CHLORINATION OF NATURAL RUBBER. I. PREPARATION AND PROPERTIES OF CHLORINATED RUBBER *

G. J. VAN AMERONGEN, C. KONINGSBERGER, AND G. SALOMON

RUBBER FOUNDATION, DELFT, HOLLAND

INTRODUCTION

The chlorination of rubber has been the subject of extensive investigations[1], the rubber being commonly treated in solution with gaseous chlorine at a given temperature and pressure. The properties of the products of rubber thus treated vary in close dependence on the chlorine content, which may be as much as 70 per cent. The drawback to a low chlorine content is that, as a rule, the chlorine is loosely bound, with the result that, when exposed to heat or light, it splits off as HCl, with formation of discolored and cyclized products and serious deterioration of the mechanical properties. But the higher the chlorine content, the more stable are these chlorinated rubbers. The stability of chlorinated products of natural rubber containing approximately 65 per cent of chlorine is such that they are used commercially as a component of anticorrosive paint.

The instability of chlorinated rubber of low chlorine content is closely connected with its chemical constitution and the mechanism of reaction. The current opinion ten years ago[2] was that chlorine first adds to the double bond of the rubber, and that this primary product, while splitting off HCl, enters into further reaction with chlorine; but reexamination of this reaction in the laboratory of our affiliated English organization[3] and independently in our own laboratory has led to very different views. It was realized that rubber dichloride (the addition product of chlorine and rubber) is far too stable to act as an unstable intermediate product during the chlorinating reaction. Bloomfield[4] argued that, during the primary reaction, the chlorine is attached by substitution to an α-methylenic carbon atom of the rubber molecule and that there is a considerable amount of cyclization.

It was not our sole concern to study the mechanism of reaction; we were also bent on following the chlorination of rubber under the most diverse conditions, starting from dry rubber, rubber in solution, and rubber in latex, and with highly diversified sources of chlorine such as from liquid chlorine, gaseous chlorine, hypochlorites, and sulfuryl chloride.

The normal course of reaction, involving the formation of unstable intermediate products, is discussed in Part I of this series; methods of producing comparatively stable rubber chlorides by adding chlorine onto the double bond are considered in Part II.

THE ANILINE TEST

The reaction of halides with organic bases has been used in this laboratory for the kinetic identification of halide groups in polymers[5]. It is sufficient for

---

* Reprinted from the *Journal of Polymer Science*, Vol. 6, No. 6, December 1950; Part I from pages 639–651; Part II from pages 653–665. These papers are Communications No. 114 and No. 115 of the Rubber Foundation, Delft.

the purpose of this and the subsequent papers to state that allylic chlorides and tertiary chlorides react with aniline at 100° C in a very short time, while dichlorides with vicinal chlorine and polychlorides of the chlorinated rubber type split off only part of the chlorine and at much lower rates. Certain polychlorides with the $>CCl_2$ group are, however, unstable at 100° C in aniline, and this can interfere with the kinetic separation. The reactivity of typical mono- and dichlorides is summarized in the left-hand part of Figure 1; the analogous reaction of some polymers with a polychloride structure is given in the right-hand half.

A polymer or a mixture of polymers consisting of allylic and (or) tertiary groups react very fast until all the reactive chlorine has been split off. This, in fact, is observed in the chlorination products of rubber (see Figure 2).

Polymers with 30–55 per cent total chlorine content split off part of their chlorine very fast, while the "slow" fraction reacts frequently with a rate found for chlorinated rubber with 64 per cent Cl (curve 4, Figure 1). The exact amount of reactive chlorine can be determined by an extrapolation to time zero.

