THE CHLORINATION OF HIGH POLYMERS OF ISOPRENE

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by

Gerard Kraus

Bachelor of Science, Southern Methodist University, 1943
Master of Science, University of Cincinnati, 1945

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

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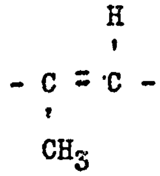
INTRODUCTION

Chlorinated rubber has, in the last thirty years, become a resin of considerable technical importance.

The polymer is produced commercially by passing chlorine into a rapidly circulated solution of the rubber in carbon tetrachloride at reflux temperature. The chlorine content of the commercial products (Parlon, Raclin) ranges from 65-68%; these are hard, brittle powders, soluble in many organic solvents. Because of their strong adhesion to metals and chemical resistance to acids they are used extensively in the paint industry. Other inportant applications are their use in cements for the bonding of rubber to steel and in flame proofing compositions.

During the second world war, with the Allies cut off almost entirely from the world's supply of natural rubber, chlorinated synthetic polyisoprene (Pliochlor) appeared on the market in the United States as a substitute for chlorinated rubber. Simultaneous attempts to chlorinate butadiene-styrene copolymers (GRS) to yield a substitute for chlorinated rubber were unsuccessful. Such products are insoluble gels of considerably lower chlorine content. This appears to be due to the fact that, for high chlorination, the structure must appear in the polymer,



$$-\underset{CH_3}{C}=\overset{H}{C}-$$

i.e. a double bond attached to a carbon atom carrying two additional carbons.

The essential structure for high chlorination appears in natural rubber, gutta percha, balata and synthetic polyisoprene, which is structurally similar to natural rubber, differing in the fact that whereas the unsaturated bonds of natural rubber have essentially the cis configuration, the unsaturated bonds in polyisoprene are partly cis and partly trans. Gutta Percha and Balata represent the other extreme, having unsaturated bonds entirely in the trans configuration.

The synthetic polyisoprene also contains a certain amount of side chains due to 1-2 and 3-4 rather than 1-4 addition during polymerization, whereas rubber is predominantly the 1-4 polymer.

Nevertheless, chlorinated polyisoprene appears to be almost identical with chlorinated rubber. Apparently chlorination in the side chains causes no profound change. The difference in cis-trans configuration might be expected to be of no importance since, after addition of chlorine, the structures are identical.

Because of their interesting adhesive properties, chlorinated rubber and polyisoprene received early attention in an investigation of rubber to metal adhesion conducted at the Applied Science Research Laboratory, University of Cincinnati, under the sponsorship of the Inland Mfg. Division of the Gereral Motors Corporation.

It was discovered that chlorinated polyisoprene and rubber can be used uncompounded to give bonds of excellent strength provided a second coat of highly reinforced rubber cement is used to insure a gradual step-down in hardness.

Unfortunately difficulties are often encountered in the preparation of chlorinated rubber and polyisoprene. Depending on the conditions of chlorination products of widely different properties such as solubility, viscosity in solution, hardness, stability against loss of hydrogen chloride and adhesive properties have been obtained. Considering the complexity of the situation this is not surprising.

The constitution of chlorinated rubber and the mechanism of the chlorination reaction have been subjects of considerable controversy.

As a result very little is known with certainity concerning the unsaturation of chlorinated rubbers of varying chlorine content, their structure, the course of the chlorination and its dependence on the conditions under which the reaction is carried out. The chlorination of synthetic polyisoprene has never been investigated.

Synthetic polyisoprene lends itself better to a fundamental investigation because its physical properties can be controlled in the preparation and because its purification can be achieved with ease. Since synthetic polyisoprene represents the most general example of a high polymer of isoprene, the chlorination of natural rubber and gutta percha should merely represent special cases of the same reaction. For these reasons most of the research reported in this paper was done with polyisoprene.

A study of the mechanism of chlorination of polyisoprene and rubber was thought to be likely to reveal some pertinent information not only with respect to the structure of the chlorinated polymers in general, but also concerning their unsaturation. In fact there appears to be no other method available for estimating the unsaturation of chlorinated polyisoprenes and rubber, since direct methods cannot be relied upon to give correct results for the chlorinated polyisoprenes and rubbers.[1] Iodine chloride addtion to a highly chlorinated polymer may be inhibited by the chlorine atoms already present in the molecule. Ozonolysis would be very difficult, due to the great variety of products that might be expected to form. Spectrophotometric methods are likewise difficult in application. The absorption band due to the non-conjugated double bond lies at about 2000Å -- the very limit of the Beckmann Spectrophotometer.

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(1) Kolthoff, I.M. and Meehan, E. J., Univ. of Minnesota, private communication

At this frequency benzene and chloroform as well as other solvents for chlorinated polyisoprenes are opaque. Heptane, which is usually used in polymer work (GRS, Neoprene), is not a solvent for chlorinated polyisoprenes.

The synthesis of chlorinated polyisoprene and rubber, was found to be dependent on reaction conditions such as light, temperature, and the presence of oxygen, peroxides, and antioxidants. Therefore, a study of the effect of these variables on the chlorination mechanism represents an essential part of the present investigation.

HISTORICAL

The first definite production of chlorinated rubber seems to be that of Engelhard and Day[2] in 1859. They described two processes for chlorinating rubber: (1) subjecting crude rubber to a stream of chlorine, and (2) chlorination of rubber in solution in chloroform, benzene, or naphtha. The identical processes were again patented only four days later by Havemann[3].

Gladstone and Hibbert[4] discovered that chlorine is not only added to the rubber but is also substituted, as shown by the formation of large quantities of hydrogen chloride.

McGavack[5] investigated the amount of hydrogen chloride given off during chlorination using flowmeters to measure the chlorine input and hydrogen chloride evolved. Although the accuracy of measurement was

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(2) Engelhard, G.A. and Day, H.H., British Patent 2,734 (1859).

(3) Havemann, British Patent 2,762 (1859).

(4) Gladstone and Hibbert, J. Chem. Soc., 53, 682 (1888).

(5) McGavack, Ind. Eng. Chem., 15, 961 (1923).

admittedly low, the results gave clear indications that substitution occurs first, practically to the exclusion of addition. McGavack proposed $(C_{10}H_{13}Cl7)_n$ as the empirical formula of chlorinated rubber.

Kirchhof[6] suggested that chlorine first adds to the double bond. One or two molecules of hydrogen chloride are then split off causing reformation of one or two double bonds per isoprene unit. Further addition of chlorine results in a mixture of $(C_5H_6Cl_4)_n$ and $(C_5H_7Cl_3)_n$ which contain 68% and 61.5% chlorine respectively. The completely chlorinated polymer may thus be considered as a mixture of the trichloro and tetrachloro and tetrachloro derivatives.

Nielsen[7] proposed a similar mechanism involving the initial formation of an additive dichloride which splits off hydrogen chloride with reformation of the double bond. The process repeats itself leading to a product containing four chlorine atoms per isoprene unit. In the splitting off of hydrogen chloride, free radicals are formed transiently, and these can unite with one another, In this manner chlorination may result in the formation of a network structure[8]. Daubigny[9] essentially supports Nielsen's theory.

Baxter[10] made a comprehensive study of the physical properties of chlorinated rubber. He also measured the relative amounts of addition and substitution of chlorine. He gives 4.3 atoms of chlorine added and 3.2

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(6) Kirchhof, Gummi. Ztg., 46, 497-8 (1932).

(7) Nielsen, Chlorkautschuk und die uebrigen Halogenverbindungen des Kautschuks, pp. 38-52, Leipzig, Verlag Hirzl, 1937.

(8) Schweitzer, Kautschuk, 15, 152 (1939).

(9) Daubigny, Rev. gen. Matieres plast., 14, 17 (1938).

(10) Baxter, Chem. and Ind., 55, 407-414 (1936).

atoms substituted for two isoprene units as present in the completely chlorinated rubber molecule.

Chlorinated rubbers have very low intrinsic viscosities even if no effort is made to depolymerize the rubber before or during chlorination by mastication[11], oxidation[12], or exposure of the solution to ultra-violet light[13]. Accordingly it was assumed by Staudinger[14] that, in the chlorination of rubber, the labile carbon chains are subject to rupture, which can take place easily in the rubber molecule because of the allyl grouping of the double bonds.

The most recent papers on the constitution of chlorinated rubber and the mechanism of chlorination present results in open contradiction to those reported in the earlier publications. It appears that much of the earlier work was conducted in a rather crude fashion with many important variables uncontrolled and that quite often theories were based on insufficient experimental data.

Staudinger and Staudinger[15] measured the molecular weight of chlorinated rubber and found it to be of the same order of magnitude as that of the rubber hydrocarbon chlorinated. The chlorination was carried out in the strict absence of oxygen. Staudinger, modifying his earlier views, suggests that, since obviously no depolymerization takes place, the low intrinsic viscosity of the products must be attributed to a cyclization of the

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(11) Dyche-Teague, British Patent 305,968 (1929); U.S. Patent 1,819,136 (1931).

(12) Metallges, A.G., British Patent 413,559 (1934).

(13) Chemische Fabrik Bruckau, British Patent 416,252 (1934)

(14) Staudinger, Ber., <u>57</u>, 153 (1924); Kautschuk, <u>17</u>,101 (1941)

(15) Staudinger, H. and Staudinger, Hansjürgen, J.prakt. Chem., <u>162</u>, 148 (1943); Rubber Chem. Tech., <u>17</u>, 15 (1944)

rubber molecule. Thus a shortening of the chain is effected without decreasing the molecular weight, but giving rise to lower intrinsic viscosities.

The work of Bloomfield[16,17] has definitely shown the inadequacy of the chlorination mechanisms proposed by Kirchhof[18] and Nielsen[19]. The chlorination of natural rubber involves a completely substitutive initial reaction, followed by simultaneous substitution and addition, and is terminated by substitution:

$$C_{10}H_{16} + 2\ Cl_2 \rightarrow C_{10}H_{14}Cl_2 + 2\ HCl$$

$$C_{10}H_{14}Cl_2 + 2\ Cl_2 \rightarrow C_{10}H_{13}Cl_5 + HCl$$

$$C_{10}H_{13}Cl_5 + 2\ Cl_2 \rightarrow C_{10}H_{11}Cl_7 + 2\ HCl$$

Carbon-hydrogen analyses[20] on the completely chlorinated rubber favor the empirical formula $C_{10}H_{11}Cl_7$ over the formula proposed by McGavack[21]. Bloomfield suggests that the lower than theoretical unsaturation of chlorinated rubber as observed by iodine chloride titration is due to a cyclization mechanism. Halogenation experiments with dihydromyrcene, squalene, cyclohexene, and 1-methylcyclohexene support this view.

D'Ianni[22] and coworkers compared the physical properties of chlorinated

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(16) Bloomfield, J. Chem. Soc., <u>1943</u>, 289.

(17) Bloomfield, J. Chem. Soc., <u>1944</u>, 114.

(18) Kirchhof, <u>op</u>. <u>cit</u>.

(19) Nielsen, <u>op</u>. <u>cit</u>.

(20) Bloomfield, Farmer, and Miller, Journal Soc. Chem. Ind., <u>54</u>, 26Ct (1935).

(21) McGavack, <u>op</u>. <u>cit</u>.

(22) D'Ianni, Naples, Marsh, and Zarney, Ind. Eng. Chem., <u>38</u>, 1171 (1946).

synthetic polyisoprene with those of chlorinated rubber and found a close similarity between the two polymers.

Field^{23} measured the unsaturation of completely chlorinated polyisoprene and rubber spectrophotometrically. No double bonds could be detected in either polymer.

There is no indication that anyone has studied the mechanism of chlorination of synthetic polyisoprene. Nor has anyone been able to propose a complete chlorination mechanism based on experimental results for natural rubber. The influence of several inportant variables on the chlorination reaction such as light, oxygen, peroxides, and antioxidants has been treated only very incompletely^{24}.

PRESENT INVESTIGATION

A. Scope.

The chlorination of polyisoprene has been studied with regara to

a) additive and substitutive reaction

b) cyclization during chlorination, and

c) unsaturation of the chlorination products.

Intrinsic viscosities were obtained for several of the chlorinated polyisoprenes. These represent supporting evidence for the cyclization.

A mathematical analysis of the cyclization process has been made and a general mechanism for the chlorination has been proposed.

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(23) Field, The Goodyear Tire & Rubber Co., unpublished work quoted in D'Ianni's paper.

(24) Bloomfield, J. Chem. Soc., 1943, 289.

The influence of the following variables on the chlorination of polyisoprene has been investigated:

a) Antioxidants

b) Temperature

c) Small amounts of oxygen

d) Light, and

e) Peroxides

For the sake of comparison some data on the chlorination of natural rubber and gutta percha have been obtained.

Benzene solubilities were determined on all chlorinated polymers.

B. Method.

1. Determination of Substitutive and Additive Reaction.

The relative amounts of substitutive and additive reaction can be easily calculated from the weight of polymer chlorinated, the amount of hydrogen chloride evolved and the chlorine content of the chlorinated product. Let

w = weight of polymer chlorinated in grams

s = weight of chlorine split out as HCL in grams

x = the weight fraction of chlorine in the final product

Then the number of chlorine atoms of substitutive origin N_s per isoprene unit is

$$N_s = \frac{s}{35.45} \cdot \frac{68.1}{w} = \frac{1.92s}{w} \qquad \text{-----------------(1)}$$

where 68.1 is the molecular weight of isoprene and 35.45 is the atomic weight of chlorine.

