[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dielectric Dispersion and Absorption in Neoprene Gum and Tread Stocks

BY W. C. SCHNEIDER, W. C. CARTER, M. MAGAT AND C. P. SMYTH

It is well known that the dielectric constants and the dielectric losses of rubbers reinforced with carbon black are very high in the frequency regions where measurements have been made.[1] However, no explanation has ever been offered to account for this behavior. In order to obtain an indication as to the possible mechanisms involved, we have investigated the dielectric properties of Neoprene-GN, both gum and tread, at three different temperatures, 20, 40 and 60°, over a wide range of frequencies, extending, in certain cases, from 60 cycles to 3000 megacycles.

Experimental

Between 500 cycles and 100 megacycles a technique[1a] similar to that of Yager was used. The measurements were made with a capacitance bridge (0.5 to 300 kc.), a Twin-T impedance measuring circuit (0.5 to 40 mc.) and a Q-meter (40 to 120 mc.). As can be seen from Fig. 1 the data obtained with the three different instruments give a perfectly smooth curve. At our request, Drs. R. M. Fuoss and D. J. Mead of the General Electric Company were kind enough to make some measurements in the range from 60 to 540 cycles using a Schering bridge and their technique of "Aquadag" electrodes. The measurements at 3000 mc. on the pure gum were carried out in the Palmer Physical Laboratory by Dr. M. H. Nichols and Mr. R. Blizzard whom we wish to thank for their valuable assistance. Although at this frequency the experimental technique is quite different from those employed at the lower frequencies, the measured points fall exactly on our extrapolated curves.

In order to be able to carry out high frequency dielectric measurements at temperatures different from room temperature, without notably increasing the length of the leads, a Dewar was constructed with a hole in the bottom and a concentric cable system connecting the inside and the outside. The cell with the sample was heated by water circulating in a copper coil surrounding the cell. The water was heated in a thermostat held to ±0.1°. The thermostat temperature was maintained slightly higher than the desired measuring temperature in order to compensate for heat losses in the line leading to the cell. The temperature was measured with a thermocouple placed in contact with the sample.

The work at temperatures different from room temperature required a slight modification of the original method.[1a] Yager used a simple substitution method, balancing the bridge once with the cell containing the sample of thickness d_s and then rebalancing the bridge with the cell containing air, by changing the electrode distance. If the air distance necessary for the balancing of the bridge is d_a, the dielectric constant, ϵ, of the sample is given by $\epsilon = d_s/d_a$.[1b] This requires that the sample be placed in the cell and removed for each frequency. With the length of time necessary for temperature equilibrium to be established, it is impractical to use this procedure. Hence, we have calibrated the readings of the measuring condenser as a function of the electrode distance in the cell for each frequency used and balanced the bridge once without the cell and once with the cell containing the sample. The corresponding air thickness was determined from a graph. The calibration remained sufficiently stable over long periods of time. By measuring the dielectric properties of a sample kindly given us by Dr. Yager it was found that the results obtained by the original Yager method and by our modification were in excellent agreement.

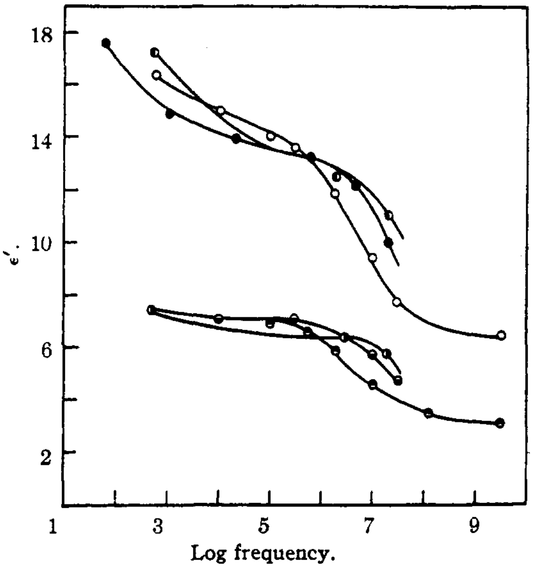

Fig. 1.—The dielectric constant of Neoprene-GN gum and tread at various temperatures: tread—○, 20°, ●, 40°, ◐, 60°; gum—◓, 20°, ◑, 40°, ◒, 60°.

