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PHOTOELASTIC PROPERTIES OF SOFT, VULCANIZED RUBBER

By Wilfred E. Thibodeau and Archibald T. McPherson

ABSTRACT

A study of double-refraction under tensile stress was made on transparent, vulcanized rubber at about 25° C by means of a Babinet compensator, using light of wave length, 5461 A. The relative retardation per unit thickness and the stress-optical coefficient were found to be related to the stress by equations of the form, $\Delta n = aT + bT^2 + cT^3$, and $C = a + bT + cT^2$, where Δn is the retardation coefficient, C the stress-optical coefficient, T the stress, and a, b, and c are constants for any given rubber compound. Formulas of the compounds investigated, in parts by weight, were: pale crepe rubber, 100; stearic acid, 1; and zinc oxide, 1, to which was added—(A) "captax" (mercaptobenzothiazole), 1, "tuads" (tetramethylthiuramdisulphide), 0.5, selenium, 0.5, and sulphur, 0.3; (B) "tuads", 0.3, and sulphur, 2.0; (C) "tuads", 0.3, and sulphur, 4.0; (D) "captax", 0.5, and sulphur 2.5; (E) "captax", 0.5, and sulphur, 4.0; (F) to (J), inclusive, sulphur, 3 to 7, respectively. Compounds (K), (L), and (M) were made from rubber hydrocarbon with 4, 6, and 8 percent of sulphur, respectively. The parameters, a, b, and c, were functions of the type of compound. A term in c was needed, if at all, only at stresses above 65 bars. For compounds A to E, inclusive, values of $a \times 10^4$ were 2.059, 2.092, 2.233, 2.155, 2.242, respectively; values of $b \times 10^4$ were 0, 0, −0.00354, 0, −0.00146, respectively. For compounds F to M, inclusive, a and b were functions of the percentage of combined sulphur, and the retardation coefficient was given by the equation,

$$\Delta n \times 10^4 = (1.960 + 0.0250\ S_c)\ T - (0.00540 + 0.00112\ S_c)\ T^2,$$

where S_c is the percentage of combined sulphur.

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I. INTRODUCTION

This paper describes an exploratory study of the photoelastic properties of transparent, soft, vulcanized rubber. The work was originally undertaken to obtain data on rubber samples that were used in an investigation of stresses in models by the photoelastic

[1] W. E. Thibodeau, unpublished work.

method,[1] and was extended to provide general information on the relation of the photoelastic properties to the composition of rubber.

Measurements of the photoelastic behavior of rubber have been made by several previous investigators whose work points to a functional relation between double-refraction and stress. Bjerken [2] made measurements on rubber of unspecified composition at stresses from 5 to 69 bars, which corresponded to elongations from 66 to 434 percent. Rossi [3] observed the behavior of three types of rubber compositions, (1) crude rubber, (2) the same, mixed with oil and wax, and (3) rubber vulcanized with 15 percent of sulphur and subsequently extracted with benzene. Rossi's measurements extended only to stresses of 5 to 7 bars, which corresponded to elongations of 50 to 100 percent. The measurements of the coefficient of relative retardation by both Bjerken and Rossi, when plotted as functions of stress, give smooth curves which are either linear or nearly so. Van Geel and Eymers,[4] however, working with sheets of rubber made by the evaporation of latex, obtained a discontinuous relation between relative retardation and stress. Other investigators have studied the double-refraction of rubber in relation to the structure. This latter work is summarized in a recent paper by Rowland.[5]

The contribution of the present investigation lies in the fact that it presents measurements made over relatively wide ranges of stress and composition, and indicates that for any given rubber compound the relation between relative retardation per unit thickness and stress can be expressed by a simple equation. For certain compounds made with organic accelerators the relation may be simplified to a linear one, while for rubber-sulphur compounds the relation is a function of the combined sulphur content.

The present investigation leaves untouched a number of factors which may have important bearing on the photoelastic behavior of rubber. The measurements were all made at approximately the same temperature, that of the room, and with light of one wave length, the green line of mercury. The results obtained represent the behavior of rubber samples being stressed for the first time, and under conditions which produced no appreciable optical creep.