The total number of chlorine atoms N per isoprene unit is given by

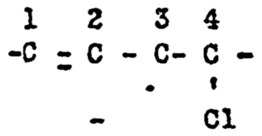
$$N = \frac{68.1 - N_s}{35.45} \cdot \frac{x}{1-x} \qquad \text{-----------------(2)}$$

The number of chlorine atoms of additive origin N_a per isoprene unit is obviously

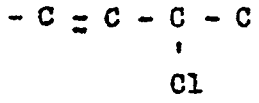
$$Na = N - N_s \qquad \text{--------------------}(4)$$

2. Estimation of Cyclization and Unsaturation. The amounts of additive and substitutive chlorine alone give some indication of possible cyclization of the polyisoprene during chlorination. However, combined with measurements of unsaturation by iodine chloride titration and intrinsic viscosity data considerable supporting evidence can be gathered concerning the cyclization of the molecule.

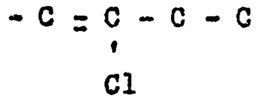
The applicability of the iodine chloride titration to chlorinated olefins and chlorinated rubber has been investigated by Bloomfield[25]. Of the following groups



$$\overset{1}{-\mathrm{C}} = \overset{2}{\mathrm{C}} - \overset{3}{\mathrm{C}} - \underset{\mathrm{Cl}}{\overset{4}{\mathrm{C}}} -$$



$$-\mathrm{C} = \mathrm{C} - \underset{\mathrm{Cl}}{\mathrm{C}} - \mathrm{C}$$



$$-\mathrm{C} = \underset{\mathrm{Cl}}{\mathrm{C}} - \mathrm{C} - \mathrm{C}$$

only the last one inhibits iodine chloride addition to the double bond. Since in the case of chlorinated rubbers of low chlorine content (not more than one Cl atom per isoprene unit) practically all the substitutive chlorine is removable with alcoholic silver nitrate[26], the chlorine must be in the 3-position[27] and the iodine value should give a true measure of unsaturation.

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(25) Bloomfield, J.Chem.Soc., 1944, 114

(26) ibid

(27) Ziegler et al., Ann. 551, 80 (1942)

With chlorinated polyisoprenes containing more than one chlorine atom per isoprene unit the applicability of the iodine chloride method becomes very doubtful.

The percent unsaturation of a chlorinated isoprene polymer as determined from the iodine value, is calculated as follows:

$$\text{Iodine value} = \frac{\text{number of centigrams of iodine taken up}}{\text{wt. of sample}} \quad \text{------(5)}$$

Let M_0 be the base molecular weight of the polymer. Then for 100% unsaturation the iodine value would be

$$I_{100} = \frac{126.9 \times 2 \times 100}{M_0} \quad \text{--------------(6)}$$

Thus the percent unsaturation u is

$$u = \frac{I}{I_{100}} \times 100 = \frac{I\ M_0}{253.8} \quad \text{--------------(7)}$$

M_0 can be calculated from the amount of chlorine in the polymer (N) and the amount of HCL split out ($=N_S$).

M_0 = base molec. wt. of polyisoprene - loss of hydrogen weight of chlorine introduced ---------------(8)

Thus

$$M_0 = 68.1 - N_s \times 1.008 + N \times 35.45 \quad \text{---------------(9)}$$

Substituting (9) into (7) we obtain

$$u = \frac{I\ (68.1 - 1.008\ N_s + 35.45\ N)}{253.8} \quad \text{--------------(10)}$$

A decrease in unsaturation upon chlorination may be ascribed to two factors - cyclization and additive reaction. Denoting by N_c the number of double bonds per isoprene unit lost due to cyclization and by u_0 the initial unsaturation of the polymer chlorinated, the percent unsaturation can be written as

$$u = u_0 - (N_c + \frac{Na}{2})\ 100 \quad \text{--------------(11)}$$

The degree of cyclization N_c can then be calculated from equations (10) and (11). It must be borne in mind however, that equation (10) can only be expected to give reasonably accurate results for polymers of relatively low chlorine content (below 40% Cl). For polymers containing over 40% of chlorine equation (11) can be used to calculate the unsaturation provided N_c can be estimated independently. It will be shown that it is possible to do this.

It has been found by Staudinger and Staudinger[28] that when rubber is chlorinated in the absence of oxygen and light, no appreciable depolymerization takes place. Introduction of chlorine into the chain should cause no change in intrinsic viscosity provided the solvation of the chlorinated rubber molecule is the same as for the rubber and no shortening of the chain by cyclization takes place. Experiments with squalene and squalene hexa-hydrochloride show that the intrinsic viscosity increases slightly with introduction of chlorine apparently due to the fact that the chlorine atoms are more solvated than the hydrogen atoms. Consequently, if no cyclization took place in the chlorination of polyisoprene or rubber one would expect the intrinsic viscosity to increase with the degree of chlorination. If, however cyclization occurs, leading to a reduction in chain length, a drop in intrinsic viscosity might be expected.

This provides another method for determining whether, and at what stage in the chlorination, cyclization occurs. There are two limitations to the method: (1) chlorinated polyisoprenes and rubbers of low chlorine content (approximately below 50% Cl) become insoluble once they are isolated from solution, and (2) at approximately 45% Cl a gel is formed

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(28) Staudinger H, and Staudinger Hansjürgen, op. cit.

in the reaction which can only be broken down by further chlorination. The first difficulty can be overcome by making the intrinsic viscosity determination on the polymer in the original carbon tetrachloride solution without first isolating the dry polymer. The second limitation definitely rules out the method for polymers of more than 45% chlorine content. Fortunately, as will be shown later, the cyclization is essentially complete below 45% Cl.

C. Results and Discussion.

1. Chlorination of Polyisoprene in the Dark and in Absence of Oxygen.

When polyisoprene in dilute carbon tetrachloride solution is chlorinated slowly in the absence of light and oxygen the reaction proceeds initially in a strictly substitutive manner. Addition sets in slowly after about 0.8 mol of chlorine have been reacted with one base molecular weight of polymer, and eventually becomes the dominant mode of reaction. Addition ceases abruptly after reaction of 2.3 mols of chlorine and further chlorination is again strictly substitutive.

This behavior is well illustrated by the data of Table 1. As an additional safeguard against oxidation 0.10 mol percent of phenyl-β-naphthylamine was used in the chlorination experiments. By chlorinating slowly the temperature was kept within the range from 25-30°C. Nitrogen was used as a diluent for the chlorine in order to flush out the hydrogen chloride formed and prevent its secondary addition to the rubber molecule.

Table 1

Chlorination of Polyisoprene in the Dark and in Absence of Oxygen

Mols of Cl_2 reacted per base mol of polyisop.	% Chlorine Product	Total Cl Atoms per isoprene unit	Substitutive Cl atoms per isoprene unit	Additive Cl atoms per isoprene unit
0.38	16.6	0.38	0.38	0.00
0.46	19.0	0.46	0.46	0.00
1.33	43.6	1.46	1.19	0.27
1.48	46.8	1.65	1.30	0.35
1.79	52.6	2.08	1.51	0.57
2.13	58.4	2.62	1.65	0.97
2.28	60.3	2.84	1.71	1.13

When nitrogen containing 0.3% of oxygen by volume was used no effect could be observed as long as antioxidant was used (Table 2). The data of Tables 1 and 2 are plotted in Figure 1.

Table 2

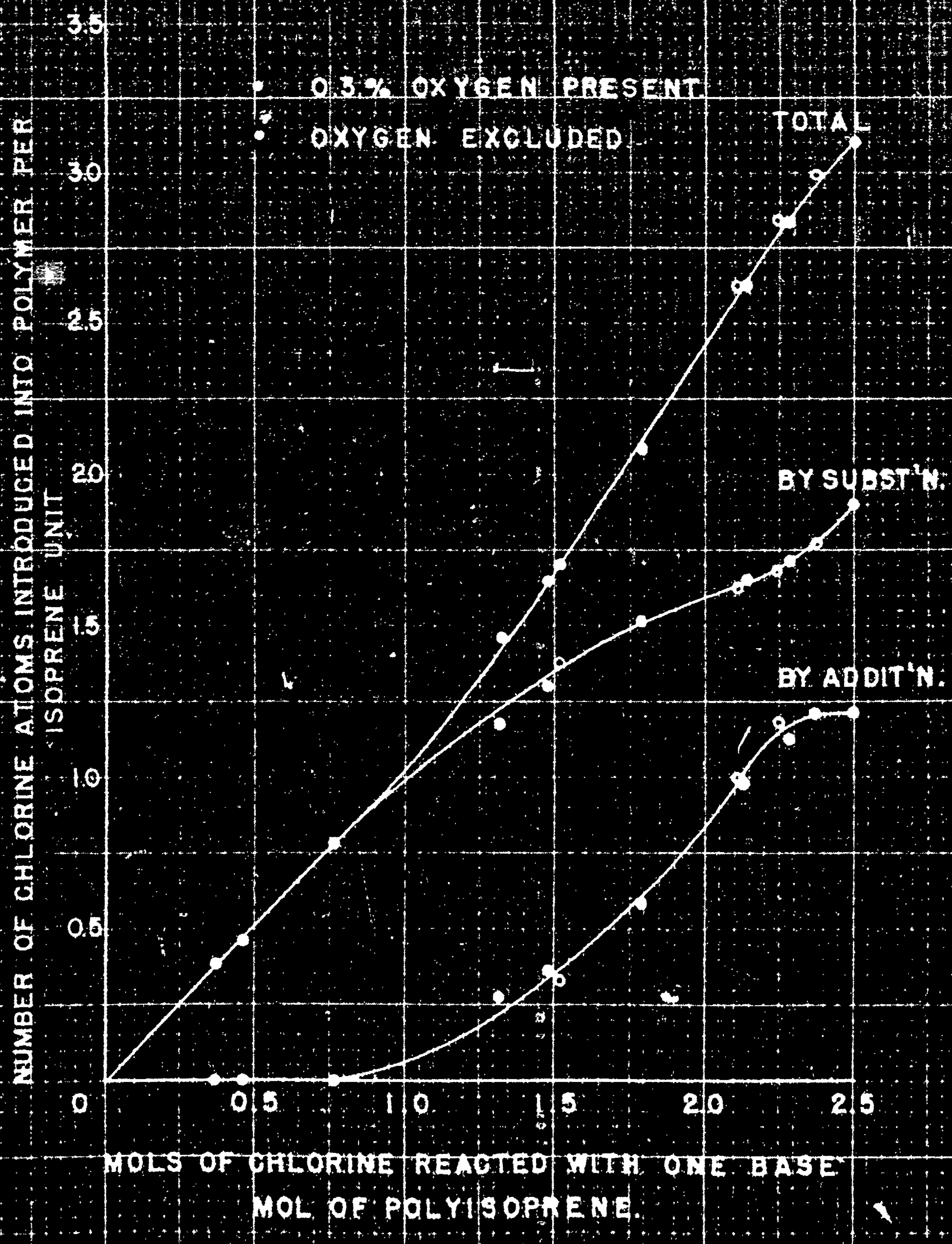
Chlorination of Polyisoprene in the Dark with Antioxidant in the Presence of Small Amounts of Oxygen

Mols of Cl_2 reacted per base mol of polyisop.	% Chlorine Product	Total Cl Atoms per isoprene unit	Substitutive Cl atoms per isoprene unit	Additive Cl atoms per isoprene unit
0.77	28.6	0.76	0.78	0.00
0.90	32.6	0.91	0.89	0.02
1.43	45.6	1.57	1.30	0.27
1.53	47.6	1.70	1.37	0.33
1.97	56.0	2.38	1.56	0.82
2.12	58.3	2.62	1.63	0.99
2.25	60.3	2.84	1.67	1.17
2.37	61.5	2.98	1.77	1.21
2.50	62.5	3.10	1.89	1.21

Chlorination products of relatively low chlorine content (0 - 40% Cl)

FIG. I

EXTENT OF SUBSTITUTIVE AND ADDITIVE CHLORINATION OF POLYISOPRENE IN DARKNESS WITH ANTIOXIDANT AT 30° C.



still possess some rubberlike characteristics. These of course decrease with increasing chlorine content. There is a tendency for these polymers to split out hydrogen chloride upon aging.

Products of 40 to 55% Cl are tough white solids having practically no rubberlike characteristics. They are thermoplastic and quite stable to splitting out of hydrogen chloride at ardinary temperatures.

Polymers of more than 55% chlorine content are white, flaky resins, are only slightly thermoplastic and can be molded into hard, brittle solids.

Inspection of the data shows that the total amount of chlorine which can be added to the double bonds is only somewhat more than one half of the amount that could be expected to add on the basis of the initial unsaturation of the polyisoprene chlorinated. Since the unsaturation of fully chlorinated polyisoprene is zero[29], about half of the unsaturation is lost due to causes other than addition of chlorine to the double bonds. A cyclization involving two neighboring isoprene units to yield a six-membered ring containing one double bond offers a possible explanation for this behavior.