Neoprene was selected for our investigation because its dielectric constant is moderately high, and its dispersion region is situated in an easily accessible frequency region. On the other hand, carbon black is known to reinforce this elastomer only slightly, if at all, so that the interaction between Neoprene and carbon black ought to be fairly small. The two samples of Neoprene-GN, gum and tread, were kindly prepared for us by

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[1] Yerzley, *Ind. Eng. Chem.*, **35**, 330 (1943).

[1a] Yager, *Trans. Am. Electrochem. Soc.*, **74**, 117 (1938).

[1b] Assuming that the fixed capacity of the cell and edge effects are identical at each electrode setting.

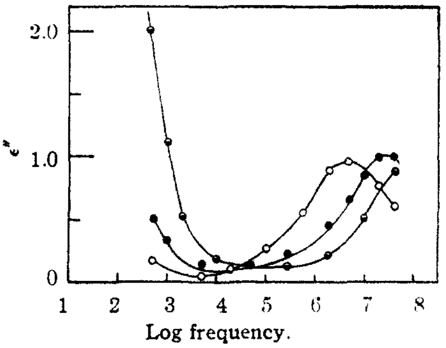

Fig. 2.—The dielectric losses of Neoprene-GN gum at various temperatures: ○, 20°, ●, 40°, ⊖, 60°

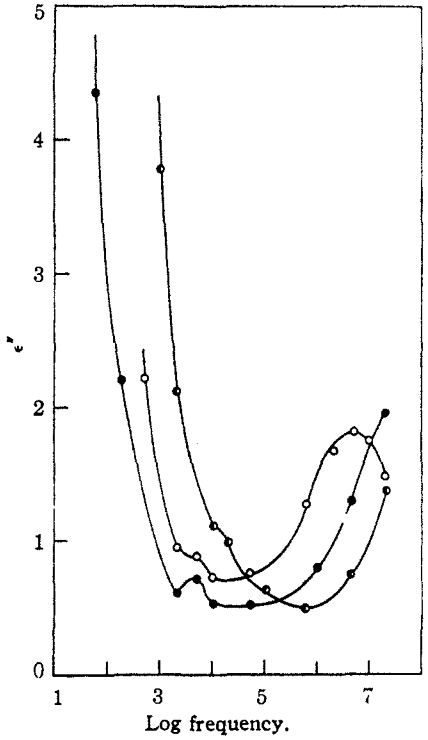

Fig. 3.—The dielectric losses of Neoprene-GN tread at various temperatures: ○, 20°, ●, 40°, ⊖, 60°.

Dr. R. F. Dunbrook and Dr. J. H. Dillon of the Firestone Tire and Rubber Company, the two recipes being as similar as possible. Each sample contained, for every 100 parts by weight of Neoprene-GN, 5.0 parts of zinc oxide, 0.5 stearic acid, 1.0 agerite powder (phenyl-β-naphthalamine), 2.5 cottonseed oil, 4.0 calcined light magnesia, 0.75 altax (benzothiozal disulfide), and 0.5 pip pip (piperidinium pentamethylene carbamate), and the tread contained 50.0 parts of channel black. Both samples had been cured for 75 minutes at 270°F. The results are summarized in Fig. 1 (dielectric constants) and Figs. 2 and 3 (dielectric losses).