The definitions, symbols, conventions, and literature on photoelasticity up to 1931 are to be found in a recent comprehensive text on the subject by E. G. Coker and L. N. G. Filon, entitled "A Treatise on Photoelasticity", Cambridge University Press (1931).

II. PREPARATION OF SPECIMENS

The specimens for photoelastic measurement were made from three types of rubber compounds. Compounds of the simplest type were prepared from rubber hydrocarbon and sulphur, and were vulcanized so as to bring practically all of the sulphur into combination with the rubber. These are represented in table 1 by formulas K, L, and M, which were prepared in connection with an investigation on the electrical properties of rubber.[6] Compounds of another type were made from crude rubber and sulphur, together with small amounts of zinc oxide and stearic acid; the

[2] Ann. Phys. [3] **43**, 808 (1891).
[3] Il nuovo Cimento [5] **20**, 226; 268 (1910).
[4] Z. Phys. Chem. **3**, 240 (1929). English translation, Rubber Chem. Tech. **2**, 545 (1929).
[5] Ind. Eng. Chem. **22**, 1182 (1930); also, Rubber Chem. Tech. **4**, 83 (1931).
[6] BS J. Research **11**, 173–209 (1933); RP585.

two latter ingredients were introduced to render these compounds more nearly comparable to those of the third type in which accelerators were employed. The compounds made from crude rubber and sulphur are represented by formulas F to J, inclusive, and the compounds made with accelerators, by formulas A to E, inclusive. The accelerators employed were tetramethylthiuram disulphide and mercaptobenzothiazole, each with two different percentages of sulphur. One additional compound, A, was made using a combination of the two accelerators and a small percentage each of sulphur and selenium.

TABLE 1.—*Composition of samples*

Composition and treatment	Designation of rubber compounds												
	A	B	C	D	E	F	G	H	I	J	K	L	M
Constituents (parts by weight):													
Pale crepe rubber	100	100	100	100	100	100	100	100	100	100	----	----	----
Rubber hydrocarbon	----	----	----	----	----	----	----	----	----	----	96	94	92
Zinc oxide (Kadox)	1	1	1	1	1	1	1	1	1	1	----	----	----
Stearic acid	1	1	1	1	1	1	1	1	1	1	----	----	----
Tetramethylthiuram disulphide	.5	.3	.3	----	----	----	----	----	----	----	----	----	----
Mercaptobenzothiazole	1	----	----	.5	.5	----	----	----	----	----	----	----	----
Sulphur	.3	2	4	2.5	4	3	4	5	6	7	4	6	8
Selenium	.5	----	----	----	----	----	----	----	----	----	----	----	----
Conditions of vulcanization:													
Time (min)	45	30	40	60	60	300	300	300	300	300	(a)	(a)	(a)
Temperature (°C)	134	126	126	134	134	148	148	148	148	148	----	----	----
Composition:													
Free sulphur, percent	----	.10	1.28	1.06	1.38	.04	.05	.09	.08	.08	(a)	(a)	(a)
Combined sulphur, percent	----	2.05	2.40	1.60	2.46	2.85	3.69	4.65	5.35	6.19	----	----	----

[a] The preparation and composition of these samples are discussed in the paper cited in footnote 6.

The specimens were prepared in the familiar dumb-bell shape commonly used for tensile tests. The thinner specimens were cut with a die from molded sheets, but in the case of thicker specimens the preparation in this manner resulted in curved edges, so recourse was had to molding and vulcanizing such samples in the desired form. The molds consisted of frames provided with sheets of polished aluminum for covers. In making samples an excess of stock was placed in a mold which was pressed between the platens of a vulcanizing press at a temperature of about 100° C. All stock which overflowed was carefully removed and the mold then placed in a press at the requisite temperature for vulcanization. The specimens so prepared were uniform in thickness to a high degree. Fine reference lines were printed on the specimens at the time of vulcanization by ruling scratches on the aluminum sheets used for covering the mold, and filling these scratches with carbon black.

Specimens from 0.7 to 2.7 mm in thickness were employed. The constricted portion of the specimens was about 6.5 mm in width; the length between the reference marks was about 50 mm.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental observations which were made included the determination of the dimensions of the specimens, both in the unstressed and in the stressed condition, and the measurement of the relative retardation of the light vibrations respectively parallel and perpendicular to the direction of stress in the specimens.