2. Cyclization during Chlorination. At first glance it appears that if complete cyclization into six-membered rings occured the amount of additive chlorine at complete chlorination should be two chlorine atoms per ring, or one atom per original isoprene unit. Closer analysis shows this not to be so.

Let us assume a chain of n isoprene units and that initially the chain is attacked by chlorine at random points. At the point of attack cyclization with a neighboring isoprene unit takes place. As the reaction proceeds some of the isoprene units will become isolated by virtue of

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(29) Field, op. cit.

being surrounded on both sides by units which have already cyclized. The isolated units retain their double bonds and these can in turn be saturated by the addition of chlorine.

It is possible to calculate statistically the fraction of isoprene units which become isolated. The problem is similar in nature to that of the condensation of polymethylvinylketone upon heating[30] or the removal of chlorine from polyvinyl chloride with zinc dust [31].

The complete calculation is given in the appendix. The result is that for chains of more than eitht isoprene units the following relation holds:

Fraction of isoprene units uncyclized $= 0.1353 \left(1 + \frac{2}{n}\right)$ ----------------(12)

For shorter chains (n smaller than 8):

Fraction of isoprene units uncyclized $= \frac{1}{n} \sum_{s=0}^{n-1} \frac{(-2)^s}{s!} (n-s)$ --------------(13)

For long, uninterrupted chains of isoprene units, such as can be expected to occur in natural rubber the fraction of uncyclized units would be approximately 0.135. Hence the theoretical limit of additive chlorination would be 1.135 additive chlorine atoms per isoprene unit. It is significant in this connection that the unsaturation of completely cyclized rubber (Thermoprene SL) is 57% [32], in excellent agreement with equation (12).

In the case of polyisoprene the case is more complicated. Polyisoprene prepared by emulsion polymerization contains approximately 10% external

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(30) Marvel and Levesque, J.A.C.S. 60, 280, (1938)

(31) Flory, J.A.C.S., 61 1518, (1939)

(32) Davis and Blake, "Chemistry and Technology of Rubber" Reinhold Publishing Corp., 1937, p. 659.

double bonds due to 1-2 and 3-4 addition during polymerization. These cannot be expected to undergo cyclization in the same manner as the normal 1-4 isoprene units. Assuming that these side chains are lost to cyclization, it is possible to estimate the total amount of additive chlorine in the following manner:

The unsaturation of the polyisoprene used in the chlorination experiments was 96%. This means that of 100 isoprene units

4 are saturated
10 are 1-2 and 3-4 addition units (external double bonds)
86 are available for cyclization

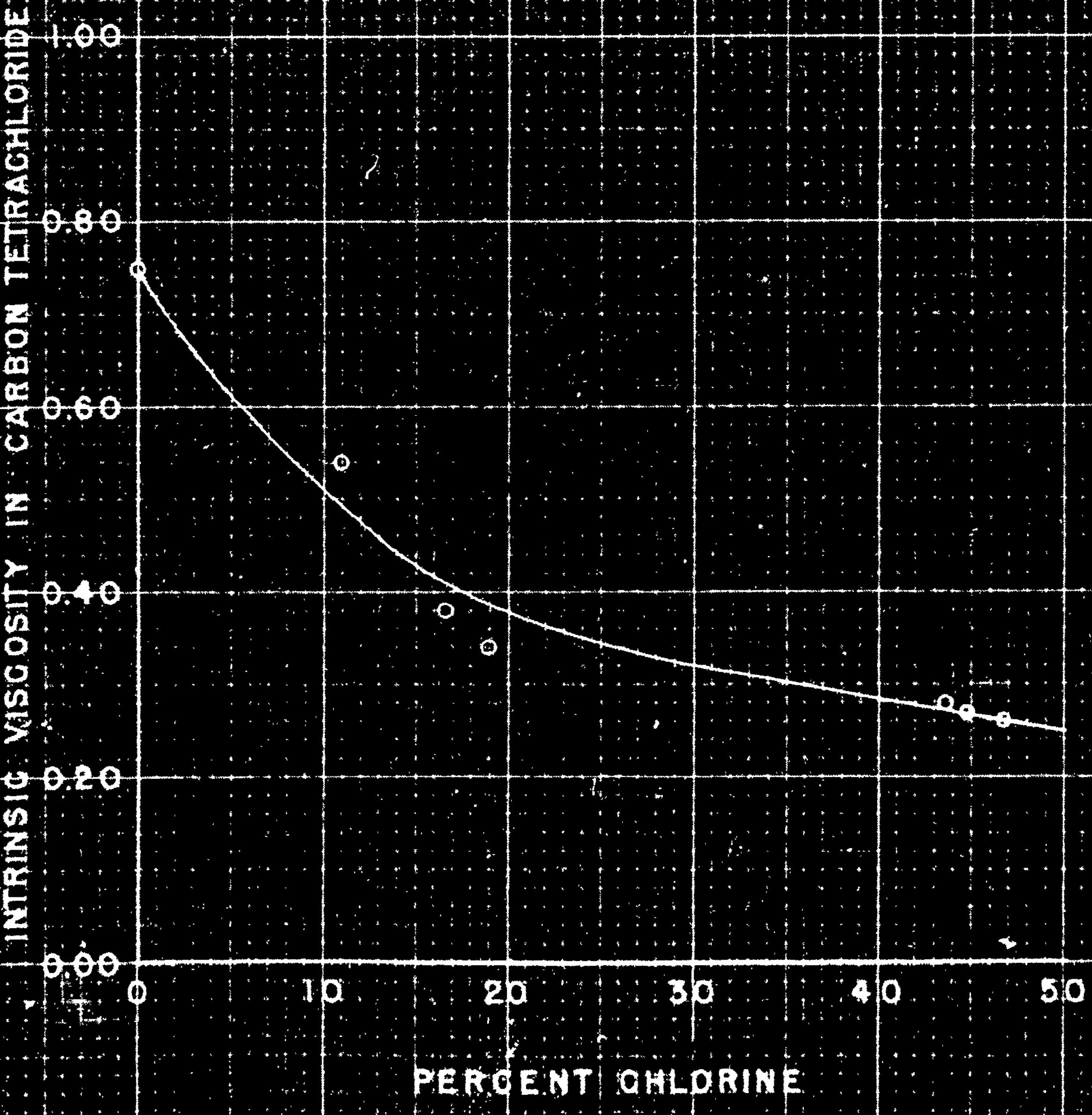
On the average the length of each section of the chain containing only consecutive normal isoprene units is then slightly more than 6. According to equation (13) the fraction of isoprene units left uncyclized is 0.18. Thus for 100 isoprene units the number of chlorine atoms reacting by addition is

20 due to addition to vinyl side chains
$2 \times 0.18 \times 86 = 31$ due to addition to isolated units
$0.82 \times 86 = 71$ due to addition to cyclized units

The total number of additive chlorine atoms thus should be 1.22 per isoprene unit. The observed value of 1.21 is well within the limits of experimental error. The number of double bonds lost due to cyclization is approximately 0.36 per isoprene unit.

Intrinsic viscosity measurements provide further evidence for the cyclization. The theoretical considerations have been discussed (p. 12) The intrinsic viscosity of the polymer shows a sharp drop during the early stages of chlorination and levels off still within the limits of initial substitutive reaction (Table 3, Figure 2).

FIG 2



INTRINSIC VISCOSITY DROP IN EARLY STAGES OF CHLORINATION.

Table 3

Intrinsic Viscosities of Chlorinated Polyisoprenes
(in carbon tetrachloride)

Polymer	% Cl	Cl-Atoms per Isoprene unit	Intrinsic Viscosity
Polyisoprene	0	0	0.75
Chlorinated Polyisoprene	11.0	0.24	0.54
	16.6	0.38	0.38
	19.0	0.46	0.34
	43.6	1.46	0.28
	44.8	1.53	0.27
	46.8	1.65	0.26

It thus appears that cyclization is essentially complete before the bulk of the additive reaction sets in. This is in agreement with the assumption made in the theoretical calculation of the limit of additive reaction.

The decrease in unsaturation due to cyclization in the early stages of chlorination should, on the basis of the arguments given previously (p. 10), be measurable by iodine chloride titration. Such a decrease in iodine value was observed (Table 4). Unsaturation was calculated by equation (10) and the degree of cylization was estimated from equation (11).

Table 4

Loss of Unsaturation due to Cyclization as
Determined by Iodine Chloride Titration

Polymer	% Cl	Cl atoms per isop, unit	Iodine No.	% unsat. (by Iodine number)	Degree of cyclization (double bonds lost per isop. unit)
Polyisoprene	--	--	357	96	---
Chlorinated Polyisoprene	11.0	0.24	314	94	0.02
"	16.6	0.38	265	85	0.11
"	19.0	0.46	247	81	0.15
"	28.6	0.76	191	71	0.27
"	32.6	0.91	171	68	0.29

Theoretical limit of cyclization = 0.36.

The results again point to cyclization at the beginning of the chlorination . It is well to interpret the results presented in Table 4 in a qualitative way and to consider the values for degree of cyclization as rough estimates. However, combined with the viscosity data the results show clearly that cyclization is essentially complete below 40% Cl.

3. Unsaturation of Highly Chlorinated Polyisoprenes. The iodine values of polymers containing more than one chlorine atom per isoprene unit fall considerably below the theoretical values calculated on the basis of total possible cyclization and additive reaction (equation 11).

Table 5

Unsaturation of Highly Chlorinated Polyisoprenes

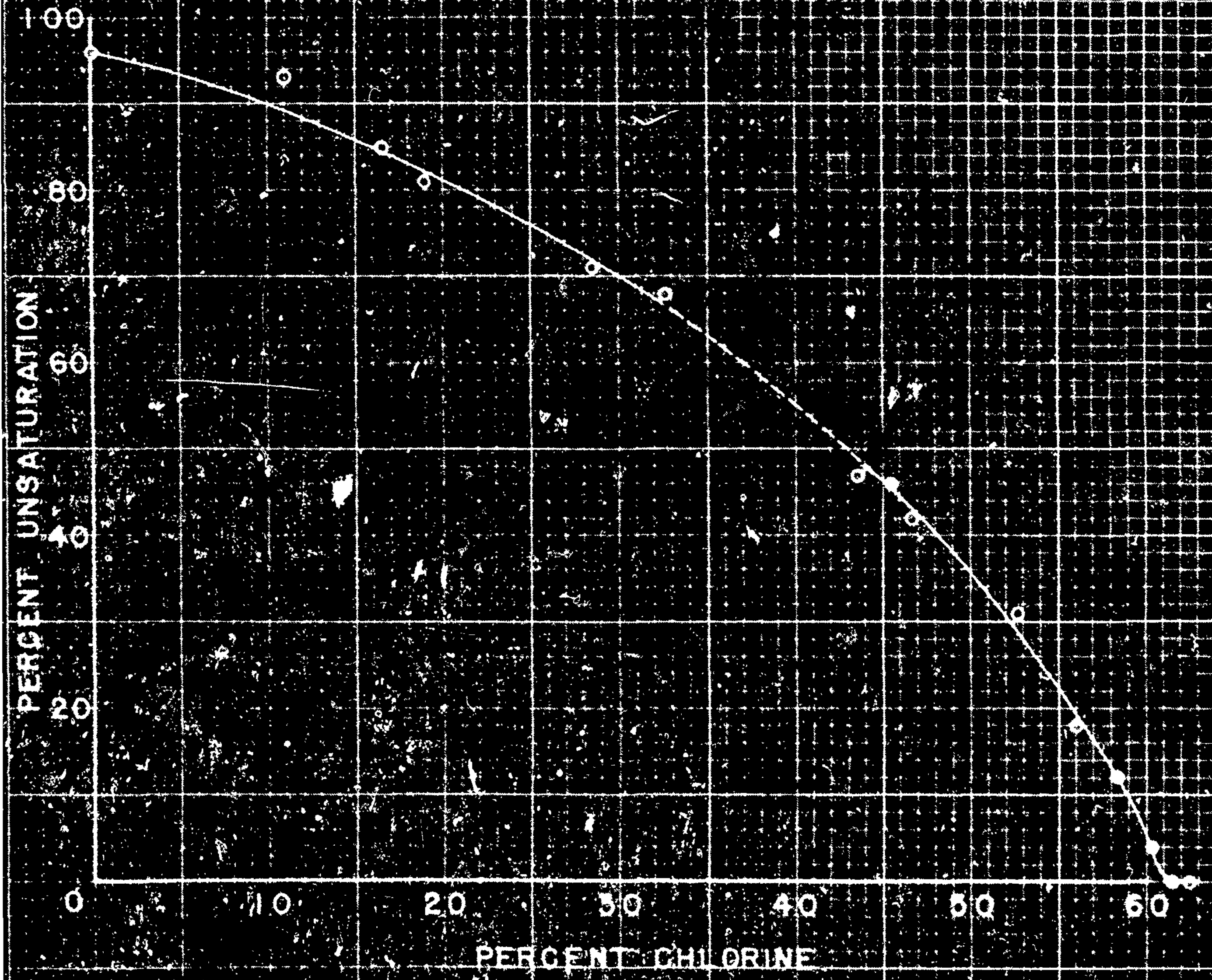
% Cl	Cl atoms per isop. un.	Additive Cl atoms	Unsaturation	
			by Iodine #	by cycl. & addition
43.6	1.46	0.27	44	47
45.6	1.57	0.27	33	46
46.8	1.65	0.35	35	42
52.6	2.08	0.57	12	31
56.0	2.38	0.82	7	19
58.4	2.62	0.97	2	12
60.3	2.84	1.13	0	4
61.5	2.98	1.21	0	0
62.5	3.10	1.21	0	0

For example the unsaturation as given by the iodine value of a sample of 56% chlorine content is 7%. However further chlorination of the sample results in an additive uptake of 0.39 chlorine atoms per isoprene unit, showing that the actual unsaturation is at least 19.5%. This demonstrates clearly that in the range of high chlorination the iodine value is no longer applicable.