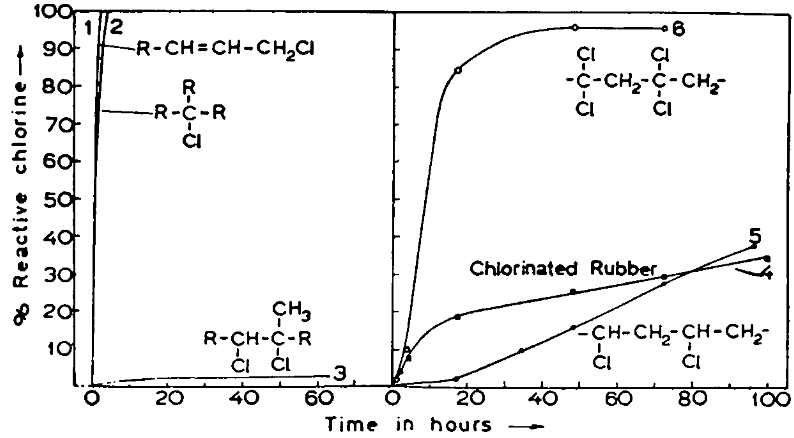


FIG. 1.—Reactivity of chlorides with aniline at 100° C. *Model Compounds:* 1, allylic chlorides; 2, tertiary chlorides; 3, vicinal dichlorides. *Polymers:* 4, chlorinated rubber with about 64 per cent chlorine; 5, polyvinyl chloride; 6, polyvinylidene chloride.

Above a total chlorine content of 55 per cent, this reactivity with aniline becomes less significant for two reasons: (1) the bend in the reaction time curve becomes less pronounced and extrapolation to time zero therefore becomes uncertain; and (2) $—CCl_2$ groups may be present and can interfere with the determination of the allylic fraction.

The reactivity with aniline by itself does not prove that the reactive fraction is allylic. Additional kinetic experiments[6] would be necessary to distinguish between allylic and tertiary chlorine in cases where it is not obvious from the type of reaction (chlorination or hydrochlorination, respectively).

Experiments were performed by heating 0.1–0.2 gram of polymer with 4 cc. of purified aniline in a sealed tube. The contents of the tube were rinsed in a beaker with dilute (1:1) nitric acid and silver nitrate added. The dyestuffs formed from aniline were removed with charcoal and the filtered solution was titrated according to Volhard.

As a matter of convenience we have usually determined the amount of reaction of chlorinated rubber with aniline after a heating time of 17 hours at 100° C. It is clear from Figure 2 that this value may be 4 to 7 per cent higher than the extrapolated value, an inaccuracy which does not influence our conclusions.

CHLORINE GAS WITH RUBBER IN SOLUTION

With the object of discovering the optimum conditions for the production of chlorinated rubbers of greater stability than usual, a large number of experiments were carried out in which rubber in solution was made to react with gaseous chlorine. These experiments, which are recorded in Tables I and II, were carried out quite simply by introducing gaseous chlorine into roughly 100 cc. of a rubber solution stirred vigorously. In some cases a solution of gaseous chlorine in carbon tetrachloride was added dropwise instead of introducing gaseous chlorine as such. The natural rubber used was masticated standard sheet or crepe; the deproteinized rubber a commerical crepe grade; the gutta-percha specially purified by recrystallization of first quality commercial gutta-percha. The reaction product was reprecipitated for analysis by dissolving it in benzene or chloroform and precipitating with alcohol. The Carius method was employed to determine the chlorine content. Generally, these determinations were accurate within 0.5 per cent.

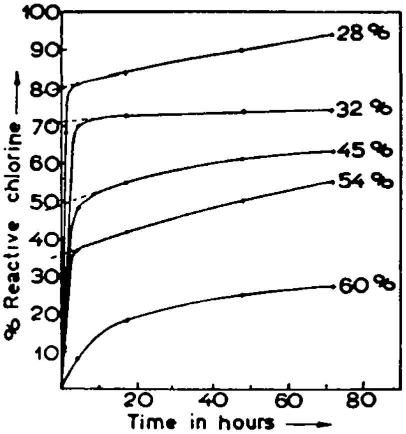


FIG. 2.—Reaction of chlorinated rubber with aniline at 100° C. The figures on the curves refer to the total chlorine content of the polymer.