Results and Discussion

The gum shows the usual behavior of plastic materials as described by the theories of Cole and Cole[2] and Fuoss and Kirkwood.[3] According to the latter, the existence of a distribution of relaxation times requires a linear relationship between the logarithm of the frequency, ν, and the quantity

$$\cosh^{-1}\frac{[\mathrm{H}(0)]}{[\mathrm{H}(x)]} = \cosh^{-1}\frac{\epsilon''_m[2 + 1/\epsilon'^2_m]}{\epsilon''[2 + 1/\epsilon'^2]}$$

where ϵ''_m = maximum dielectric loss, ϵ'_m = dielectric constant at frequency of maximum loss, ϵ'' = dielectric loss, ϵ' = dielectric constant. Figure 4 shows that this relation actually is obeyed for both Neoprene gum and tread. A striking fact is that the plots for gum and tread at 20° are identical, suggesting that there is no interaction between carbon black and Neoprene.

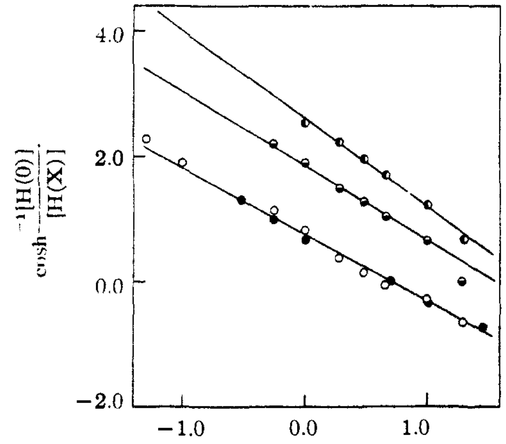

Fig. 4.—Plot of the Kirkwood–Fuoss function for Neoprene-GN gum and tread at various temperatures: gum—○, 20°, ⊖, 40°, ◐, 60°; tread—●, 20°.

Using the slope of the straight line obtained from the above plot, it is possible to calculate the dipole moment per monomer unit by means of the Kirkwood–Fuoss theory. The calculated value for the monomer unit containing the C–Cl is 1.99 × 10^{-18}, as compared to 1.69 observed for 2-chloropropylene, 1.71 for *cis*-1-chloropropylene and 1.97 for *trans*-1-chloropropylene,[4] structures rather similar to that of the monomer unit —CH_2—CCl=CH—CH_2—. The agreement can be considered satisfactory, especially since the Debye theory gives a calculated moment of 8.50*D*, which is 490% in error.

The relaxation times and free energies of activation for Neoprene gum at two temperatures are summarized in Table I. These values were obtained by the method of Eyring and Powell.[5] From the free energy of activation at 20° it is possible to obtain an indication as to the length of the moving units giving rise to the re-

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(2) Cole and Cole, *J. Chem. Phys.*, **9**, 341 (1941).

(3) Fuoss and Kirkwood, This Journal, **63**, 385 (1941).

(4) Hannay and Smyth, unpublished measurements.

(5) Powell and Eyring, "Advances in Colloid Science," Interscience Publishers, New York, N. Y., 1942, pp. 217–220.

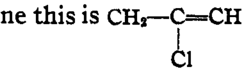
TABLE I

RELAXATION TIMES AND FREE ENERGIES OF ACTIVATION FOR NEOPRENE-GN GUM

Temp., °C.	τ_0	$\Delta F^{\pm}$, kcal.
20	3.97×10^{-8}	8.28 ± 0.17
40	6.10×10^{-9}	7.80 ± 0.17

laxation. Assuming that the free energy of activation for dielectric relaxation is identical with that for viscous flow,[5] it is possible to calculate the energy of vaporization, $\Delta E_{\text{vap.}}$, for one mole of the moving units by use of the relation[6]