Figure 3 shows a plot of unsaturation vs. percent chlorine. For samples of low chlorine content the values given in Table 4 were used,

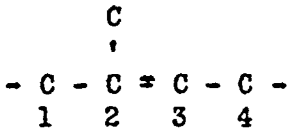
FIG 3

UNSATURATION OF
CHLORINATED POLYISOPRENES

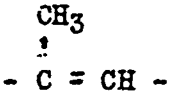


for highly chlorinated polymers those of Table 5 were used. The dotted portion of the curve represents the interpolation in the range in which the iodine value is no longer representative of unsaturation and in which the cyclization may not yet be complete.

4. *Mechanism of Chlorination.* The quantity of hydrogen chloride given off in the initial stages of chlorination far exceeds the amount accountable for by the cyclization reaction alone. Hence simultaneously with the cyclization straight substitution of one chlorine per isoprene unit is taking place. As has been mentioned (p. 10) this substitution apparently occurs in the number 1 or 4 positions since the chlorine is removable with alcoholic silver nitrate.



$$\begin{array}{ccccccc} & & C & & & & \\ & & | & & & & \\ -C & - & C & = & C & - & C- \\ 1 & & 2 & & 3 & & 4 \end{array}$$

Further evidence for substitution in these positions can be gathered from the chlorination of simple olefins containing the  $\begin{array}{c} CH_3 \\ | \\ -C=CH- \end{array}$ group.

Burgin and coworkers[33] chlorinated isobutylene both in the liquid and gaseous phases. In each case they obtained a yield of 87% of methallyl chloride and only 7% saturated dichlorides, the rest being unsaturated dichlorides, trichlorides etc. Secondary addition of HCl amounted to about 1%. The formation of methallyl chloride was not due to splitting out of HCl from 1,2-dichloroisobutane, as the equilibrium between methallyl chloride and HCl was found to be far on the side of 1,2-dichloroisobutane. Likewise the chlorination of "tertiary amylene" (a mixture of 2-methylbutene-2 and 2-methylbutene-1) resulted in a yield

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(33) Burgin, Engs, Groll, and Hearne; Ind.Eng.Chem., 31, 1413 (1939)

of 80% of unsaturated allyl type monochlorides (2-methyl, 3-chloro butene-1 and 2-methyl, 1-chlorobutene-2).

Dihydromyrcene (di-isoprene), squalene and 1-methylcyclohexene[34] likewise chlorinate predominantly by substitution (80-90%).

The course of the chlorination of polyisoprene as far as the normal isoprene units are concerned, is then:

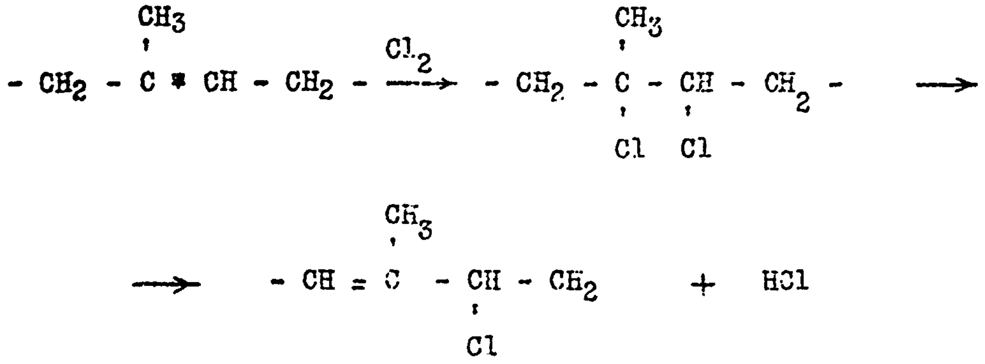
1.) Initial substitution

2.) Simultaneous cyclization accompanied by evolution of HCl

3.) Addition to the point of saturation

4.) Substitution

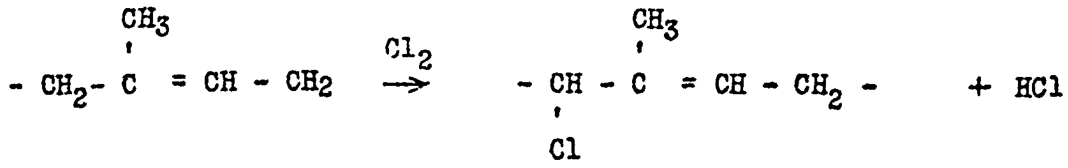
The exact mechanism by which the initial substitution takes place is uncertain. An additive dichloride may be formed, which by splitting out hydrogen chloride and reformation of the double bond goes over into a chlorine substituted isoprene unit:



$$-CH_2-\overset{CH_3}{C}=CH-CH_2- \xrightarrow{Cl_2} -CH_2-\underset{Cl}{\overset{CH_3}{C}}-\underset{Cl}{CH}-CH_2- \longrightarrow$$

$$\longrightarrow \quad -CH=\overset{CH_3}{C}-\underset{Cl}{CH}-CH_2 \quad + \quad HCl$$

The result is obviously the same as direct substitution in the 1-position (analogy with 2-methyl butene 2).



$$-CH_2-\overset{CH_3}{C}=CH-CH_2 \xrightarrow{Cl_2} -\underset{Cl}{CH}-\overset{CH_3}{C}=CH-CH_2- \quad + HCl$$

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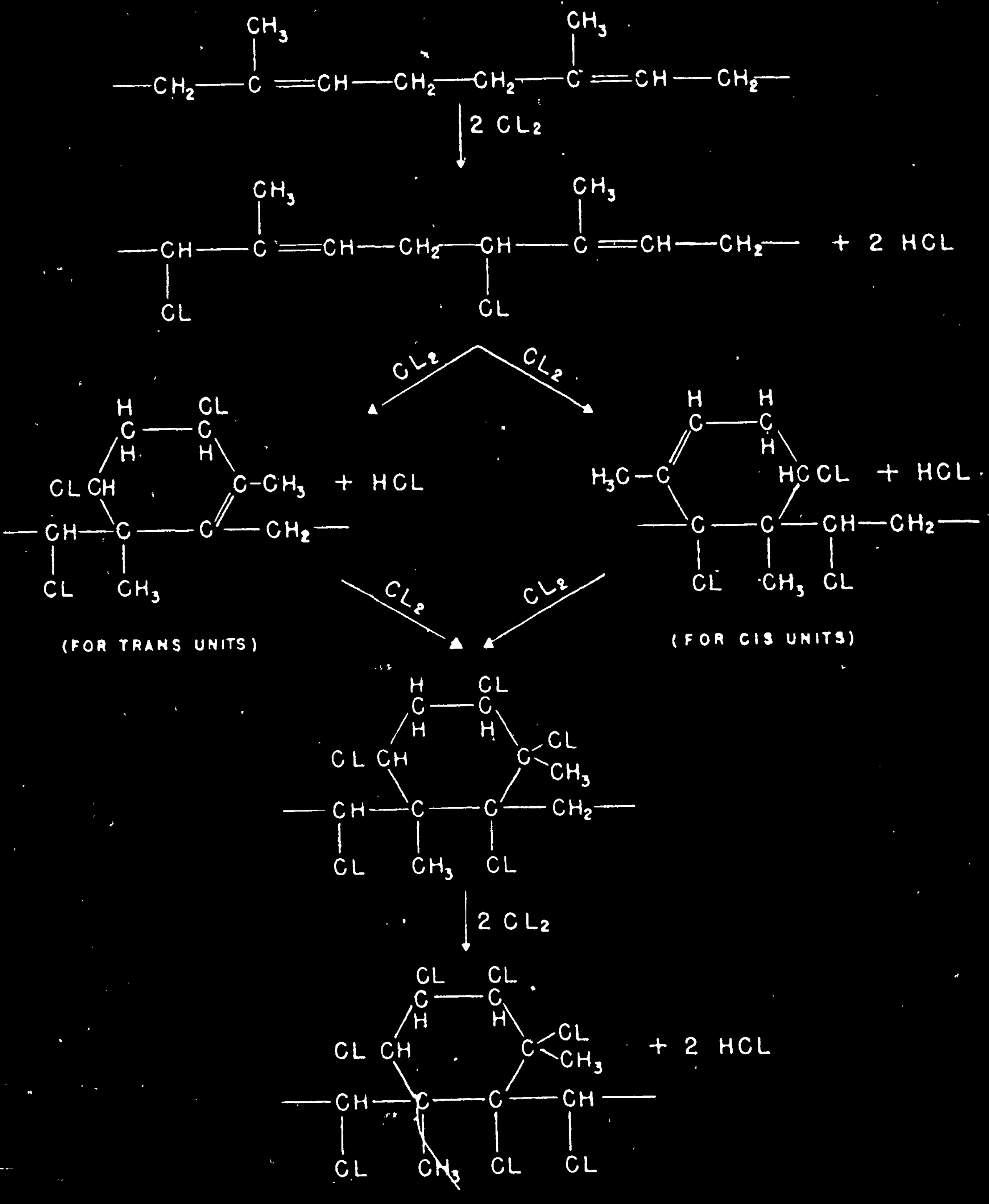
(34) Bloomfield, J.Chem.Soc., 1943, 289.

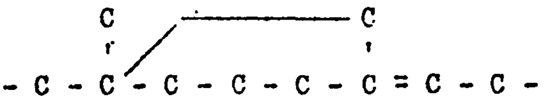
FIG. 4.

"PROPOSED SCHEME FOR COMPLETE CHLORINATION OF 1-4 ISOPRENE UNITS



Burgin's [35] experiments with isobutylene favor the direct substitution.

The main cyclization cannot be effected through the methyl groups since such a shortening of the chain would hardly be sufficient to explain the large drop in intrinsic viscocity. A cyclization with the main chain is a more plausible alternative. Figure 4 shows a possible scheme for the chlorination of two adjacent isoprene units. A study of molecular models shows that cis and trans units must cyclize in a slightly different manner. In both cases pratically strainless structures result which on further chlorination become identical. There is a further possibility of forming a strainless ring through the methyl groups:



Possibly such a cyclization also occurs to some extent. The final structure having the empirical formula $C_{10}H_{11}Cl_7$ would contain 63.7% Cl. Since this figure refers only to the normal isoprene units which undergo cyclization, it is apparent that no definite chlorine content can be specified for completely chlorinated polyisoprene. In the dark and in strict absence of oxygen chlorination can not be carried much farther than 62.5%. Chlorinated polyisoprene of higher chlorine content can however be prepared by changing the reaction conditions.

5. Influence of Temperature of the Chlorination in Darkness and Absence of Oxygen. Within the range from 0° to 77°C the temperature of chlorination has little effect on the relative amounts of addition and substitution but does effect the rate of the reaction. The chlorination in the cold proceeds faster. A comparison of results obtained by chlorination at three different temperatures is given in Table 6.

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(35) Burgin et al., op. cit.

Table 6

Effect of Temperature on Chlorination of Polyisoprene in the Dark and in Absence of Oxygen

(Data for 30°C are taken from Figs. 2 and 4)

% Cl	Temp. °C	Substit. Cl atoms per isop. unit	Additive Cl atoms per isop. unit	Unsaturation (by iodine value)
11.0	0°	0.24	0	94
	30°	0.24	0	94
43.9	0°	1.20	0.24	--
	30°	1.24	0.24	--
60.6	0°	1.71	1.17	--
	30°	1.69	1.17	--
36.2	77°	0.99	0.08	66
	30°	0.98	0.08	62
41.5	77°	1.07	0.27	48
	30°	1.12	0.17	53
48.3	77°	1.42	0.33	--
	30°	1.39	0.40	--

6. Influence of Small amounts of Oxygen and Light. Oxygen has a pronounced effect on halogenation reactions. It inhibits the substitutive chlorination of ethylene[36] and combined with the action of light brings about the rapid halogenation of a considerable number of organic compounds such as cyclopropane, toluene, phenanthrene and others[37].

When the chlorination of polyisoprene is carried out in diffuse daylight, without antioxidant and in an atmosphere of about 0.3 volume percent of oxygen, certain deviations from the behavior described for the chlorination in the dark with antioxidant can be observed:

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(36) Stewart and Smith, J.A.C.S., 51, 3082 (1929)

(37) Kharasch, Fineman and Mayo, J.A.C.S., 61, 2139 (1939)

(1) Additive reaction sets in somewhat earlier

(2) The total extent of additive reaction is noticeably larger

(3) Chlorination can be carried farther.