The nature of the reaction products is characterized by the percentage of reactive chlorine, *i.e.*, the portion of combined chlorine which is reactive in the aniline test (17 hours 100° C). It is found that the stability of the products toward aniline is quite independent of the experimental conditions. Although the percentages of reactive chlorine vary strongly, the responsible factor has been found on careful investigation to be the total chlorine content of the reaction product. This chlorine content of chlorinated rubbers is governed by the duration and intensity of chlorination. A somewhat larger chlorine content is usually obtained at higher temperatures, *e.g.*, 50 to 70° C, than at 0 to 20° C. The addition of benzoyl peroxide (Bz_2O_2) as a catalyst does not affect the nature of the chlorine and certainly does not help to increase the chlorine content. Experiments with purified gutta-percha have proved that exhaus-

TABLE I

CHLORINATION OF NATURAL RUBBER AND GUTTA-PERCHA IN 5 PER CENT SOLUTION WITH CHLORINE GAS

Polymer	Solvent	Catalyst	Time (hours)	Temp. (° C)	% Cl in product	% reactive Cl of total
Natural rubber	$CHCl_3$	—	17	−70	41.5	55
Deproteinized rubber	CCl_4	—	1	5	43.5	70
		—	2	5	49.5	65
		—	4	5	62.0	30
		—	7	5	64.0	15
		O_2	2	5	50.5	58
		O_2	7	5	50.5	57
Natural rubber	CCl_4	—	1	20	36.5	79
		2% Bz_2O_2	1	20	27.0	80
		—	2	20	48.0	57
		—	7	20	62.5	17
Gutta-percha	CCl_4	—	0.5	20	22.5	75
		5% Bz_2O_2	0.5	20	22.0	74
		—	1.5	20	58.5	19
Natural rubber	CCl_4	—	1	77	49.0	37
		5% Bz_2O_2	1	77	35.0	63
		—	4	77	60.5	13
		—	8	77	65.5	14
		—	16	77	68.0	21

tive purification of the polyisoprene hydrocarbon also has no visible effect. Oxygen has a slight inhibiting effect during continued chlorination. Exposure to the light of an ordinary tungsten lamp hardly influences the rate of reaction, but ultraviolet light has a considerable influence, as is evident from Table II.

SOME EXPERIMENTS ON FRACTIONATION

Products of about 30 per cent chlorine content, when fractionated, are found to be nonhomogeneous. A more regular reaction appears to result from the dropwise introduction of chlorine dissolved in carbon tetrachloride instead of in the gaseous form, but it is clear from the following experiments that even then the products are nonhomogeneous.

1. At −10° C, 10 grams chlorine, dissolved in 86 cc. CCl_4, were added drop by drop to 20 grams masticated crepe dissolved in 400 cc. CCl_4, the material being stirred constantly. The resulting product contained 18.5 per cent of chlorine. This product was fractionated by solution in $CHCl_3$ (3 per cent

TABLE II

INFLUENCE OF LIGHT ON CHLORINATION WITH GASEOUS CHLORINE OF NATURAL RUBBER IN 5 PER CENT CCl_4 SOLUTION (REACTION TIME, 7 HOURS)

	Dark		100-watt electric bulb		U.V. light quartz	
Temp. (° C)	% Cl in product	% reactive Cl	% Cl in product	% reactive Cl	% Cl in product	% reactive Cl
0	59.0	40	62.0	17		
20	62.5	19	64.0	17		
50	60.5	30	64.0	17	66.5	18
77	65.0	16	65.0	18	70.0	57

solution) and precipitating with progressive amounts of isoamyl alcohol. The following were obtained:

42% of a fraction with 41.3% Cl
7% of a fraction with 35.0% Cl
38% of a fraction with 1.5% Cl
13% of a fraction with 0.5% Cl

2. Another chlorinated rubber, treated in the same way, contained 18.0 per cent of chlorine. This was fractionated by dissolving in benzene and precipitating in fractions with acetone and then with ethyl alcohol. The following were obtained:

37% of a fraction with 1.1% Cl
27% of a fraction with 22.5% Cl
36% of a fraction with 30.5% Cl

The chlorine in the two latter fractions was found to be reactive in the aniline test to the extent of 90 to 95 per cent, which means that the fractions contain approximately that amount of allylic chlorine.

A few experiments were also performed in a film reactor, but with the same result, *viz.*, the formation of nonhomogeneous products. We shall see in Part II of this series that it is possible to obtain homogeneous products by chlorinating with SO_2Cl_2.