$$\Delta E_{\text{vap.}} = 2.45\,\Delta F^{\pm}_{\text{vis.}}$$

The value of $\Delta E_{\text{vap.}}$ obtained is 19.8 kcal./mole. The value of $\Delta E_{\text{vap.}}$ in cal./cc. has been determined by Gee[7] from the swelling of Neoprene in various solvents. The value obtained is 67.2 cal./cc. Since the density of Neoprene gum is 1.27, $\Delta E_{\text{vap.}}$ in cal./g. is 53.0. Dividing the energy of vaporization per mole by the energy of vaporization per gram, a value for the molecular weight of the moving units is obtained, 374 g./mole. The simplest repeating unit of the polymer is known as the base mole. In the case of Neoprene this is  $CH_2{-}\underset{\text{Cl}}{\underset{|}{C}}{=}CH{-}CH_2$. A quantity representing the distributed molecular weight per chain carbon atom is obtained by dividing the molecular weight of the base mole by the number of chain carbon atoms in the base mole. For Neoprene this quantity is 22 g./chain C atom. The number of carbon atoms moving as a segment is then found by dividing the molecular weight of the moving unit by the base molecular weight per chain carbon atom. The value obtained is 17 carbon atoms. Other workers[8,9] have estimated that the moving segments contain 20 to 40 carbon atoms. It must be remembered, however, that the accuracy of the above calculations is dependent upon the assumption that Eyring's relations are valid for the case under consideration.

The energy, $\Delta E^{\pm}$, and the entropy, $\Delta S^{\pm}$, of the relaxation process calculated by the methods of Eyring and Kauzmann[10] are $\Delta E^{\pm} = 14.3$ kcal. and $\Delta S^{\pm} = 23.5$ e. u. The distribution in the free energy of activation, $\delta(\Delta F^{\pm})$, giving rise to the distribution of relaxation times, and the value of $\delta(\Delta S^{\pm})$ obtained from the temperature variation of $\delta(\Delta F^{\pm})$ were found to be $\delta(\Delta F^{\pm}) = 1390$ cal./mole at 20°, 1270 cal./mole at 40°, and 890 cal./mole at 60° and $\delta(\Delta S^{\pm}) = 17.0$ e. u. Comparing the entropy values, it is seen that most, if not all, of the entropy change accompanying the relaxation process arises from the distribution of relaxation times.

A most striking fact is the appearance in the loss curve of the carbon black loaded stock of two maxima, one at 5 mc. at 20°, very close to the loss maxima in the gum stock, and the other, much smaller, at about 7 kc. This second maximum is fairly independent of the temperature. It is more pronounced at 40° because here the overlapping of the first maximum, which we shall call the Debye maximum, is smaller. At frequencies below 2 kc. the loss curve rises rather steeply, and the sample possesses a definite d. c. conductivity. The interpretation of the results is fairly simple if one considers that carbon black loaded samples represent essentially a mixture of two dielectrics with fairly different dielectric properties, *e. g.*, different dielectric constants and conductivities. In such a mixed dielectric medium we have to expect the appearance of the Maxwell–Wagner effect.

The origin of this effect is an a. c. current which is in phase with the applied potential. This current, resulting from the differences in the conductivities and dielectric constants of the substances composing the dielectric, introduces a time factor in the charging of the boundary surfaces between the different substances. The formal equations relating ϵ', ϵ'' and τ, the relaxation time, are independent of the manner in which the mixture is obtained. They are identical for successive layers (Maxwell) and for colloidal mixtures (Wagner), which best approximate the conditions prevailing in carbon black loaded rubber stocks.[11] If $\omega = 2\pi\nu$ cycles, the equations are

$$\epsilon' = \epsilon_\infty\left(1 + \frac{k}{1 + \omega^2\tau^2}\right)$$

$$\epsilon''/\epsilon' = \tan\delta = \frac{k\omega\tau}{1 + k + \omega^2\tau^2}$$