The thickness and the width of samples in the unstressed state were measured by means of screw micrometer gages [7] which were thought to be reliable to about 0.0002 inch or 0.005 mm. Measurements of the length of rubber specimens, both before and during the application of stress, were made by means of an improvised cathetometer which operated with a precision of about 0.2 mm.

A few direct measurements of the thickness and the width of specimens under stress were made with the screw-micrometer gage, but in most instances these dimensions were computed from the original thickness and width, and the elongation, as will be discussed in a subsequent part of this paper.

The relative retardation, or the distance by which the extraordinary or slow wave lags behind the ordinary wave in passing through the sample under stress, was measured by means of the well-known Babinet compensator. The optical system consisted of a light source, a polarizing nicol furnishing light vibrating at 45 degrees to the direction of stress, the compensator, the sample under stress, an analyzing nicol at a position of extinction relative to the polarizer, together with a ground-glass screen and accessory projection components. The light source was a mercury arc from which light of wave length 5461 A was isolated by the use of an optical filter. The compensator had an aperture about 3 cm square. Its range was 11 bands, 0.479 cm apart, so the constant was 5461/0.479 or 11,400 A per cm. The position of a band could be read to about 0.01 wave length.

The procedure in making stress-optical measurements was the following: A sample on which measurements of dimensions had been made was mounted between the crossed nicols; the compensator was set with the central band on a cross hair (zero retardation), and its scale reading noted. The specimen was then stressed, by attaching to it a pan to which weights were added, and the compensator then adjusted to bring the central band on the cross hair, and the scale read. After the length between the reference marks on the specimen was read by means of the cathetometer, the compensator reading was again checked to ascertain whether optical creep had occurred. Successive additions of weight were made until optical creep was observed or until the sample broke, as happened with some of high sulphur content. The upper support which held the specimen was adjusted after each addition of weight to keep the constricted portion centered in the optical path. The pan was clamped before each addition of weight, and was released gently so as not to permit oscillation. No definite time schedule was followed in conducting the operations. The observations on a given specimen were usually made without interruption at 10 to 20 increasing stresses, and occupied about one to two hours. The temperature at which measurements were made was not controlled, but it was regularly observed and recorded.

IV. COMPUTATION OF COEFFICIENT OF RELATIVE RETARDATION, STRESS-OPTICAL COEFFICIENT, AND STRESS

The relative retardation per unit thickness is expressed by the relation,

$$\Delta n = \frac{R}{d},$$

Holt, BS J. Research 10, 575 (1933) RP549.

where R is the observed relative retardation, and d, the thickness in the same units. When the relative retardation is measured by means of the compensator mentioned above, and the thickness is found from the thickness in the unstressed state and the elongation, this equation becomes,

$$\Delta n=\frac{(11{,}400\ \Delta x)}{d_0}\sqrt{\frac{L}{L_0}}$$

where Δx is the change in setting of the compensator, 11,400, the compensator constant, L_0 and L, the original length and the length under stress, respectively, and d_0, the original thickness.

The stress-optical coefficient is defined by the relation,

$$C=\frac{R}{Td}=\frac{\Delta n}{T},$$

where C is the coefficient, and T, the tensile stress. The stress-optical coefficient has the dimensions of the reciprocal of a stress. When the relative retardation is expressed in Angstrom units, the stress in bars, and the thickness in millimeters, the stress-optical coefficient is given in brewsters.

The stress in bars was usually found from the relation,

$$T=980.7\times10^{-6}\left(\frac{mL}{d_0w_0L_0}\right),$$

where T is the stress, m, the load in grams, and d_0 and w_0, the thickness and the width, in cm, respectively, of the sample in the unstressed state. This stress relates, of course, to the actual cross section, not the original cross section which is commonly used in connection with stress-strain curves for rubber.

This equation for the stress, as well as the one for the coefficient of relative retardation involves the assumption that the reduction in thickness and the reduction in width of a stressed specimen are each proportional to the square root of the increase in length. In the case of one compound, designated as B in table 1, this assumption was verified by direct measurements with the screw micrometer gage on a number of specimens. These measurements gave an average value for Poisson's ratio as 0.502 at elongations up to 350 percent. The amount by which this differs from 0.500 was less than the probable error of the determination.