The extremely rapid reaction between rubber and chlorine is in all probability responsible for this nonhomogeneity. This reaction, betrayed by the evolution of HCl, is seen to occur as soon as gaseous chlorine or a chlorine solution is mixed with the rubber solution, and it is a tenable conjecture that the conversion takes place in a matter of a fraction of a second. Then, the viscosity of the solution stands in the way of rapid intensive mixing, with the result that, even with intensive stirring, there are likely to be local high concentrations of chlorine, in the vicinity of which the rubber reacts with greater ease than elsewhere in the solution.

CHLORINATION UNDER PRESSURE

There was good reason to believe that if the pressure of the chlorine gas was raised, the reaction of chlorine with rubber would be accelerated and the chlorine content of the chlorinated rubber increased. A special device was made by which rubber in solution can be chlorinated under pressure—see Figure 3.

The apparatus comprises a couple of bronze autoclaves. A glass jacket in an autoclave of 200 cc. capacity contains about 100 cc. of a rubber solution. It is necessary to have chlorine gas flowing continuously through the solution to keep the latter sufficiently saturated and homogeneous, and also to evacuate the HCl formed during the reaction. An exhaust is accordingly provided for the surplus gas *via* a condenser through a regulated pressure valve. The required chlorine is in the liquid state in the other autoclave connected by pressure pipe with the reaction autoclave. The autoclaves can be heated to any temperature required. By keeping the temperature of the chlorine autoclave 10 to 20° C below that of the reaction autoclave, a constant stream of chlorine gas can be made to bubble through the solution *via* a silver inlet tube.

It was found expedient to chlorinate the rubber solution in the ordinary way for some time before applying pressure. The impression from a comparison of Table III with Table I is that the application of pressure certainly does produce

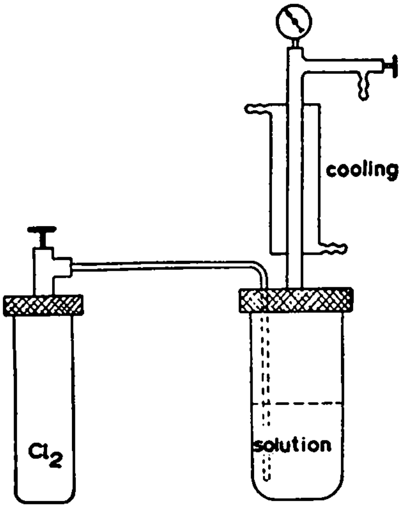


FIG. 3.—Apparatus for chlorinating rubber solutions under pressure.

a higher chlorine content in less time. An added advantage is that the material can thus be chlorinated at temperatures far above the boiling point of the solvent. On the evidence of the recorded intrinsic viscosities, the solubility of the resulting products is satisfactory. Without exposure to light it is exceedingly difficult to obtain chlorine contents above 65 per cent at ordinary pressure, so large-scale production of chlorinated rubber of a high chlorine content would without doubt benefit by the application of pressure.

CHLORINATION WITH LIQUID CHLORINE

The next point on our program was to discover how rubber responds to chlorination with liquid instead of gaseous chlorine. We can see from Table IV what happens when liquid chlorine reacts at relatively low temperature with rubber in solution. In these experiments 10 cc. liquid chlorine was mixed with 10 cc. solution at $-70°$ C and, if necessary, was then warmed up in a closed tube to the desired reaction temperature. Apparently, the reaction, in the main, occurs at $-70°$ C. The chlorine content does not differ appreciably from that resulting from chlorination with gaseous chlorine, which proves that the

TABLE III

INFLUENCE OF PRESSURE ON CHLORINATION OF NATURAL RUBBER IN 3 PER CENT CCl_4 SOLUTION

First phase: chlorination at atmospheric pressure for 4 hours at 45° C

Pressure, atm.	Second phase temp. (° C)	Time (hours)	Per cent Cl in product	$[\eta]$[a]
7	70	5	65.5	0.48
11	70	2	67.5	0.18
12	120	2	66.5	0.14
13	90	2	68.5	0.09

[a] Intrinsic viscosity of the polymer solution in $CHCl_3$, determined at 25° C in an Ostwald viscometer.