The experimental results are given in Table 7 and plotted in Figure 5.

Table 7

Effect of Light and Small Amounts of Oxygen on the Chlorination of Polyisoprene

Mols of Cl_2 reacted per base mol of polyisop.	% Chlorine Product	Total Cl Atoms per isoprene unit	Substitutive Cl atoms per isoprene unit	Additive Cl atoms per isoprene unit
1.06	37.4	1.13	0.99	0.14
1.34	44.0	1.48	1.21	0.27
1.67	51.3	1.79	1.56	0.23
2.06	56.9	2.47	1.65	0.82
2.11	58.4	2.62	1.60	1.02
2.33	61.5	2.98	1.69	1.29
2.46	62.7	3.14	1.78	1.36
2.47	62.9	3.16	1.79	1.37
2.65	64.3	3.35	1.95	1.40
3.04	66.5	3.69	2.30	1.39

In view of the result of Kharasch's work the increase in additive reaction of chlorine with polyisoprene due to oxygen is not surprising. The additive reaction probably follows a free radical course similar to the halogenations described by Kharasch.[38]

The increased amount of addition decreases the number of isoprene units available for cyclization and thus affects the entire course of the reaction.

As could be expected the final substitutive reaction of chlorine with the saturated chlorinated polyisoprene is catalyzed by light and the chlorination proceeds farther.

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(33) ibid.

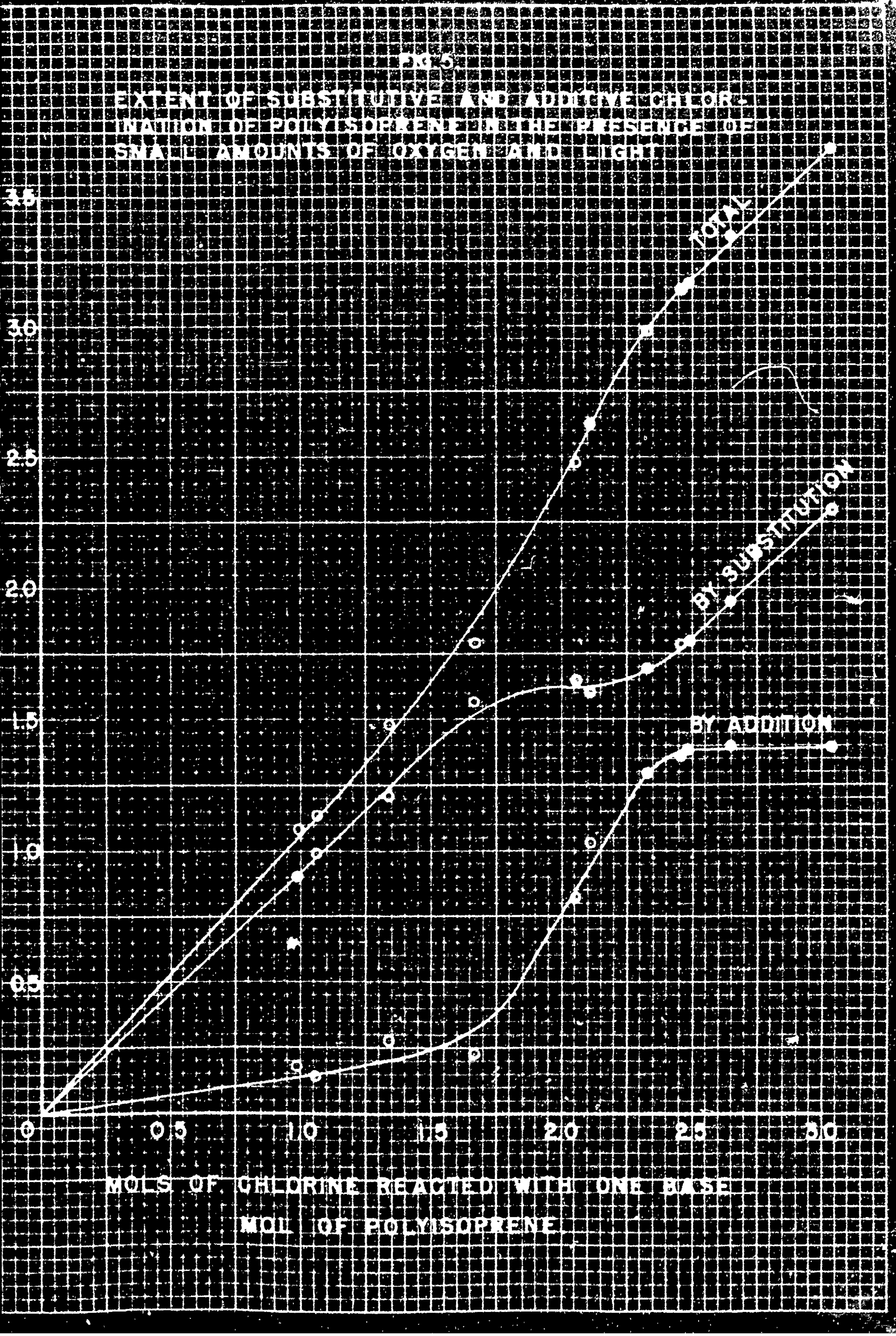

FIG. 5

EXTENT OF SUBSTITUTIVE AND ADDITIVE CHLORINATION OF POLYISOPRENE IN THE PRESENCE OF SMALL AMOUNTS OF OXYGEN AND LIGHT

7. Solubility. It has been mentioned that in the chlorination of polyisoprene some gel is formed after about 1.5 mols of chlorine have been reacted with one base mol of polyisoprene. This gel gradually disappears upon further chlorination.

A more pronounced solubility loss takes place when polymers of low chlorine content are isolated from solution. These products although initially soluble in carbon tetrachloride become almost completely insoluble in any organic solvent. It is believed that this behavior is due to oxidation during drying of the polymers leading to cross-linking of the chains with accompanying loss in solubility. The higher chlorination products, possessing less unsaturation do not oxidize as readily and consequently do not exhibit this property. Table 8 gives benzene solubilities for a number of chlorinated polyisoprenes.

Table 8

Benzene Solubilities of Chlorinated Polyisoprenes

Conditions of Chlorination			%Cl	Benzene Solubility %
Illumination	Temp. °C	Oxygen		
Dark	25-30°	negligible, antioxidant used	16.6	19
			19.0	23
			43.6	42
			46.8	63
			52.6	71
			58.4	100
			60.3	95
Dark	0°	"	11.0	22
			44.8	5
			60.6	92
Dark	77°	"	36.2	30
			41.5	44
			48.3	96

FIG. 6

BENZENE SOLUBILITIES OF CHLORINATED POLYISOPRENES

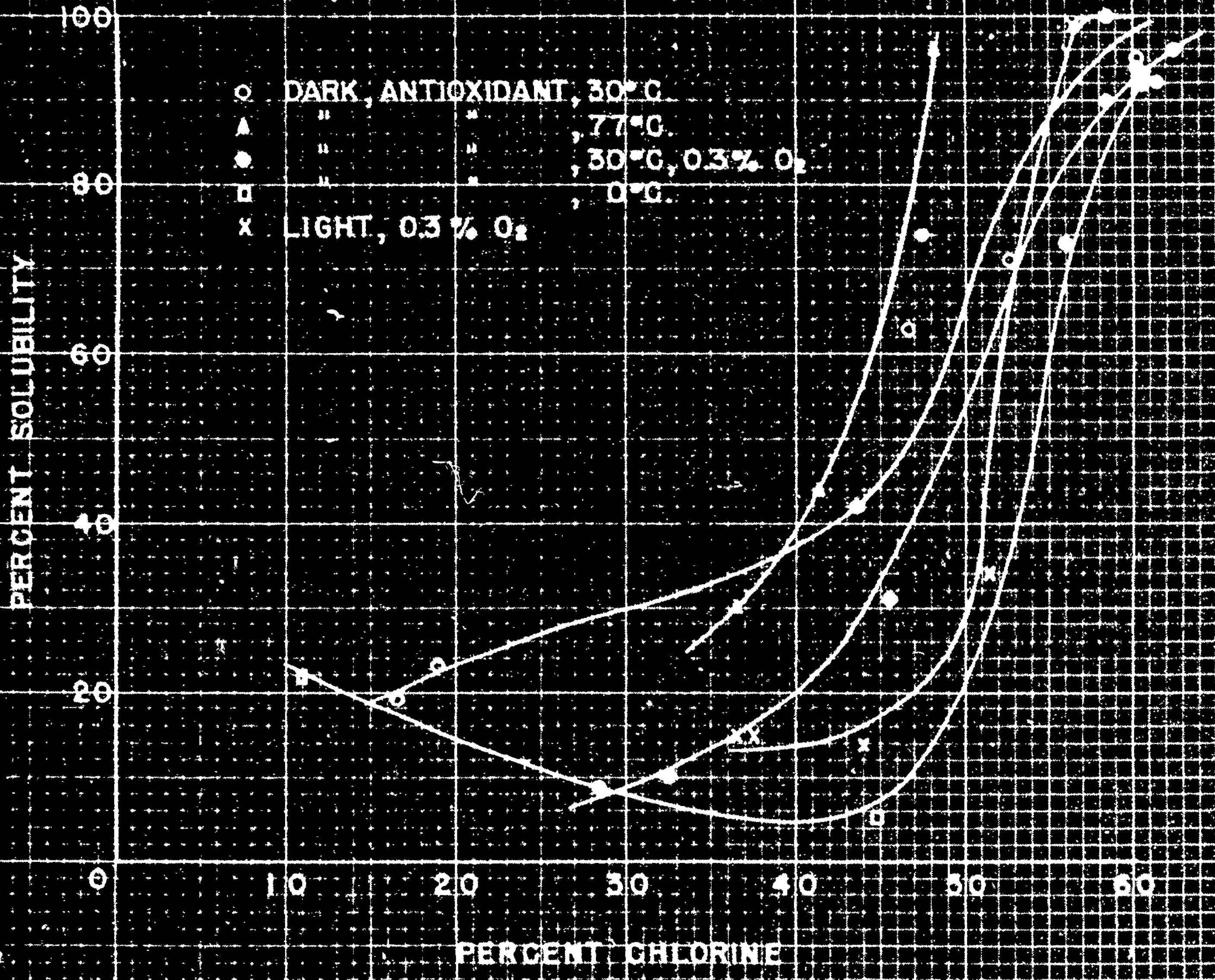

Table 8
(Cont.)

Conditions of Chlorination			% Cl	Benzene Solubility %
Illumination	Temp. °C	Oxygen		
Dark	25-30°	0.3%, but with 0.1% antioxidant	28.6	9
			32.6	10
			45.6	31
			47.6	74
			56.0	73
			58.3	90
			60.3	94
			61.5	92
			62.5	96
Diffuse Day-light	25-30°	0.3%	36.4	15
			37.4	15
			44.0	14
			51.3	34
			56.9	99
			above 58.4	100

Some variation is seen to arise due to differences in chlorination procedure. Chlorination at reflux leads to higher solubilities. Chlorination without antioxidant in daylight causes a decrease in benzene solubility. These differences are not easily explained. In the case of chlorination without antioxidant the polymers are more susceptible to oxidation during working up of the sample which may explain the solubility loss. This is substantiated by results obtained with polymers prepared with benzoyl peroxide as a chlorination catalyst. The solubility of these polymers will be discussed at a later point.

8. The Chlorination of Polyisoprene in the Presence of Ultraviolet Light and Peroxides. If the increase in additive reaction due to oxygen and diffuse daylight is due to a free radical chain reaction then one should expect a further shift toward additive chlorination under conditions favoring the formation of free radicals and atomic chlorine. Such conditions are readily established by carrying out the chlorination

in the presence of a peroxide catalyst with simultaneous irradiation by ultraviolet light.

Indeed, profound changes in both the mode of chlorination as well as the physical properties of the products were observed when chlorination was carried out in the presencd of 1% of benzoyl peroxide and in the light of a 100 watt high pressure mercury arc lamp. The general increase in additive reaction is striking, the total uptake of additive chlorine being 1.76 atoms per isoprene unit. The chlorination proceeds much faster and can be carried to a chlorine content of more than 70% (Table 9, Figure 7). Within the limited temperature range of 0°-77°C no significant difference in the amounts of additive and substitutive chlorination can be observed.