Further evidence regarding Poisson's ratio may be adduced from measurements of the change of volume of rubber on stretching, provided the assumption is made that the ratio is the same in the thickness and in the width dimension. This latter assumption is reasonable in view of the well-known isotropic character of mold-cured rubber of the "pure-gum" type.

Measurements of the volume change on stretching were made on compounds B, D, F, and G.[8] None of these showed any appreciable change of volume at elongations up to 350 percent. At an elongation of 400 percent, compounds B and D decreased in volume by 1 or 2 parts per 1,000; at 500 percent, the decrease was 5 to 8 parts per 1,000; and at 600 percent, it was 10 to 15 parts per 1,000. Compounds F and G, on the other hand, showed no significant change of volume at 500 percent elongation, while at 600 percent the volume decreased by 1 to 2 parts per 1,000.

[8] Holt and McPherson, Unpublished work.

With the majority of the compounds the photoelastic measurements were terminated at elongations below 400 percent. Neglect of the volume change on stretching probably occasioned no appreciable error in the case of these compounds, or in the case of compounds F and G which were measured at elongations up to 550 or 575 percent. Compounds H and K were measured at elongations up to about 580 percent, but in the absence of definite data on the volume relations for these compounds no definite estimate can be made of the probable error entailed by neglecting the change of volume on stretching at the higher elongations. It was, however, probably not great.

V. RELATION OF COEFFICIENT OF RELATIVE RETARDATION AND STRESS-OPTICAL COEFFICIENT TO STRESS

When the retardation coefficients of the different rubber compounds were plotted against the stress, the relation was in some instances linear, while in other cases it showed a greater or less deviation from a linear function. It was found that the relations could be expressed by equations of the form,

$$\Delta n = aT + bT^2 + cT^3$$

where Δn is the retardation coefficient, T the stress, and a, b, and c are constants for any given rubber compound under specified conditions of measurement. For some compounds b and c are zero; the measurements on other compounds at stresses below about 65 bars are adequately represented by making c equal to zero, while at higher stresses c was not zero.

The coefficients, a, b, and c, of the above equation were determined for all the specimens investigated and are here employed as a means of presenting the results of the investigation in concise form. The values of the parameters are given in table 2, along with other data regarding the determinations, including the temperature at which the measurements were made, the range of stresses employed, and the corresponding elongations produced in the samples. The range of stress covered extended to between 50 and 100 bars in the case of most compounds, and to 164 bars in one instance. Values of the retardation coefficient ranged up to 100 to 200×10^{-4} in most instances.

Curves showing the relation of the coefficient of retardation to stress for a typical sample of each compound are presented in figure 1. The smooth curves were computed from equations using values of a, b, and c from table 2, while the points shown represent observations. In most cases the points cannot be distinguished from the curves on the scale of the figure. The differences, however, were computed, and are summarized in the last two columns of table 2. The average discrepancies range from 0.1 to 0.45×10^{-4} unit of the retardation coefficient for the different compounds, while the maximum discrepancies are from 0.25 to 2.0×10^{-4}. These relate to values of the retardation coefficient ranging up to 100 or 200×10^{-4}. The results obtained with specimens of compounds G and H are expressed by second-degree equations at stresses below 65 bars, and by third-degree equations for the complete range of observations which extend to about 100 bars. The second-degree equations were found in order that the parameters a and b might be correlated with the composition, as is discussed in a subsequent part of this paper.