TABLE IV

CHLORINATION OF NATURAL RUBBER IN SOLUTION WITH LIQUID CHLORINE

Solvent	% rubber in solution	Temp. (° C)	% Cl in product	
			1 hour	17 hours
$CHCl_3$	5	−70	51.0	54.5
	20		50.0	54.0
CCl_4	5	+20	52.5	58.5
	20		51.0	56.0

chlorine concentration does not have a great influence on the course of the reaction. A higher temperature would be needed to obtain larger chlorine content.

It was tempting to allow liquid chlorine to react direct with solid rubber, thus obviating the tedious and costly process of solution involved in the production of chlorinated rubber[7]. The technique in these experiments was to add about half a gram of rubber to roughly 10 cc. of liquid chlorine at −70° C in a small autoclave, and then to warm it up gradually to the desired temperature. It was found incidentally, that liquid chlorine is an excellent swelling agent for rubber. When the reaction has ceased, the chlorine is evaporated and the resulting chlorinated rubber purified by dissolving it in $CHCl_3$ and precipitating with alcohol.

It will be seen from the data of Table V that the reaction proceeds with greater velocity at higher temperatures, when the normal chlorine contents for commercial chlorinated rubber are obtained and surpassed. There is, however, one serious drawback to this method: if the rubber and liquid chlorine are warmed too quickly, the reaction is likely to be too violent and to cause charring. There may even be signs of kindling when finely divided pieces of rubber or gutta-percha are introduced into liquid chlorine at −50° C. It is, therefore, necessary to be on guard against any reaction of chlorine with rubber in anything like large quantities, and one should, in any case, beware of letting liquid chlorine react at the more elevated temperatures with major amounts of rubber all at once, as the reaction is likely to become uncontrollable[8]. The products are generally insoluble, only those containing a very large percentage of chlorine (65–70 per cent) being soluble. Apparently, cross-linking reactions are apt to occur during chlorination as a secondary reaction, but this is a much rarer occurrence with chlorination in dilute solution because the solvent molecules keep the rubber molecules further apart. The solubility of products of large chlorine content is due to chlorinolysis. Under the severe conditions employed, the chlorine disrupts C—C bonds of the chlorinated rubber molecules with the formation of smaller fragments.

TABLE V

CHLORINATION OF SOLID NATURAL RUBBER WITH LIQUID CHLORINE

Temp. (° C)	Time (hours)	% Cl in product	% reactive Cl
−70	17	38–43	50–40
−40	17	49–57	50–20
20	3–60	50–60	40–20
50	5	60	20
70	3–6	63–64	14–25
100	3–6	68–70	30–41
120	1–3	68–69	35

CHARACTER OF THE CHLORINE-RUBBER BOND

Some experiments were performed to discover how much chlorine is combined by substitution. This can be deduced fairly easily from the quantity of hydrochloric acid generated, since one molecule of HCl is liberated for every chlorine atom combined by substitution.

In these experiments, the results of which are given in Figure 4, a solution of chlorine gas in carbon tetrachloride of known concentration was dripped into a given amount of rubber solution in carbon tetrachloride at 60° C. It would seem that it is especially in the initial stages of chlorination (below 30 per cent of combined chlorine) that the reaction proceeds almost entirely by substitution. In the case of products with 50–55 per cent of combined chlorine, the chlorine is bound additively to the extent of 40 per cent. This is consistent with the view that addition of chlorine on the double bond follows substitution of one chlorine atom per isoprene unit. The possibility remains, however, that there may be a certain amount of splitting-off of HCl from the chlorinated rubber during the reaction. The aniline test indicates that the primarily bound substitution chlorine possesses a reactivity which, according to experiments with model substances, fits in with a linkage at the allylic position.

