U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP786

Part of Journal of Research of the National Bureau of Standards, Volume 14, May 1935

REFRACTIVE INDEX OF RUBBER

By Archibald T. McPherson and Arthur D. Cummings

ABSTRACT

The refractive index of rubber was measured on an Abbe refractometer by a method of total reflection. For plantation Hevea rubber and purified rubber average values of n_D^{25} are 1.5188 and 1.5190, respectively. The index of crude rubber is not altered by the introduction of insoluble fillers. Sulphur in solution increases n_D^{25} of crude rubber by 0.0016 for each percent, and phenyl-β-naphthylamine, by 0.0015 for each percent. The refractive index of vulcanized compounds of purified rubber and sulphur is given by,

$$n_D^t = 1.5190 + 0.00370\ S_c - 0.00035\ (t-25)$$

where S_c represents the percentage of combined sulphur, between 0 and 16, and t, the temperature in degrees centigrade, between 10 and 75° C. The curve relating refractive index to temperature for a compound containing 19 percent of sulphur undergoes a change in slope at about 17° C. Preliminary measurements on compounds containing 19 to 32 percent of sulphur indicate that the transition from soft to hard rubber is accompanied by a decrease in the slope of the curve relating refractive index to temperature.

CONTENTS

I. INTRODUCTION

This paper presents an exploratory study of the refractive index of rubber. Previous observations on the refractive index of rubber have been, for the most part, restricted to transparent samples.[1] In the present investigation, however, by using reflected light rather than light at grazing incidence, it was found possible to extend the range of measurements to rubber samples that were somewhat dark in color or that were very nearly opaque. Such being the case, determinations of refractive index were made not only on translucent

[1] References to several previous publications on the refractive index of rubber are given in two papers by Kirchhof, Kautschuk 8, 137 (1932), and 9, 172 (1933); English translations, Rubber Chem. Tech. 6, 92 (1933) and 7, 608 (1934). Other publications on the refractive index of rubber are: Ayrton and Perry (and Jellett) Phil. Mag. [5], 12, 196 (1881); Gladstone and Hibbert, J. Chem. Soc. Trans. 53, 680 (1888); Curtis and McPherson, Tech. Pap. BS 19, 698 (1925) T299; Tanaka, Trans. Inst. Rubber Ind. 2, 330 (1927); and Shacklock, Trans. Inst. Rubber Ind. 7, 354 (1932). Preliminary mention of the present work was made in BS Tech. News Bul. 194, p. 66 (June 1933).

samples of unvulcanized or soft vulcanized rubber, but also on binary mixtures of rubber and different compounding materials, and on compounds of rubber and sulphur containing 0 to 19 percent of sulphur and covering the range from soft to semihard rubber.

Different samples of unvulcanized Hevea rubber, of plantation origin, all showed approximately the same refractive index, irrespective of considerable variations in the nonhydrocarbon constituents. The index was not appreciably altered by the amount of mastication which rubber ordinarily receives in processing and mixing with compounding ingredients. Mixtures of rubber with substances insoluble in it showed the same index as the rubber itself, while mixtures with soluble substances differed in index from rubber by an amount which depended upon the index of the substance and the amount in solution. Measurements of refractive index, therefore, afford a means of measuring the solubility of substances in rubber and were employed for determinations of the solubility of sulphur and of a common antioxidant, phenyl-β-naphthylamine.

Sulphur in combination with rubber had a relatively greater effect on the refractive index than did sulphur in solution. For vulcanized rubber-sulphur compounds in the soft-rubber range the refractive index was a simple linear function of the percentage of sulphur and also of the temperature. Preliminary measurements on vulcanized compounds in the hard-rubber range indicate that the change in physical properties of rubber-sulphur compounds from soft to hard was accompanied by a decrease in the slope of the curve relating refractive index to temperature.

