dye addition; II—pure solution.

chemical decomposition yielding a free radical. On the other hand, in solvents photochemically more stable, like petroleum fractions or benzene, the gelling is slow.<sup>573,576</sup>

Concerning the photogelling of polybutadiene, very little experimental material is available. Zhukov, Komarov, and Sibirakova<sup>570</sup> observed that the viscosity of fresh as well as aged polybutadiene solutions (more or less free of oxygen), when exposed to direct sunlight at room temperature, first decreases and then, after about 25 days, increases; after 30 days, the solu-

### 3. Photochemical Effects: Photogelling

In the case of *Hevea* rubber, the effect of sunlight or ultraviolet light is well known: at room temperature, in the absence of all but small amounts of oxygen, the solution gels, that is, the cross-linking reaction leading to a three-dimensional polymer predominates. If larger amounts of oxygen are present, the degradation reaction (scission) dominates the picture, the intrinsic viscosity going down more rapidly than when the solution is kept in the dark. The gelling reaction goes faster in the presence of ketones, aldehydes, carbon tetrachloride, chloroform, and peroxides—all substances which suffer photo-

<sup>575</sup> V. Margaritov, *Acta Physicochim. U.R.S.S.*, 9, 917 (1938).

<sup>576</sup> E. H. Farmer, *Rubber Chem. Tech.*, 15, 774 (1942).

tion gels. In the same lapse of time, the viscosity of solutions kept in diffuse light or in darkness decreases inappreciably.

Pavlushina<sup>577</sup> has investigated the kinetics of the photogelation process somewhat more carefully. She found that the most active light has a wave length somewhat below 4000 Å. The process itself consists of two stages. In the first stage, during the initial absorption, an activation of the polymer takes place which leads to a depolymerization and produces the observed drop in the intrinsic viscosity of rubber solutions. In the second stage, the activated molecules polymerize again, forming a brittle, three-dimensional polymer which is insoluble in benzene (as was also observed by Zhukov *et al.*<sup>572</sup>).

#### 4. Effect of Electrical Field

The changes occurring in dissolved rubber when exposed to silent electric discharges were first investigated by Hock<sup>578</sup> and Fromandi.<sup>579</sup> They observed a breakdown of the molecules, characterized by a considerable decrease in the viscosity of the rubber solutions. Further experiments<sup>580</sup> have shown, however, that this depolymerization occurs only when oxygen is present, if only in traces. If the electrical treatment takes place in oxygen-free inert gases such as hydrogen or nitrogen, on the contrary, a further polymerization takes place.<sup>565, 580</sup>

Hock and Leber<sup>580</sup> have carefully investigated the changes occurring as a function of "electrification time" and of concentration of the polymer for *Hevea* and sodium polybutadiene (Buna 85). The apparatus used is in principle a Siemens ozone tube, purified hydrogen passing through a fritted-glass plate in the discharge chamber, where it breaks up the reaction mixture into fine particles and creates a foam which is greatly increased by application of the high-tension discharge. The liquid circulates between the discharge chamber and two foam traps, where it is broken up and again flows into the reaction chamber. The reaction chamber is 5 mm. wide; the voltage applied is 5000 volts; and the frequency is about 500 cycles per sec. The solutions used were mainly benzene solutions of 3, 6, and 9%.

In order to record the changes occurring, Hock and Leber measured the time of flow through a capillary (for such concentrated solutions in which the structural viscosity is important it is not useful to calculate intrinsic viscosity), the iodine

<sup>577</sup> A. Ā. Pavlushina, *Kauchuk-i Resina*, 3, No. 3, 57 (1939).

<sup>578</sup> L. Hock, *Z. Elektrochem.*, 34, 664 (1928).

<sup>579</sup> G. Fromandi, *Kolloidchem. Beihefte*, 27, 189 (1928).

<sup>580</sup> L. Hock and H. Leber, *Kolloid-Z.*, 90, 65 (1940); *Rubber Chem. Tech.*, 13, 831 (1940).

number, the "perspiration" temperature, and the heat of combustion, and made an elementary semimicroanalysis which proved that the chemical composition of the treated product was identical with that of the initial polymer.

The results for *Hevea* rubber and for sodium polybutadiene, which are given in table IV-28, are fairly parallel. We see from the table that the iodine number (measuring unsaturation) and the heat of combustion both

TABLE IV-28

EFFECT OF ELECTRICAL TREATMENT ON THE PROPERTIES OF POLYBUTADIENE (BUNA 85)

Concentration of benzene solution	Time of exposure, hours	Solubility	Iodine number	"Perspiration" temperature	Heat of combustion, kcal./g.
Solid	0	Soluble	316.2	150	10.615
3	7	Soluble	226.0	164	10.52
6	3	Soluble	220.0	164	10.45
9	1	Soluble	230.0	164	10.44
9	1	Insoluble	160.1	210	8.20

decrease, while the C:H ratio remains the same, which means that more or less extensive cross linking of the polymer at the double bonds takes place—more so for concentrated solutions which form gels than for more dilute ones. This concentration effect appears also in the viscosity data. The

TABLE IV-29

EFFECT OF THE ELECTRICAL TREATMENT ON TENSILE STRENGTH AND MAXIMUM ELONGATION OF BUNA-85 TREAD<sup>a</sup>

Compound	Sulfur content, 2%		Sulfur content, 3.4%	
	Tensile strength, p.s.i.	Maximum elongation, %	Tensile strength, p.s.i.	Maximum elongation, %
Buna 85				
Untreated	1420	400	1980	380
Treated	2020	390	2750	420
Pale crêpe	2520	400	2840	300

<sup>a</sup> Amount of carbon black and the exact recipe are not specified.

time of flow increases by 25% after a 7-hour treatment of a 3% solution of Buna 85, and by 400% in a 9% solution of a lower polymer (Buna 32).

The amount and rate of gelling were found to be the same in toluene, decalin, and benzene solutions. Neither is the reaction influenced by temperature variation between  $-25^{\circ}$  and  $+50^{\circ}$  C., showing that the

changes which take place during these treatments depend fundamentally on the activation of molecules by electrical bombardment. If a partly gelled, 9% polybutadiene solution is separated into sol and gel and the sol is again subjected to electrical treatment, a new gel fraction is formed which has the same characteristics (perspiration temperature and iodine number) as the gel formed in the first treatment. The same is true for the sol fraction.

Hock and Leber also investigated the effect of electrical treatment on the tensile strength and the maximum elongation. Their results pertaining to tread stocks and optimal cure are listed in table IV-29. An improvement of the tensile strength is undeniable.

The favorable effect of electrical treatment on the "tackiness" of polybutadiene solutions has already been discussed (page 275).



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