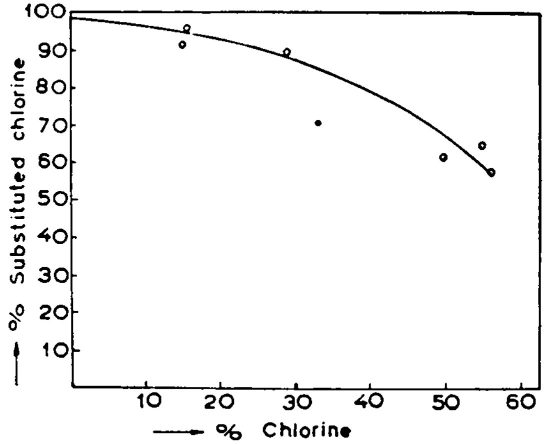


FIG. 4.—The quantity of substituted chlorine as a function of the chlorine content.

It will be seen from Figure 5 that the quantity of reactive chlorine split off in the aniline test decreases with increasing chlorine content. Products containing about 30 per cent of chlorine show that roughly 80 per cent of this chlorine is reactive in the aniline test. This reactivity drops to approximately 15 per cent in chlorinated rubbers with 60–66 per cent, but begins to increase again above 67 per cent of chlorine.

The remarkable point about this is that the results recorded in Figure 5 are those obtained with chlorinated rubbers produced under the most divergent reaction conditions with variation of temperature, pressure, source of chlorine (gaseous or liquid), rubber (solid or in solution), exposure to light, and catalysts. It is evident, therefore, that however much we varied these conditions, we were unable to combine chlorine with rubber in any fundamentally different way. The minor variations found in Figure 5 may be due in part to lack of homogeneity of the chlorinated rubber. In Part II we shall discuss methods that do make it possible to combine chlorine with rubber in a different way and to which the relation found in Figure 5 does not apply.

The results of the aniline test tend to show that in all instances the chlorine is first mainly bound by substitution at an allylic position. With 50 per cent of chlorine, chlorinated rubber contains, on an average, two chlorine atoms per isoprene unit. We have to assume that roughly half the isoprene units contain only one loosely bound allylic chlorine atom, whereas the other half of the isoprene units contain three atoms far more firmly attached. This is compatible with an average reactivity of the total chlorine in a chlorinated rubber of this kind with aniline of approximately 45 per cent. The increase in reactivity with aniline of chlorinated rubber containing more than 67 per cent of chlorine may be due to the formation of —CCl_2 groups, which are very reactive with aniline, as has been shown in Figure 1 for polyvinylidene chloride.

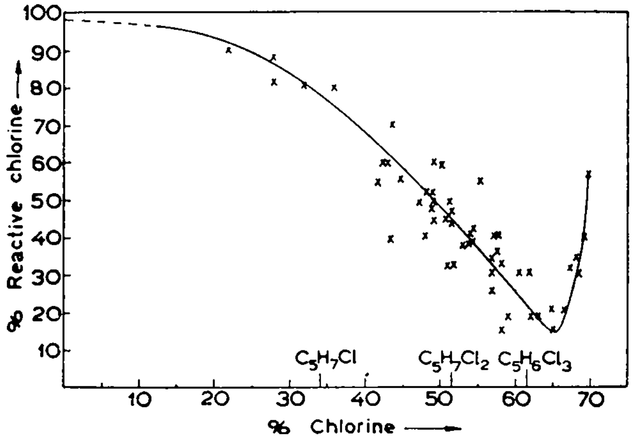
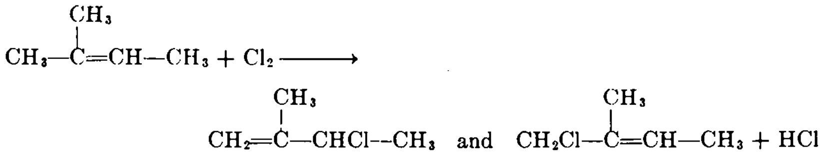


FIG. 5.—Percentage of reactive chlorine in the aniline test as a function of chlorine content.