II. METHOD OF MEASURING REFRACTIVE INDEX OF RUBBER

The measurements of refractive index were made on critical-angle refractometers of the Abbe type, but the border-line characteristic of rubber was obtained by using reflected light rather than light at grazing incidence. Two instruments were used. One was designed for this type of measurement, but it had the practical limitation that the prism was not jacketed to permit the circulation of water for temperature control. This instrument was used in a constant-temperature room at approximately 25° C. In order to make observations over a range of temperature a standard Abbe refractometer having a water-jacketed prism was employed. Since there was no provision for admitting light into the prism from the face opposite the one on which the specimen was mounted, a slab of plane-parallel glass having ground edges was interposed between the specimen and the prism. Light was introduced through the edge of this slab, as illustrated in figure 1. The illuminating prism was, of course, removed. The specimen and glass slab were enclosed on three sides by a cored metal housing. The control of temperature was secured by circulating water through this housing and the jacket around the prism. The glass slab had a refractive index of 1.65, which was significantly higher than that of the rubber, as required by the optical system. α-Bromonaphthalene was employed to obtain optical contact between the glass slab and the prism.

Samples of rubber for measurement were mounted on the prism of the refractometer or on the glass slab without employing a contact liquid. No difficulty was experienced in obtaining good optical contact between soft rubber and glass, provided the surface of the rubber was clean and smooth. This condition was met by molding the specimens between sheets of polished aluminum, and by removing the aluminum just before the rubber was to be attached to the glass. In preparing crude-rubber specimens, the rubber was milled until it ran smoothly on the rolls, compounding ingredients, if any, were added quickly, and the resultant batch was pressed out between thin aluminum sheets in a vulcanizing press at about 100° C. Vulcanized specimens were cured between the aluminum sheets.

Samples of hard or semihard rubber did not give good contact when pressed against glass at room temperature. These were prepared in sheets about 0.25 mm in thickness and were mounted on the

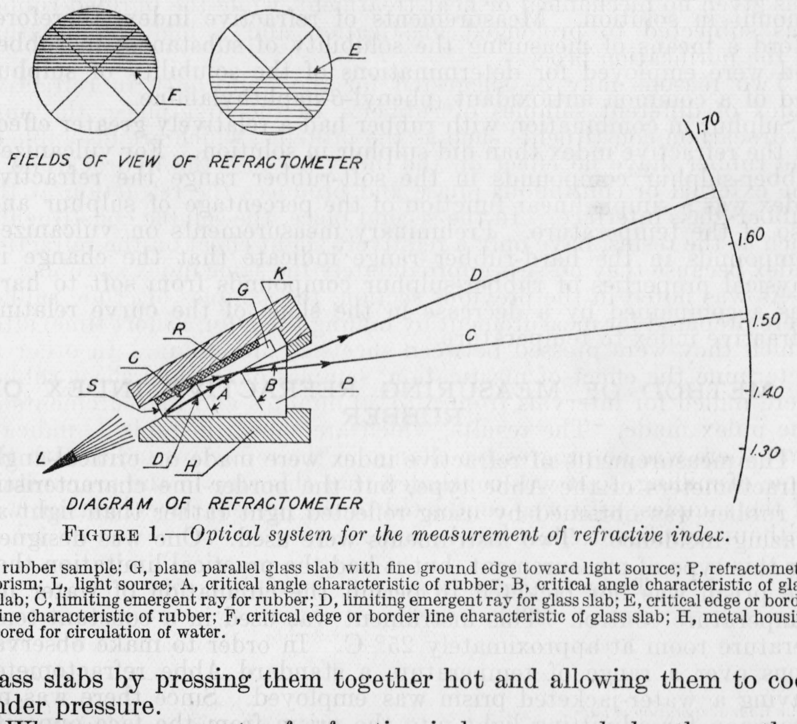

FIGURE 1.—*Optical system for the measurement of refractive index.*

R, rubber sample; G, plane parallel glass slab with fine ground edge toward light source; P, refractometer prism; L, light source; A, critical angle characteristic of rubber; B, critical angle characteristic of glass slab; C, limiting emergent ray for rubber; D, limiting emergent ray for glass slab; E, critical edge or border line characteristic of rubber; F, critical edge or border line characteristic of glass slab; H, metal housing cored for circulation of water.

glass slabs by pressing them together hot and allowing them to cool under pressure.

When measurements of refractive index are made by the method here employed the contrast between the two halves of the field, seen in the telescope of the refractometer, is not great. This contrast is diminished as the samples become darker in color or increase in opacity, and the boundary often becomes less distinct. This constitutes a limitation of the method, both as to the range of samples that can be employed and as to the precision of measurement.