TABLE 2.—*Summary of photoelastic measurements*

Compound	Sample number	Temperature	Range of elongation	Range of stress [1]	Parameters of equation,[2] $\Delta n = aT + bT^2 + cT^3$			Difference between values of Δn (obs.) and Δn (calc.) $\times 10^4$	
					$a \times 10^4$	$b \times 10^4$	$c \times 10^4$	Max	Avg
		° C.	Percent	Bars					
A	1	26.1	26 to 308	2.78 to 45.65	2.059	0	0	0.5	0.2
	2	27.7	26 to 324	2.77 to 51.1	2.044	0	0	.4	.2
	3	30.5	25 to 299	2.78 to 44.95	2.019	0	0	.85	.3
B	1	24.0	26 to 323	2.73 to 55.0	2.092	0	0	.4	.1
	2	25.5	25 to 335	2.95 to 54.3	2.092	0	0	.4	.15
	3	24.2	25 to 260	2.95 to 38.6	2.097	0	0	.3	.15
	4	22.4	13 to 261	1.68 to 40.0	2.108	0	0	.7	.2
	5	27.8	14 to 273	1.69 to 41.15	2.084	0	0	.5	.2
	6	24.0	25 to 258	2.96 to 39.5	2.091	0	0	.6	.2
	7	22.5	6 to 129	0.73 to 15.65	2.108	0	0	.2	.05
C	1	24.0	13 to 308	1.76 to 63.2	2.233	−0.00354	0	.3	.15
D	1	28.8	31 to 365	2.70 to 44.6	2.158	0	0	.7	.15
	2	24.4	33 to 348	2.82 to 40.45	2.155	0	0	.8	.25
E	1	--------	30 to 365	2.72 to 49.4	2.267	−0.00175	0	.3	.15
	2	24.5	30 to 362	2.75 to 49.65	2.242	−0.00146	0	.3	.15
F	1	26.9	69 to 572	3.87 to 65.2	2.660	−0.00820	0	.3	.1
G	1	21.8	40 to 470	2.91 to 65.0	2.895	−0.01000	0	.65	.25
	1	21.8	40 to 556	2.91 to 96.95	2.895	−0.01127	0.000023	1.3	.45
H	1	25.6	30 to 403	2.84 to 64.2	3.120	−0.01075	0	.95	.35
	1	25.6	30 to 506	2.84 to 109.5	3.120	−0.01258	0.000029	.6	.3
	2	31.7	34 to 582	3.29 to 163.6	2.988	−0.01170	0.000026	1.95	.45
I	1	27.2	27 to 380	2.92 to 74.15	3.297	−0.01138	0	.75	.4
	2	27.3	27 to 383	2.95 to 74.6	3.275	−0.01110	0	.8	.3
J	1	27.9	19 to 345	2.20 to 68.5	3.509	−0.01216	0	.75	.35
K	1	26.0	58 to 581	3.41 to 68.4	3.005	−0.00909	0	.7	.3
L	1	25.3	32 to 296	2.83 to 35.95	3.531	−0.01313	0	.25	.1
M	1	25.0	31 to 142	3.57 to 17.3	4.108	−0.01466	0	.25	.1

[1] Stress refers to actual cross section.
[2] Δn is relative retardation per unit thickness, and T, stress.

Measurements on specimens of compounds A and B were made at temperatures covering ranges of 4° or 5°. The results indicate a decrease in retardation coefficient of the order of 0.25 to 0.5 percent per

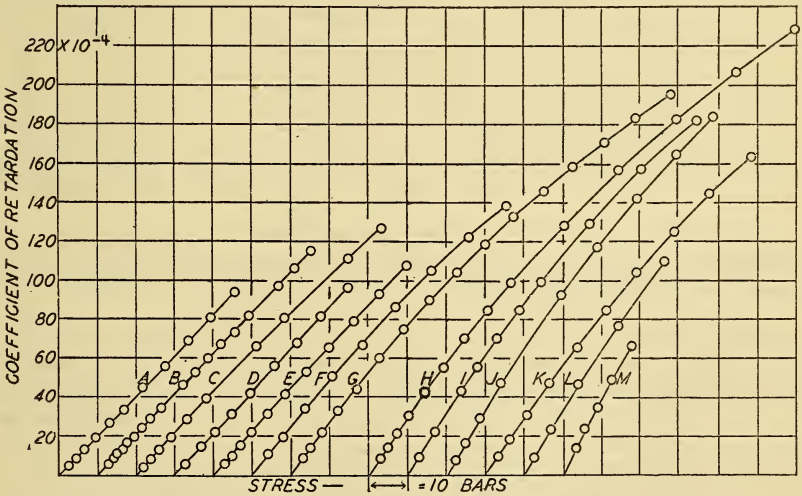

FIGURE 1.—*Relation of coefficient of relative retardation to tensile stress.*

Compounds A to E represent rubber compounds made with organic accelerators, F to J, compounds of crude rubber and sulphur, K to M, compounds of purified rubber and sulphur. Each curve is plotted from a separate origin to avoid confusion. The stress relates to the actual cross section.

degree, but are not sufficiently precise to warrant the computation of temperature coefficients.