It has been stated[9] that a substitution of chlorine at the allylic position is likely to occur at very low temperatures (0 to −60° C), with great rate of reaction in the chlorination of branched olefins, such as isobutene and trimethyl ethylene, in the liquid phase. The following two chlorides are formed from trimethyl ethylene:

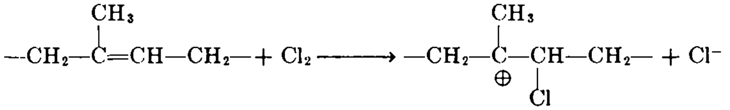


$$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 + Cl_2 \longrightarrow}$$

$$\mathrm{CH_2=\overset{CH_3}{\overset{|}{C}}-CHCl-CH_3 \text{ and } CH_2Cl-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 + HCl}$$

when at the same time allylic rearrangement between the two products takes place. This substitutive chlorination of isobutylene and trimethyl ethylene illustrates a fairly general rule formulated by Kondakoff[10] in 1891 to the effect that olefins which combine readily with mineral acids yield monochloroolefins, whereas those which do not, yield the normal addition products on treatment with chlorine. Natural rubber and gutta-percha possess a structure very similar to that of trimethylethylene, and these polymers combine readily with a mineral acid such as HCl. Thus the primary substitutive reaction of these polymers is in line with the behavior of olefins in general.

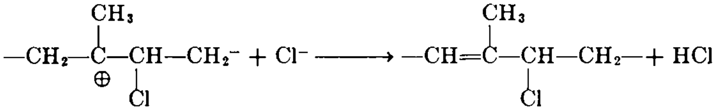
Although the chlorination of hydrocarbons generally constitutes a free radical type of reaction, it is nevertheless a tenable conjecture that, with olefins, the primary reaction in chlorination is of an ionic nature[11]. It has been found that the normal primary chlorination of rubber and like olefins with chlorine cannot be accelerated by normal free-radical chain-initiating agents. Nor can the chlorination be arrested by the known chain reaction inhibitors. Arguments can be advanced[12] to show that the rate-determining step is addition of a positive chlorine ion to the double bond to form a carbonium ion and a negative chlorine ion.



$$-CH_2-\overset{CH_3}{C}=CH-CH_2- + Cl_2 \longrightarrow -CH_2-\underset{\oplus}{\overset{CH_3}{C}}-\underset{Cl}{CH}-CH_2- + Cl^-$$

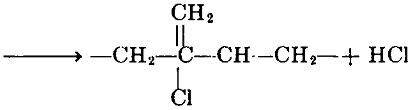
The intermediate carbonium ion follows several distinct reaction courses. It may be that a proton splits off. The double bond resulting from the elimination of the proton is formed preferentially between the carbon bearing the positive charge and that adjacent carbon atom which is the most richly endowed with electrons, and it is from this carbon atom that the proton splits off[12]. We may then obtain the following chlorinated rubber structures:

(a)



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

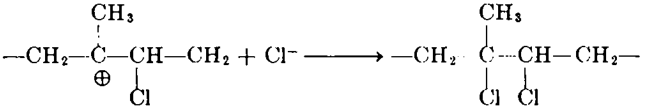
(b) and



$$\longrightarrow -CH_2-\overset{CH_2}{\overset{\|}{C}}-\underset{Cl}{CH}-CH_2- + HCl$$

Apart from this, we have to allow for the possibility of the carbonium ion's reacting with a Cl⁻ ion with the formation of a normal chlorine addition product, as follows:

(c)

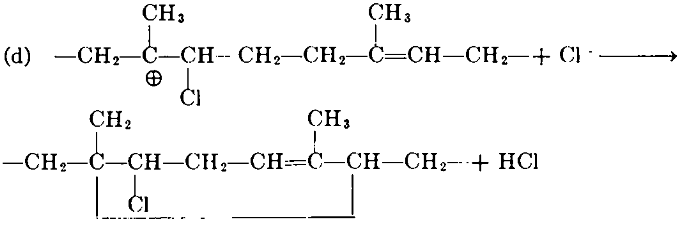


$$-CH_2-\underset{\oplus}{\overset{CH_3}{C}}-\underset{Cl}{CH}-CH_2 + Cl^- \longrightarrow -CH_2-\underset{Cl}{\overset{CH_3}{C}}-\underset{Cl}{CH}-CH_2-$$

On the evidence of the quantity of HCl split off and the results of the aniline test, however, it is quite certain that only infinitesimal amounts of this rubber dichloride are formed, if at all.