III. REFRACTIVE INDEX OF UNVULCANIZED RUBBER

Several different samples of unvulcanized rubber, of plantation Hevea origin, were examined and all were found to possess approximately the same refractive index, irrespective of their hydrocarbon content or method of preparation. This is shown by the results given in table 1. Two samples of rubber obtained by the evaporation of ammonia-preserved latex from different sources gave indices, n_D^{25}, of 1.5187 and 1.5192, respectively. Different samples of commercial smoked sheet and pale crepe gave indices from 1.5187 to 1.5189, with an average of 1.5188, while for purified rubber the index ranged from 1.5189 to 1.5191, with an average of 1.5190.[2] The various samples of unvulcanized rubber differed materially in composition and in the treatment which they were accorded in preparation. The latex rubber contained about 10 percent of resins, proteins, and soluble serum constituents, while the purified rubber contained about 0.5 percent of nonhydrocarbon constituents. The smoked sheet and pale crepe contained intermediate but not identical amounts of nonhydrocarbon constituents. The rubber from latex was given no mechanical or heat treatment, while the purified rubber was subjected to prolonged mastication and a high temperature in the purification process.

Two reasons may be suggested for the uniformity in refractive index of different samples of rubber. In the first place, the nonhydrocarbon constituents such as the proteins, which are insoluble in the rubber, have no effect on the index because the hydrocarbon is the external or continuous phase and produces the refraction at the rubber-glass interface. In the second place, the soluble constituents, such as the resins, have only a relatively slight effect on the refractive index because they possess approximately the same index as rubber.

As was noted in the previous section, the samples of crude rubber were prepared for measurement by milling them for a short time, after which they were pressed between sheets of aluminum. In order to determine the effect of mastication, samples of smoked sheet rubber were milled for intervals from 5 to 30 minutes and measurements of the index made. The results, which are shown in table 1, indicate that there was no progressive change in the refractive index with the time of milling, so it was concluded that this step in the preparation of the samples, as it was conducted in the present investigation, was without significant effect on the index.

TABLE 1.—*Refractive index of unvulcanized rubber*

Kind of rubber	Sample no.	Treatment of sample	n_D^{25}
Film from evaporation of latex	1	None	1.5187
	2	do	1.5192
Pale crepe	1	Milled	1.5187
	2	do	1.5188
	3	do	1.5187
Smoked sheet	1	do	1.5188
	2	Milled 5 min	1.5188
	2	Milled 10 min	1.5188
	2	Milled 20 min	1.5189
	2	Milled 30 min	1.5188
Purified	1	([a])	1.5191
	2	([a])	1.5190
	3	([a])	1.5190
	4	([a])	1.5189

[a] See BS J. Research 11; 175 (1933) RP585.

[2] This value is a little higher than the value $n_D^{25}=1.5184$ previously reported by one of the authors, BS J. Research 8, 756 (1932) RP449.

In addition to the studies on plantation rubber, refractive-index measurements were made on twenty samples of representative types of wild rubber, which were kindly furnished by the U. S. Bureau of Plant Industry, Office of Cotton, Rubber, and Other Tropical Plants. The samples ranged in index, n_D^{25}, from 1.5191 to 1.5242, with an average value of 1.5208. The results are not here reported in detail because no study was made to correlate the indices of the various samples with their composition, or to ascertain the indices of the hydrocarbon fractions in the pure state.

All of the above measurements of refractive index relate to the D line of the spectrum. One sample of purified rubber, however, was measured on a Pulfrich refractometer with light of two other wave lengths, and the following results were obtained:

Line	Wave length in angstroms	Refractive index
C (H_α)	6, 563	1. 5153
D	5, 893	1. 5190
F (H_β)	4, 861	1. 5483

The dispersion, $H_\alpha - H_\beta$, was therefore 0.0330.

IV. REFRACTIVE INDEX OF MIXTURES OF UNVULCANIZED RUBBER WITH COMPOUNDING MATERIALS

1. RUBBER-FILLER MIXTURES

Measurements of the refractive index were made on samples of crude rubber mixed with different proportions of whiting, zinc oxide, barytes, titanium dioxide, carbon black, and zinc stearate. Only in the case of zinc oxide was there any significant difference between the index of the mixtures and that of the rubber. A freshly prepared mixture of pale crepe, $n_D^{25}=1.5188$, with 4 percent of "Kadox" zinc oxide showed an index of 1.5220. A mixture of the same rubber with 4 percent of "XX–Red" zinc oxide, however, had an index of 1.5209. With smaller percentages of the two oxides, lower values of the index were obtained. It is probable that some zinc oxide reacted with nonhydrocarbon constituents of the rubber to form salts which dissolved in the rubber and changed the index. A definite statement, however, cannot be made without further experimental work.