Table 9

The Chlorination of Polyisoprene Catalyzed by Ultraviolet Light and Benzoyl Peroxide

Mols of Cl_2 reacted per base mol of polyisop.	% Chlorine Product	Total Cl Atoms per isoprene unit	Substitutive Cl atoms per isoprene unit	Additive Cl atoms per isop. unit
Chlorinated at Room Temperature:				
0.61	25.0	0.63	0.58	0.06
0.99	36.0	1.07	0.91	0.16
1.06	38.2	1.17	0.95	0.22
1.15	40.0	1.26	1.03	0.23
1.26	43.7	1.47	1.06	0.41
1.51	49.8	1.87	1.15	0.72
1.88	57.4	2.53	1.23	1.30
2.02	59.2	2.73	1.30	1.43
2.21	62.2	3.09	1.33	1.76
2.29	62.9	3.17	1.41	1.76
2.93	67.2	3.81	2.06	1.75
3.07	67.9	3.92	2.22	1.70
3.51	70.4	4.39	2.63	1.76
Chlorinated at 77° C:				
0.15	7.9	0.16	0.15	0.01
0.36	16.3	0.37	0.35	0.02
1.53	50.6	1.93	1.13	0.80

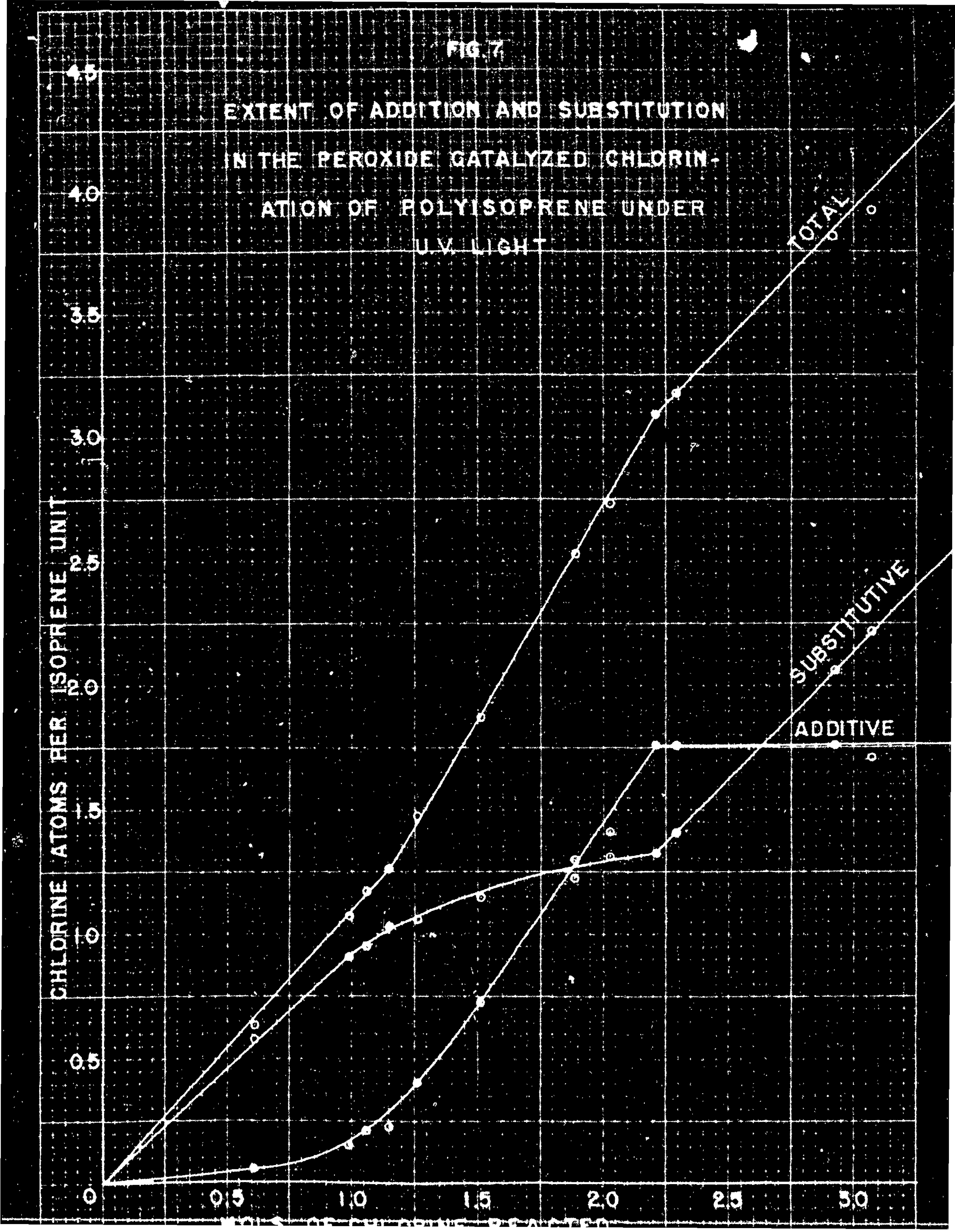

FIG. 7

EXTENT OF ADDITION AND SUBSTITUTION IN THE PEROXIDE CATALYZED CHLORINATION OF POLYISOPRENE UNDER U.V. LIGHT

Table 9
(Cont.)

Mols of Cl_2 reacted per base mol of polyisop.	% Chlorine Product	Total Cl Atoms per isoprene unit	Substitutive Cl atoms per isoprene unit	Additive Cl atoms per isop. unit
	Chlorinated at 0°C:			
0.90	34.2	0.99	0.81	0.17
2.05	59.7	2.79	1.32	1.47
3.53	70.8	4.46	2.59	1.87

It is obvious that the amount of cyclization must be considerably smaller. Unfortunately the methods used to estimate cyclization and unsaturation cannot be applied to this case since no conclusions can be drawn from intrinsic viscosities and iodine values. When a carbon tetrachloride solution of 5 g. of polyisoprene with 1% of benzene peroxide was exposed to the action of ultraviolet light for two hours, the product showed an intrinsic viscosity of the sol of 0.54 as compared with the original value of 1.01 and a drop in iodine value from 354 to 330. The sample also contained a considerable amount of gel (40%). Thus cross-linking with accompanying loss in unsaturation take place. A large increase in gel formation during chlorination was also observed. It is impossible to separate these effects from the changes caused by the catalyzed chlorination.

When the chlorination is carried out in the presence of 1% benzoyl peroxide but in total darkness the effect is a definite shift toward substitution. The cause of the increase in additive reaction when both peroxide and light are used is thus seen to be the irradiation with ultraviolet light. This is also borne out by the results obtained from chlorinations in u. v. light but without peroxide (Table 10). Indeed, there is only a small difference in the amounts of addition and substitution, whether or not a peroxide catalyst is used, as long as the chlorination is carried out in the presence of ultraviolet light. However it was found that only in the presence of both catalytic effects could the chlorination be carried to the extremely high degrees reported in Table 9.

Table 10

Separate Effects of Peroxide and U. V. Radiation

Mols Cl_2 reacted per base mol of polyisop.	Reaction Conditions	Chlorine atoms per isoprene unit		
		Total	Substitutive	Additive
1.95	uncatalyzed	2.34	1.57	0.77
	peroxide	2.18	1.72	0.46
	u.v.& perox.	2.65	1.28	1.37
2.41	uncatalyzed	3.01	1.80	1.21
	peroxide	2.82	2.00	0.82
	u.v.& perox.	3.29	1.53	1.76
0.58	uncatalyzed	0.58	0.58	0.00
	u.v. light	0.58	0.58	0.00
	u.v.& perox.	0.60	0.55	0.05
2.55	uncatalyzed	3.16	1.95	1.21
	u.v. light	3.39	1.71	1.68
	u.v.& perox.	3.42	1.66	1.76

The solubilities of chlorinated polyisoprenes prepared under the influence of ultraviolet light and benzoyl peroxide differ noticeably from those of polymers prepared in the dark and in absence of oxygen (Figure 8).

The decrease in solubility may be due to the formation of the free radicals leading to cross-linking between chains.

This is partially effected during the chlorination but probably takes place to an even higher degree during the isolation and drying of the polymers, as in the solid polymer the chains are closer together and the life of the free radicals is considerable longer.

Table 11

Benzene Solubilities of Chlorinated Polyisoprene Prepared by U.V. and Peroxide Catalyzed Chlorination.

% Cl	Benzene Solub. %	% Cl	Benzene Solub. %
7.9	39	57.4	36
25.0	26	59.2	40
36.0	3	62.2	91
38.2	7	62.9	92
40.0	8	67.2	89
43.7	8	67.9	90
49.8	10	70.4	91

That most of the cross-linking takes place in the isolated product is further evidenced by the fact that polymers containing the limiting amount of additive chlorine (and hence no double bonds) are practically completely soluble where as polymers possessing unsaturation have very low solubilities when isolated. This is borne out by the sharp solubility rise around 60% - the point at which saturation of the double bonds is essentially complete (see Figure 8).

9. Natural Rubber and Gutta Percha. On the basis of the results obtained with polyisoprene the chlorination of rubber and gutta percha is merely a special case of the same reaction. Both cis and trans oriented isoprene units are capable of cyclization and so no appreciable difference should arise in this respect. The absence of 1,2 addition units should allow cyclization to proceed to the theoretical limit of 86.5% of all units cyclized. The total number of chlorine atoms which can be introduced by addition must be

$$0.865 - 2 \times 0.135 = 1.135$$

Experimental results (Table 12) are in very good agreement with the theoretical figures. Aside from the effects due to the absence of 1-2 addition units, no deviation from the behavior of polyisoprene can

FIG 8

BENZENE SOLUBILITIES OF CHLORINATED POLYISOPRENES PREPARED BY PEROXIDE CATALYZED CHLORINATION

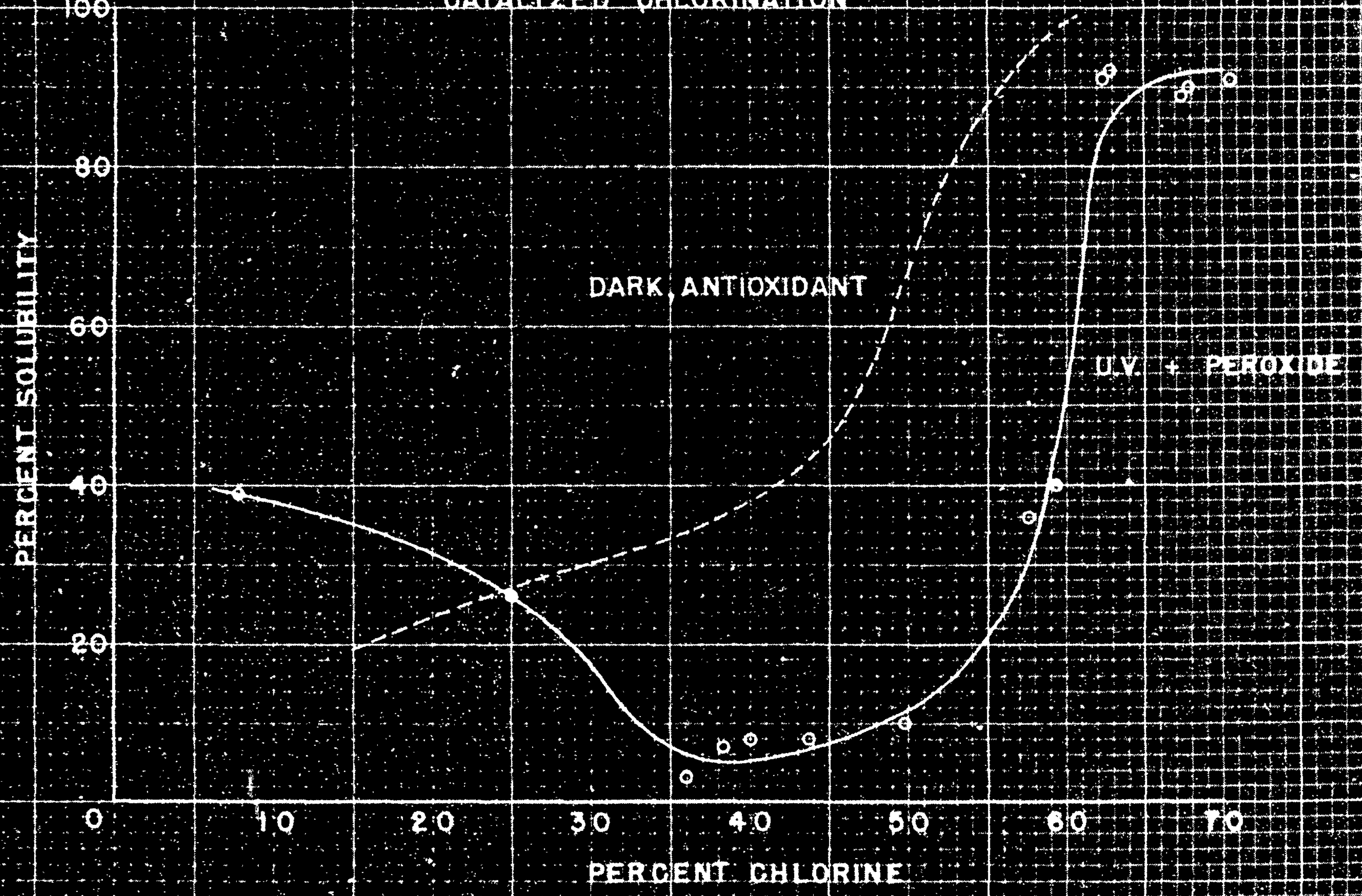

Table 12

Summary of Results with Rubber and Gutta

Polymer	Chlorination Conditions	Mols Cl_2 reacted	% Cl	Cl atoms per isoprene unit			% Unsat.	Degree of Cyclization
				Total	Subst.	Add.		
Rubber	Dark, antioxidant, 30°C	0.15	6.8	0.15	0.15	0.00	92*	.08
		0.27	12.3	0.28	0.26	0.02	76*	.23
		1.00	33.6	1.03	0.97	0.06	57*	.40
		1.45	45.0	1.54	1.35	0.19	47	.43
		2.09	57.5	2.53	1.65	0.88	13	.43
		2.14	58.8	2.68	1.60	1.08	3	.43
		2.81	64.6	3.38	2.24	1.14	0	.43
	U.V. plus peroxide	0.97	35.7	1.05	0.89	0.16	--	---
		3.31	69.0	4.11	2.52	1.59	--	---
Gutta	Dark, antioxidant, 30°C	0.71	27.6	0.72	0.70	0.02	83	.16
		1.94	55.2	2.31	1.57	0.74	20	.43