Bloomfield[4] argues from iodine number determinations that the following cyclization reaction is likely to take place:

(d)



$$-CH_2-\underset{\oplus}{\overset{CH_3}{C}}-\underset{Cl}{CH}-CH_2-CH_2-\overset{CH_3}{C}=CH-CH_2- + Cl^- \longrightarrow$$

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

In view of the fact that chlorinated rubbers in solution are of relatively low viscosity compared to their molecular weight, Staudinger and Staudinger[13] likewise come to the conclusion that considerable cyclization must have taken place during the chlorination. These authors assign a different structure to cyclized chlorinated rubber from that suggested by Bloomfield. They presume that the methyl group reacts with the main chain during cyclization, and that other unknown cyclization reactions also occur. It is certainly not difficult to see that there are alternatives to the structure assigned by Bloomfield to cyclized chlorinated rubber. The fact alone that the reaction products of liquid chlorine with solid rubber are usually insoluble shows that not only intramolecular, but also intermolecular cross-linking reactions are probably involved. Especially at the more elevated temperatures cyclization reactions are likely to predominate over the chlorination reactions (a) and (b).

It is interesting to note that, except when there is addition, combination of chlorine is invariably accompanied by a shifting of double bonds. Such displacement, with the formation of an $R_1R_2C{=}CH_2$ group, is borne out by the evidence of infrared investigations[15].

When chlorination is slow, we must be prepared to find that the HCl evolved may be added on to the original polyisoprene double bond. This side reaction, which leads to rubber hydrochloride structures, can be avoided by chlorinating quickly, or by immediately evacuating the HCl generated by means of an inert gas.

The further chlorination of the primary products of chlorination may be supposed to proceed anew *via* a carbonium ion. The smaller quantity of HCl evolved at this stage would seem to indicate that considerable addition now takes place, even though, side by side, substitution may likewise occur, with displacement of the double bond or cyclization. This greatly increases the number of conceivable chlorinated rubber structures with large chlorine contents, and the manner in which the chlorine is combined in these structures is very complicated.

ACKNOWLEDGMENT

The authors wish to express their thanks to W. H. Manger and J. V. van Ulden for their valuable assistance, and to the Rubber Foundation for permission to publish the results of the investigation.

REFERENCES

[1] Nielsen, "Chlorkautschuk", Hirzel, Leipzig, **1937**; Baxter and Moore, *J. Soc. Chem. Ind.* **57**, 327 (1938); RUBBER CHEM. & TECHNOL. **12**, 82 (1939); Bloomfield, *J. Chem. Soc.* **1943**, p. 289; **1944**, p. 114; D'Ianni, Naples, Marsh and Zarney, *Ind. Eng. Chem.* **38**, 1171 (1946).
[2] Nielsen, "Chlorkautschuk", Hirzel, Leipzig, **1937**.
[3] Bloomfield, *J. Chem. Soc.* **1943**, p. 289; **1944**, p. 114.
[4] Bloomfield, *J. Chem. Soc.* **1943**, p. 289.
[5] Salomon, Koningsberger and Ultée, *Proc. 2nd Rubber Technol. Conf. London*, **1948**, p. 109.
[6] Salomon and Ultée, *Rec. trav. chim.* **69**, 95 (1950).
[7] Ellis and Boehmer, U. S. Pat. 1,544,531 (1925); Ellis, U. S. Pat. 1,544,533 (1925); Kaganoff, British pat. 606,400 (1948).
[8] Murray, *Chem. Eng. News* **26**, 3369 (1948).
[9] Burgin, Engs, Groll, and Hearne, *Ind. Eng. Chem.* **31**, 1413 (1939).
[10] Kondakoff, *Ber.* **24**, 929 (1891).
[11] Remick, 'Electronic Interpretations of Organic Chemistry", Wiley, New York, **1945**, p. 222.
[12] Taft, *J. Am. Chem. Soc.* **70**, 3364 (1948).
[13] Staudinger and Staudinger, *J. prakt. Chem.* **162**, 148 (1943).
[14] Sheppard and Sutherland, *Discussions Faraday Soc.* **2**, 374 (1947).