These equations contain three constants ϵ_∞, k, and τ which can be calculated from ϵ' alone as measured at three different frequencies. The expressions for determining the constants may be written as

$$\varphi^2 = \frac{1 + AB}{\nu_1^2 + \nu_3^2\,AB}$$

$$\epsilon_\infty = \frac{\epsilon_2' - \epsilon_1'}{\varphi^2(\nu_2^2 - \nu_1^2)} + \frac{\nu_2^2\epsilon_2' - \nu_1^2\epsilon_1'}{\nu_2^2 - \nu_1^2}$$

$$k = 1/\epsilon_\infty\,(1 + \nu_1^2\varphi^2)(\epsilon_1' - \epsilon_\infty)$$

where

$$A = \frac{\nu_1^2 - \nu_2^2}{\nu_2^2 - \nu_3^2} \qquad B = -\frac{\epsilon_3' - \epsilon_2'}{\epsilon_2' - \epsilon_1'} \qquad \varphi = 2\pi\tau$$

The expressions indicate that φ^2 will be sensitive to slight errors in ϵ' since only differences in ϵ' are involved. This condition is greatly enhanced in the case of Neoprene since the change in ϵ' over the dispersion region is quite small (14.8 − 13.9). As the precision of the measurements is only about one per cent., considerable variations in the constants can occur. To illustrate this variation the constants have been calculated for two different series of experimental values (1, 5, 20

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[6] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 492

[7] Gee, *Rubber Chem. Tech.*, **16**, 827 (1943).

[8] Flory, THIS JOURNAL, **62**, 1057 (1940).

[9] Kauzmann and Eyring, *ibid.*, **62**, 3113 (1940).

[10] Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942).

[11] See, for instance, J. B. Whitehead, "Lectures on Dielectric Theory and Insulation," McGraw-Hill Book Co., Inc., New York, N. Y., 1927.

kc. and 2, 10, and 50 kc.), and the results summarized in Table II.

TABLE II

Series	k	ϵ_∞	$\varphi \times 10^4$	$\tau \times 10^5$	ν_c(kc.)	log ν_c
1	0.065	13.9	1.16	1.83	8.61	3.94
2	0.097	13.6	1.57	2.50	6.37	3.80

As predicted there is considerable variation in k and τ. However, this variation would not be so marked on a log frequency plot as indicated in the last column of Table II and a loss curve calculated from either of the two sets of constants would give fair agreement with the experimental curve.

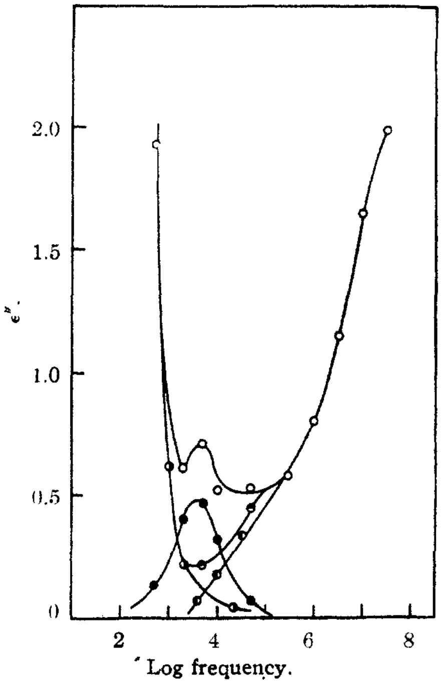

Fig. 5.—Maxwell-Wagner analysis of dielectric losses in Neoprene-GN tread at 40°: ○, $\epsilon''_{\text{obs.}}$, ●, $\epsilon''_{\text{M.W.}}$, ⊖, $\epsilon''_{\text{obs.}} - \epsilon''_{\text{M.W.}}$, ◑, $\epsilon''_{\text{d.c.}}$, ◐, $\epsilon''_{\text{Debye}} = \epsilon''_{\text{obs.}} - [\epsilon''_{\text{M.W.}} + \epsilon''_{\text{d.c.}}]$.