*by iodine value

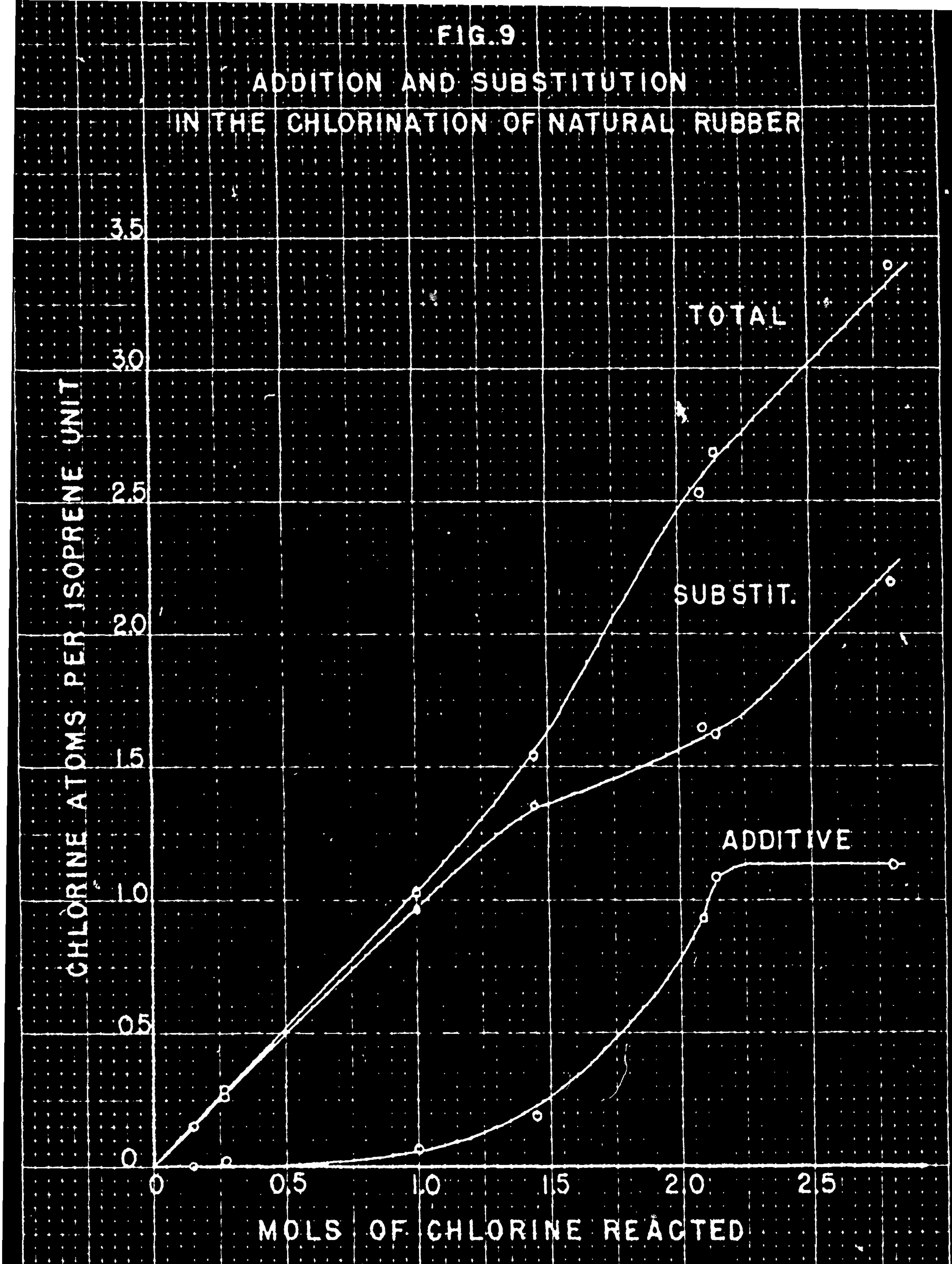

FIG. 9

ADDITION AND SUBSTITUTION IN THE CHLORINATION OF NATURAL RUBBER be observed.

Chlorinated Gutta of 29.6% chlorine content is physically indistinguishable from the corresponding chlorination products of polyisoprene and rubber. Since no appreciable addition takes place in the early stages of chlorination the apparent destruction of the cis-trans isomerism must be attributed to the cyclization. The structures proposed for the cyclized cis and trans units (Figure 4), although not identical, nevertheless show a high degree of similarity and might be expected to impart very similar properties to the polymers.

The reduced amount of addition is also apparent in the catalyzed chlorination of rubber.

EXPERIMENTAL

A. Preparation and Purification of Polymers for Chlorination.

1. Polyisoprene. Since a reproducible source of polyisoprene was required, polyisoprene was prepared in the laboratory from isoprene supplied by Newport Industries. The isoprene was distilled to remove the polymerization inhibitor and polymerized in the following emulsion recipe:

Isoprene	100.0	g
Tert. hexadecyl mercaptan	0.5	g
Water	180.0	g
Potassium Persulfate	0.3	g
Soap (SF Flakes)	5.0	g

The polymerization was carried out in 12 oz. crowncapped bottles, rotated end over end in a thermostat at 50°C for 30 hours. The latex thus obtained was short stopped with .06 g of hydroquinone, stripped of unreacted monomer by vigorous stirring at 50-60°C and 1.2 g of phenyl- β-

naphthylamine was added as antioxidant. Coagulation of the latex was effected by addition of 100 cc of 25% sodium chloride solution, followed by 600 cc of ethanol. The resulting rubber was carefully washed free of soap in warm water and dried for 24 hours in a vacuum oven at 50°C. This was followed by a 24 hour extraction (in a Soxhlet apparatus) with the azeotropic mixture of ethanol and toluene. In the extraction all but traces of antioxidant- originally added to protect the polymer during the stripping and washing operations--was removed along with residual monomer, low molecular polymers, and soap. The rubber was again dried, this time for 48 hours at 35°C in vacuo. The resulting polyisoprene hydrocarbon is a colorless, transparent, soft polymer of nearly theoretical iodine value. It was stored in the dark in an evacuated desiccator.

2, Natural Rubber. Pale crepe was purified by a method similar to that described by Kemp and Peters[39]. 50grams of crepe were placed in a cloth bag and submerged in 1500 cc of chloroform to which 0.2 grams of phenyl-β-naphthylamine had been added. Diffusion of the rubber into the solvent was allowed to take place for 5 days, after which the rubber was precipitated with methanol and redissolved in benzene. The benzene solution was now fractionally precipitated with a 50-50 mixture of ethanol and benzene and the first fraction discarded. According to Pummerer and Koch[40] all impurities are removed with the first fraction. The rubber hydrocarbon was dried for 48 hours at 35°C in a vacuum. Iodine chloride titration gave an iodine value of 370 for the final product.

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(39) Kemp and Peters, Ind. Eng. Chem. 33, 1391-8 (1941)

(40) Pummerer and Koch, Ann. 438, 294-313 (1924)

3. Gutta Percha. Crude gutta percha was dissolved in benzene and the solution filtered to remove grit and sand. The polymer was then precipitated with alcohol and extracted with the azeotropic mixture of ethanol and toluene. After two more precipitations, the gutta percha was dried in the same manner as polyisoprene and rubber. The product had an iodine value of 364, indicating a hydrocarbon content of 97%.

B. Chlorination of Polymers.

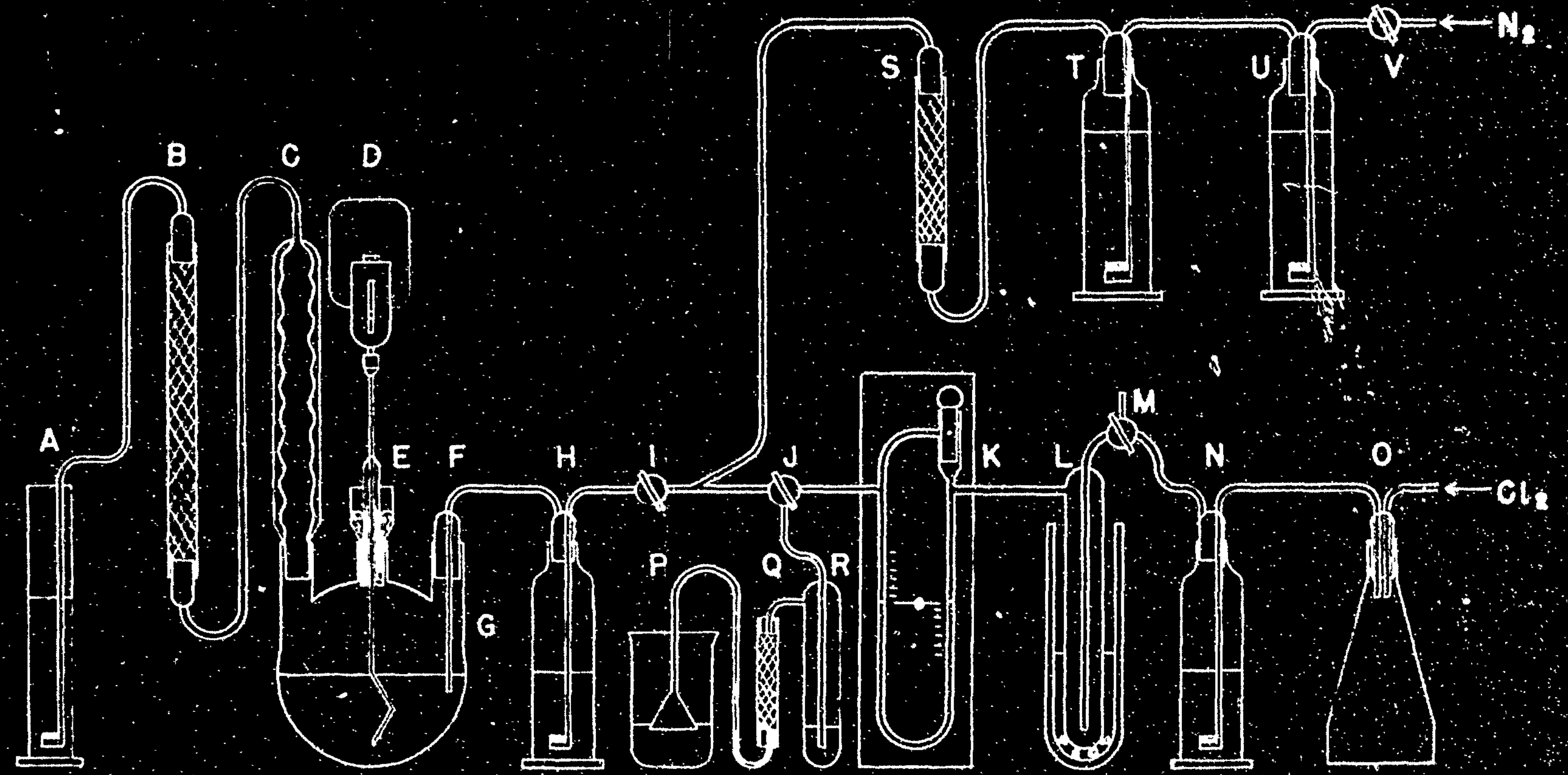
1. Chlorination Apparatus and Procedure. Chlorinations were carried out in the all glass apparatus shown in Figure 10. A slow stream of chlorine (12 - 20 cc/min.) and nitrogen in approximately equal proportions was introduced just below the surface of an agitated, dilute (20 grams/L) solution of the polymer in reagent grade carbon tetrachloride. The evolved gases were passed through the condenser (C) and up the column (B) packed with metallic antimony and glass wool. Any chlorine escaping from the solution was removed by the antimony. The hydrogen chloride passed through the antimony and into a 2N sodium hydroxide solution in the trap (A).

Special tests showed that separation of chlorine and hydrogen chloride by the above method was quantitative provided that the antimony was first saturated with anhydrous hydrogen chloride. Consequently the antimony used was first treated with anhydrous HCl and then blown free of adsorbed hydrogen chloride by a stream of dry nitrogen. As a precaution the standard alkali in the trap was checked for hypochlorite and antimony (from hydrolysis of $SbCl_5$ vapors possibly carried into the trap) after each run. Both tests were consistently negative.