Stress-optical coefficients were found corresponding to all measurements of retardation coefficient. The coefficients for typical samples of the various compounds are shown in figure 2, plotted as functions of the stress. The smooth curves were found by means of the values for the parameters, *a*, *b*, and *c*, given in table 2, while the points shown represent observations. In the case of compounds A, B, and D, the coefficient is constant and independent of stress. In the case of other compounds, the values for the coefficient decrease with increasing

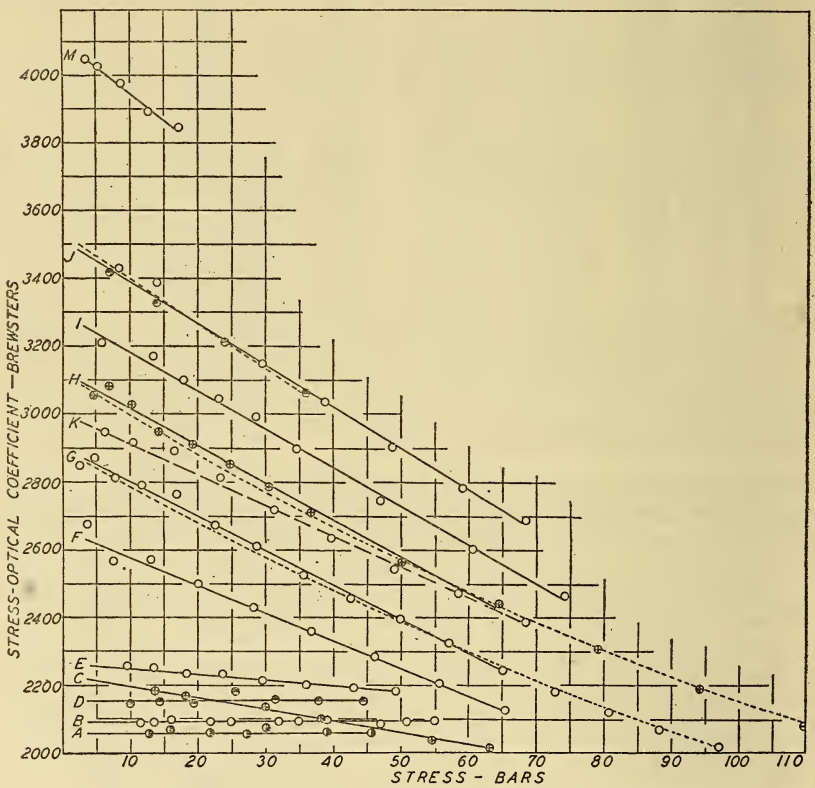

FIGURE 2.—*Relation of stress-optical coefficient to tensile stress.*

Curves for compounds J and L almost coincide; the dotted curve refers to L. The solid curves for compounds G and H were computed from equations in *a* and *b*, the dotted curves from equations in *a*, *b*, and *c*. The stress relates to the actual cross section.

stress, the slopes and intercepts varying with the compound. For compounds G and H, straight lines, in terms of *a* and *b* represent fairly well the results at stresses below 65 bars; these are shown in the figure by solid curves. Measurements on these compounds at higher stresses, however, are well fitted only by equations in terms of *a*, *b*, and *c*, which are represented in the figure by the dotted curves.

At low stresses the values for the stress-optical coefficient show considerable scattering, for the reason that they represent the ratios of small values of the retardation coefficient and stress, and hence are not of high precision. In the figure the points at stresses below 10 bars have been omitted from some of the curves, to avoid confusion.

The numerical values of the stress-optical coefficient for the compounds made with accelerators all fall between 2,000 and 2,300 brewsters. For rubber-sulphur compounds at low stresses, the values are from about 2,600 to 4,100 brewsters, but these decrease with increasing stress, and at relatively high stresses drop to as low as 2,000 brewsters.