The constants determined in series two above were used to calculate the loss curve reproduced in Fig. 5. This series was selected since the experimental frequencies involved were more symmetrically located with respect to the critical frequency than those of series one. If we subtract these losses from the total loss curve, the remainder consists of two parts. One part corresponds to pure Debye effect losses, while the low frequency portion obeys the law, $\epsilon'' = A/\omega$, where A is a constant containing the specific d. c. conductivity, Λ, which can be calculated assuming that $A = 9 \times 10^{11} \times 4\pi\Lambda$. Table III contains, besides the values for ϵ_∞, k and τ, the d. c. conductance determined from the a. c. losses and the d. c. conductance determined directly in the cell by the use of Ohm's law, which was found to be valid for voltages ranging between 0 and 90 volts. Considering the difficulty of obtaining reproducible values for the dielectric properties of carbon black loaded stocks, the agreement can be considered as satisfactory.

TABLE III

Temp., °C.	ϵ_∞	k	$\tau \times 10^4$ sec.	$\Lambda_{\text{calcd.}}$ (20°C.)	$\Lambda_{\text{obs.}}$ (27°C.)
20	14.5	0.087	0.186	8.1×10^{-10}	5.9×10^{-10}
40	13.6	.097	.250	....	....
60	13.8	.168	.182	....	....

As far as the Debye dispersion is concerned, it is interesting to note that the critical frequencies are nearly identical for the gum and the tread stock. The absolute values of the losses are naturally different but the ratios ϵ''/ϵ' are identical.

TABLE IV

	$\nu_{\text{crit.}}$ (mc.) 20°C.	ϵ''/ϵ' 20°C.
Pure gum	4.5	0.18
Loaded stock	5.0	.17

It is not possible to calculate the dielectric constants and d. c. conductivities of the pure compounds from the parameters of the Maxwell–Wagner equations since they contain unknown quantities.

It was thought that, at 3000 mc., dipole contributions could be neglected, and the dielectric constants of pure gum and tread would be equal to the square of the refractive indices of the samples. Then from the molecular refractions of the gum and tread it should be possible to calculate the refractive index of carbon black. The dielectric constant of the gum at 3000 mc. is 3.02 while that for the tread is 6.45. The value for the tread was checked by measurements on samples 0.215 cm. thick and 0.622 cm. thick, respectively. Each sample gave identical values for ϵ. A further check was obtained from the Cole and Cole plot given in Fig. 6 which gives 6.3 as the extrapolated values for ϵ_∞.[12] This value of ϵ for the tread indicates that there is another dispersion region at higher frequency and that it is impossible to calculate the refractive index of carbon black from measurements at 3000 mc.

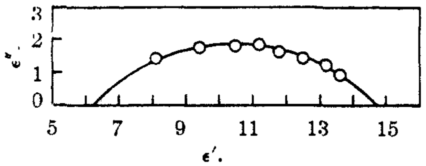

Fig. 6.—Cole and Cole plot for Neoprene-GN tread at 20°.

Acknowledgment.—The writers wish to express their indebtedness to the Firestone Tire and Rubber Company for their support of the

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[12] For a discussion of other cases where the Cole and Cole extrapolation leads to values of ϵ_∞ which are considerably larger than the index of refraction, see Mead and Fuoss, THIS JOURNAL, **63**, 2832 (1941).

work and their coöperation in supplying the samples and to the Rubber Reserve Company for additional assistance.

Summary

1. The dielectric constants and dielectric losses of Neoprene-GN gum and tread have been measured at 20, 40, 60° over a frequency range in certain cases from 60 cycles to 3000 mc.

2. The Kirkwood–Fuoss theory of dielectric relaxation has been verified over a wide frequency region. By use of this theory the dipole moment per monomer unit for Neoprene-GN gum was found to be 1.99*D*.

3. Experimental evidence has been found to confirm the assumption that there is only slight, if any, interaction between carbon black and Neoprene.

4. The free energies of activation and relaxation times have been determined for Neoprene gum. From the free energy of activation it has been calculated that there are 17 carbon atoms in the relaxing units.

5. The energy of activation and entropy of activation for Neoprene gum have been found to be $\Delta E^{\ddagger} = 14.3$ kcal. and $\Delta S^{\ddagger} = 23.6$ e. u. The distribution in the entropy of activation arising from the distribution in free energy of activation has been found to be $\delta(\Delta S^{\ddagger}) = 17.0$ e. u., which indicates that most of the entropy of activation arises from the distribution in the free energy of activation.