Commercial chlorine was used in all chlorinations. The gas was scrubbed with concentrated sulfuric acid (N) and liquified in a dry ice trap(L). Half of the liquid chlorine was distilled off and trapped in

FIG.10.

APPARATUS FOR THE CONTROLLED CHLORINATION OF POLYMERS



A..ALKALI TRAP
B..ANTIMONY TUBE
C..CONDENSER
D..STIRRING MOTOR
E..MERCURY SEAL
F..GAS INLET TUBE
G..REACTION FLASK
H..CCl_4 BUBBLER
V & I..STOPCOCKS
J..3-WAY STOPCOCK
K..FLOWMETER
L..DRY ICE TRAP
M..3-WAY STOPCOCK
N..H_2SO_4 SCRUBBING BOTTLE
O..TRAP
P..ALKALI TRAP
Q..$CaCl_2$ DRYING TUBE
R..CHECK VALVE
S..P_2O_5 DRYING TUBE
T..H_2SO_4 SCRUBBING BOTTLE
U..$CrSO_4$ BUBBLER

alkali (P). The residue, substantially free of oxygen and hydrogen chloride, was allowed to distill into the reaction flask (G). The switch from trap (P) to reactor (G) was accomplished simply by turning the three-was stopcock (J). In experiments in which total exclusion of oxygen was not desired, the distillation of the chlorine was omitted.

The purpose of using nitrogen as a diluent was twofold. Nitrogen provides a neutral atmosphere and keeps the solution in trap (A) from sucking back into the system upon absorption of HCl. At the same time, secondary addition of HCl to the rubber molecule is prevented by the flushing action of the nitrogen[41]. Oxygen was removed from the nitrogen by passing the latter rhrough a dilute solution of chromous sulfate [42] (U). The gas was then scrubbed with concentrated sulfuric acid (T) and passed through a phosphorus pentoxide drying tube (S) before being mixed with the chlorine. Again, in experiments not necessitating the strict absence of oxygen, the procedure was simplified by omitting the chromous sulfate bubbler. The nitrogen used contained 0.3% oxygen by volume.

Before starting the chlorination, the entire system was blown out with nitrogen for at least 10 hours. Likewise, the nitrogen flow was continued after chlorination until the exit gases tested entirely neutral toward moist litmus paper.

Total darkness during chlorination was insured by placing the entire apparatus into a blacked out laboratory hood.

The peroxide catalyzed chlorinations were run with the reactor flask irradiated by a 100 watt mercury arc light source, rich in ultraviolet

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(41) Bloomfield, J. Chem. Soc., 1943, 289.

(42) Rust and Vaughan, J. Org. Chem. 5, 449 (1940)

radiation.

Phenyl-β-naphthylamine was used whenever chlorination was carried out in the presence of an antioxidant. Its purification was accomplished by recrystallizing technical phenyl-β-naphthylamine (Eastman) twice from alcohol.

2. Isolation of chlorination products. The chlorinated polymers were isolated from the CCl_4 solution by dropping the solution into boiling water to flash off the solvent. The product was then divided up into small pieces and washed in boiling water for 30 minutes. This was followed by a similar wash in distilled water. The polymer was carefully dried in a vacuum oven at 50°C.

The drastic treatment to remove the solvent is absolutely essential, since chlorinated rubbers are particularly apt to retain traces of solvents[43]. It was realized that boiling of the polymers might cause hydrogen chloride to be split off. However, in all but a few cases, no chloride could be detected in the wash water. Even when the water gave a positive test for chloride, the amount was quite negligible.

It was found convenient to precipitate polymers of low chlorine content with ethanol prior to boiling them in water. This was done merely to facilitate handling of the inherently sticky polymers.

C. Analytical Methods.

1. Chlorine Analyses. The pure, dry polymers were analyzed for chlorine by sodium peroxide fusion (Parr bomb technique) followed by the Volhard method.

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(43) Houwink, R., Chemie und Technologie der Kunststoffe, p. 481, Leipzig, Akademische Verlagsgesellschaft M. B. H. (1939).

The amount of hydrogen chloride evolved during the chlorination was determined by titration of an aliquot from the standard alkali. The Volhard chloride determination was favored over back-titration with standard acid as a matter of convenience. No difficulty was encountered from traces of carbon tetrachloride swept into the alkali trap during chlorination.

2. Iodine Chloride Titrations. The limitations of the iodine chloride titration have been discussed. The method of Kemp and Mueller[44] was applied successfully without modifications to polyisoprene, rubber, and gutta percha. However, with chlorinated polymers the procedure had to be modified to insure complete iodine chloride addition. The reason for this is two-fold: (1) The reaction is considerably slower for the chlorinated polymers, and (2) the low solubility of some of the chlorinated polymers further retards iodine chloride addition and leads to erratic results, as the titration must be carried out with a gel sample. These difficulties were largely overcome by allowing 72 hours for the iodine chloride addition to take place (instead of one hour). It was found experimentally that the observed iodine value approaches a limit with increasing time of reaction. After 72 hours addition of iodine chloride was found to be essentially complete.

D. Intrinsic Viscosities and Benzene Solubilities.

Cylindrical glass jars of 150 ml capacity were equipped with screw tops lined with tinfoil. Each jar was fitted with a central glass tube extending over the whole length of the jar, the tube carrying four stainless steel wire screens (80 mesh) spaced an equal distance apart

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(44) Kemp and Mueller, Ind. Eng. Chem., Anal. Ed., 6, 52 (1934).

and fitting tightly against the side of the jar. 250 milligrams of polymer were distributed evenly over the four screens in each jar and covered with 100 ml of benzene. The lids were replaced and the samples set aside in the dark. After 24 hours, 50 ml of solution were pipetted out of the central tube and the pipette was allowed to drain onto the screens. This was done to insure uniformity of the solution. After 24 hours, 10 ml of solution were withdrawn from each jar and evaporated in 50 ml beakers at 75°C.

$$\text{Benzene solubility (in \%)} = \frac{\text{wt. of residue}}{\text{wt. of sample}} \times 1{,}000$$

Conversely, for the insoluble portion retained by the screens:

Gel content (in %) = 100 -(% benzene solubility)

An Ostwald viscosimeter immersed in a constant temperature bath (at 30°C) was employed to measure the relative viscosity (η_r) of the polymer solution.

$$\eta_r = \frac{t}{t_o}$$

where t and t_o are the times of flow of solution and solvent respectively. The difference in density between solvent and solution was neglected.

The intrinsic viscosity (η) is defined as

$$\eta = \frac{1}{c} \ln \eta_r$$

where c is the concentration of the solution in grams per 100 cc.

The intrinsic viscosities were determined in carbon tetrachloride solution (taken directly from the reactor flask), and c was calculated from the solids content of the solution.

SUMMARY

1. The extent of additive and substitutive chlorination was determined for twenty-two samples of polyisoprene chlorinated to different chlorine contents in the dark and in a nitrogen atmosphere. In all cases the reaction was found to proceed initially by substitition, followed by addition and in the last stages again by substitution.

2. The maximum amount of additive chlorine that can be introduced into the polymer is 1.21 atoms of chlorine per isoprene unit. A marked shortening of the chain length occurs during the early stages of chlorination as is evidenced by the intrinsic viscosities of the chlorination products. The unsaturation of these polymers as measured by iodine numbers falls short of the values calculated on the basis of additive reaction alone. A cyclization of two adjacent isoprene units into a six membered ring is proposed as a likely cause for this behavior.

3. The cyclization takes place in the early stages of the chlorination simultaneously with the initial substitution. The theoretical limit of cyclization calculated statistically is 86.5% of all isoprene units cyclized for natural rubber and 72% for polyisoprene containing 10% vinyl side chains. Experimental results are in excellent agreement with these figures.

4. Iodine chloride titration gives fair results for samples of low chlorine content but is not applicable to polymers containing much more than 35% Cl. Knowing the degree of cyclization, the unsaturation can however be calculated for any polymer from the extent of additive reaction.

5. A complete scheme for the chlorination of 1,4 addition units of polyisoprene has been proposed. Vinyl side chains probably chlorinate

by addition to the double bond as do isolated isoprene units not capable of undergoing cyclization.

6. Nine chlorinated polymers prepared from natural rubber and gutta percha show that natural rubber and gutta percha chlorinate in a manner analogous to polyisoprene. The situation is simpler due to the absence of 1,2 addition units. Differences due to cis-trans isomerism are minor.

7. In the presence of antioxidant, small amounts of oxygen have no effect on the reaction of polyisoprene with chlorine. Temperature has likewise no effect on the extent of addition, substitution and cyclization but does affect the rate of chlorination, the reaction in the cold proceeding faster. Polymers chlorinated at reflux show higher benzene solubilities than those chlorinated cold.

8. When polyisoprene is chlorinated in diffuse daylight and in the presence of small amounts of oxygen (no antioxidant being used) an increase in additive reaction is observed. Ten samples were prepared in this manner. The cyclization is less complete in this case. The final substitutive reaction is catalyzed by light and the reaction proceeds to higher degrees of chlorination.

9. Chlorination catalyzed by ultraviolet light and benzoyl peroxide produces a still stronger shift toward additive reaction. Twenty three polymers among them two containing over 70% Cl have been prepared in this manner. Cyclization is prevented to a considerable extent by the addition of chlorine to the double bonds. Both addition and substitution are catalyzed, the additive reaction being enhanced mainly by ultraviolet light and the substitutive reaction by the peroxide catalyst. Within the range investigated the ultraviolet and peroxide catalyzed reaction is independent of temperature.

10. Chlorinated polyisoprenes and natural rubbers of low chlorine contents become insoluble once isolated from solution. This tendency is strongest with polymers prepared by the peroxide catalyzed chlorination and least with the polymers chlorinated in the presence of antioxidants. Oxidative crosslinking during isolation from solution and drying offers a possible explanation for this behavior.

APPENDIX

Mathematical Analysis of the Cyclization Reaction

Let E_n be the number of uncyclized isoprene units at the end of the reaction in a chain of n units. Obviously $E_o = 0$, $E_1 = 1$, $E_2 = 0$ and $E_3 = 1$. If $n = 4$ either the first two or the last two units may cyclize leaving the remaining units equivalent to $n = 2$, or the second and third units may cyclize first, leaving two $n = 1$ molecules. Thus

$$E_4 = \frac{1}{3}(2E_2 + 2E_1)$$

If $n = 5$ the first two or last two units may cyclize leaving an $n = 3$ remainder in each case, or two units in the middle of the chain may cyclize leaving in each case one $n = 1$ and one $n = 2$ remainder. Then

$$E_5 = \frac{1}{4}(2E_3 + 2E_2 + 2E_1)$$

In general

$$E_n = (2/n-1)(E_{n-2} + E_{n-3} + E_{n-4} + \text{----} E_o) \qquad (1)$$

or

$$E_n = (2/n-1)\sum_{i=o}^{n-2} E_i \qquad (2)$$

It can be seen that

$$nE_{n+1} - (n-1)E_n = 2E_{n-1} \qquad (3)$$

We now construct a generating function

$$f(x) = \sum_{n=o}^{\infty} E_{n+1}\, x^n \qquad (4)$$

Differentiating

$$f'(x) = \sum_{n=o}^{\infty} nE_{n+1}\, x^{n-1} \qquad (5)$$

and

$$xf'(x) = \sum_{n=0}^{\infty} nE_{n+1}\, x^n \qquad (6)$$

$$x^2f'(x) = \sum_{n=0}^{\infty} nE_{n+1}\, x^{n+1} = \sum_{n'=1}^{\infty} (n'-1)\, E_{n'}\, x^{n'} \qquad (7)$$

$$x^2f(x) = \sum_{n=0}^{\infty} E_{n+1}\, x^{n+2} = \sum_{n'=2}^{\infty} E_{n'-1}\, x^{n'} \qquad (8)$$

From (3), (6), (7), and (8) it follows that

$$xf'(x) - x^2f'(x) - 2x^2f(x) = 0 \qquad (9)$$

Solving this simple differential equation we obtain

$$f(x) = e^{-2x}/(1-x)^2 = 1/(1-x)^2 \sum_{n=0}^{\infty} (-2x)^n \frac{1}{n!} \qquad (10)$$

But

$$1/(1-x)^2 = \sum_{n=0}^{\infty} (n+1)x^n \qquad (11)$$

E_{n+1} will be the coefficient of x^n in $f(x)$. That is

$$E_{n+1} = \sum_{s=0}^{n} \frac{1}{s!}(-2)^s \ (n+1-s) \qquad (12)$$

or

$$E_n = \sum_{s=0}^{n-1} \frac{1}{s!}(-2)^s \ (n-s) \qquad (13)$$

Rewritten

$$E_n = n \sum_{s=0}^{n-1} \frac{1}{s!}(-2)^s + 2 \sum_{s=0}^{n-1} \frac{1}{(s-1)!}(-2)^{s-1} \qquad (14)$$

For $n > 8$ this becomes very nearly

$$E_n = (n+2)\, e^{-2} = .1353\ (n+2) \qquad (15)$$

The fraction of isoprene units left uncyclized is

$$\frac{1}{n}E_n = .1353\ (1+\frac{2}{n}) \qquad (16)$$

For $n < 8$ equation (13) must be used.