VI. RELATION OF THE PHOTOELASTIC PROPERTIES OF RUBBER TO THE COMPOSITION

The examination of the results presented in the previous section indicates that the rubber compounds fall into three groups as regards

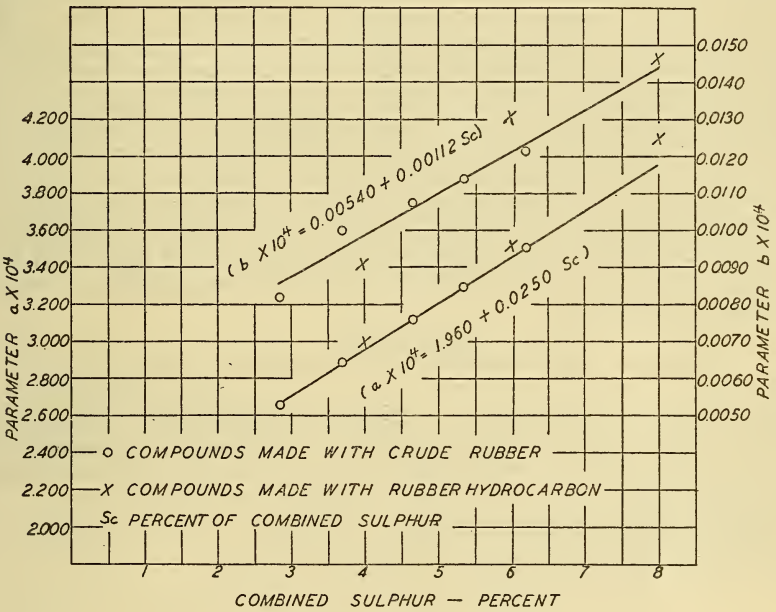

FIGURE 3.—*Relation of parameters a and b to percentage of combined sulphur in rubber-sulphur compounds.*

The parameters are the coefficients in the equation, $\Delta n = aT + bT^2$, where Δn is the coefficient of relative retardation, and T the tensile stresss. Values of b shown in the figure are negative in sign.

photoelastic properties. In one group are the compounds A, B, and D for which the parameters b and c are zero, the relation of coefficient of retardation to stress is linear, and the stress-optical coefficient is constant. A second group is made up of compounds from F to M, inclusive, for which the parameter c is either zero or has a small positive value while the parameter b has a relatively large negative value, indicating that the relation of the coefficient of retardation to the stress departs considerably from a straight line, and that the stress-optical coefficient decreases markedly with increasing stress. The third group is made up of compounds C and E, which fall between the two previous groups in respect to photoelastic properties.

This division into groups follows the mode of vulcanization. Compounds A, B, and D are vulcanized with the aid of organic accelerators, employing the minimum percentages of sulphur con-

sistent with the development of good physical properties. Compounds F to M, inclusive, on the other hand, are rubber-sulphur compounds vulcanized without the aid of organic accelerators, while compounds C and E contain accelerators, but also contain more sulphur than the minimum required to develop good physical properties, and hence partake of the character of both the rubber-sulphur and the accelerated compounds.

When the measurements on the rubber-sulphur compounds are expressed in equations of the second degree, the parameters a and b both bear approximately linear relations to the combined sulphur content, as is indicated by the curves shown in figure 3. The points representing measurements on compounds containing rubber hydrocarbon are distinguished in the figure from those on compounds containing crude rubber; they might be represented by two slightly different curves, but this has not been done because data are available on only three compounds of the rubber hydrocarbon, and are not considered adequate to define an exact relation. One straight line was drawn through values of a for the compounds F to J, inclusive, and another straight line through the corresponding values of b. These lines represent, with reasonable fidelity, the values of a and b for compounds K and L, but are somewhat too low in the case of compound M.

The equations for the relations of a and b to the percentage of combined sulphur are shown on the figure. These lead to the following expression for the coefficient of relative retardation of rubber sulphur compounds,

$$\Delta\ n \times 10^4 = (1.960 + 0.0250\ S_c)\ T - (0.00540 + 0.00112\ S_c)\ T^2$$

where S_c is the percentage of combined sulphur and T, the tensile stress. This relation is applicable to compounds containing 2.85 to 6.2 percent of combined sulphur, and to measurements at stresses up to 65 bars.

WASHINGTON, October 12, 1934.