6. The frequency variation of the dielectric loss of Neoprene tread has been explained by use of the Maxwell–Wagner theory of dielectric relaxation.

7. The high value of ϵ, 6.45, at 3000 mc. indicates that there is another dispersion region at higher frequencies.

PRINCETON, NEW JERSEY RECEIVED FEBRUARY 7, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Direct Synthesis of Organosilicon Compounds

BY EUGENE G. ROCHOW

Organosilicon compounds customarily are prepared by the action of some other organometallic compound upon a silicon halide or an ester of orthosilicic acid. Thus Kipping[1] and his coworkers have employed the Grignard reagent and silicon tetrachloride in their impressive series of investigations,[2] while the alkyls of zinc and mercury were used much earlier by Friedel and Crafts[3] and by Ladenberg.[4] The Wurtz–Fittig synthesis, first used by Polis[5] and later by Kipping and Lloyd,[6] has recently been investigated by Schumb, Ackerman and Saffer,[7] who showed that in certain cases it is advantageous to prepare an organosodium compound separately and then allow it to react with the silicon halide.[8] The action of the Grignard reagent upon ethyl silicate has been described in a series of Russian publications.[9,10]

In all these methods, it has been necessary to prepare the organometallic compound (or a series of organometallic compounds derived one from the other) and then to carry out the reaction with a covalent compound of silicon in a solvent or in an excess of the reagent. The silicon halide must in turn have been prepared from silicon and, if an ester is to be used, it requires reaction of the halide with the corresponding alcohol.

In connection with the investigation of silicone polymers in this Laboratory,[11,12] a simpler and more direct synthesis was highly desirable. Many reactions were tried with negative results, but at length it was found possible to synthesize alkyl- and aryl-substituted silicon halides by the direct reaction of the alkyl or aryl halide with elementary silicon. While this reaction was found first to proceed in the case of methyl chloride passed over an alloy of silicon and copper heated in a tube to a temperature of approximately 360°, subsequent experiments have shown that the reaction is a general one whereby hydrocarbon halides in the liquid or vapor phase are caused to react with silicon in the presence or absence of a metallic catalyst.

Under favorable conditions, the principal product of the reaction between elementary silicon and an alkyl or aryl halide RX is the corresponding dialkyl- or diaryl-dihalosilane, R_2SiX_2. This, may be obtained in yields as high as 70%. Lesser amounts of the related compounds $RSiCl_3$ and R_3SiCl are obtained at the same time, and even some R_4Si and SiX_4. Under conditions which encourage some pyrolysis of free hydrocarbon

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(1) Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904). The method also was employed at about the same time by Dilthey, *Ber.*, **37**, 319 footnote 2 (1904).

(2) See bibliography on pp. 290, 291 of Krause and von Grosse, "Die Chemie der metallorganischen Verbindungen," Berlin, 1937.

(3) Friedel and Crafts, *Ann.*, **136**, 203 (1865). See also Friedel and Ladenberg, *ibid.*, **159**, 259 (1871), and **203**, 251 (1880).

(4) Ladenberg, *ibid.*, **164**, 302 (1872); **173**, 151 (1874).

(5) Polis, *Ber.*, **18**, 1540 (1885).

(6) Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

(7) Schumb, Ackerman and Saffer, THIS JOURNAL, **60**, 2486 (1938).

(8) Schumb and Saffer, *ibid.*, **63**, 93 (1941).

(9) Andrianov and Gribanova, *J. Gen. Chem.* (U. S. S. R.), **8**, 552 and 558 (1938).

(10) Andrianov and Kamenskoya, *ibid.*, **8**, 969 (1938).

(11) Rochow and Gilliam, THIS JOURNAL, **63**, 798 (1941).

(12) Gilliam, Liebhafsky and Winslow, *ibid.*, **63**, 801 (1941).