As was mentioned previously the addition of filler to rubber increased the difficulty in reading the refractive index by reducing the contrast between the two halves of the field and by rendering the boundary between them less sharp. With carbon black satisfactory observations were obtained for mixtures containing not more than 0.1 percent. With titanium dioxide the amount was of the order of 2 percent. In the case of zinc stearate, however, fairly satisfactory observations were made on stocks containing as high as 50 percent.

2. RUBBER-SULPHUR MIXTURES

When rubber was mixed with sulphur on the mill in proportions up to 4 percent, it was possible to cool the resulting stocks to 25° C and measure the index before any separation of the sulphur or blooming took place. For such stocks the index was a linear function of the percentage of sulphur, as is indicated by the curve ABC in figure 2. This curve relates to solutions of sulphur in crude rubber and is described by the equation,

$$n_D^{25} = 1.5188 + 0.0016 S_s$$

where S_s is the percentage by weight of dissolved sulphur.

When these stocks were permitted to stand, sulphur separated from those in which it was present in larger amounts, and the index decreased. The measurements after 1 month and 14 months are

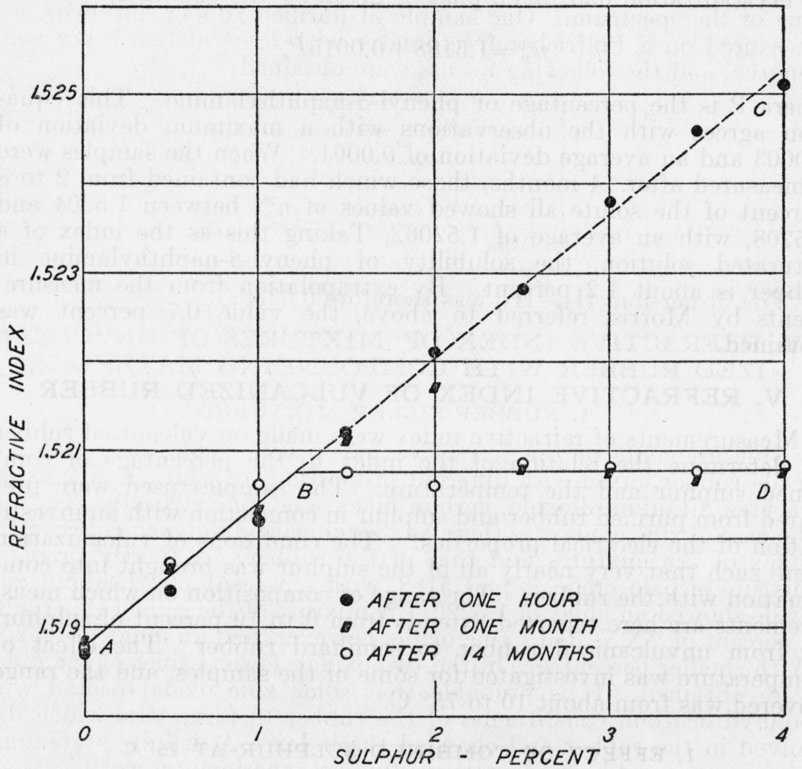

FIGURE 2.—*Refractive index of rubber-sulphur mixtures at different times after mixing.*

AB represents unsaturated solutions of sulphur in rubber; BC, supersaturated solutions; and BD, a saturated solution.

shown in the figure. At the end of 1 month the index of the samples containing from 2.5 to 4.0 percent of sulphur had dropped to the constant value 1.5208, while the index of the samples containing 2.0 percent had dropped a little, and that of the samples containing 1.5 percent was practically unchanged. After 14 months, however, the indices of these last two compositions had dropped to about 1.5208, while those of the other compositions remained practically unchanged. This indicates that the value 1.5208 is the refractive index of a saturated solution of sulphur in rubber at the temperature of the room in which the samples were stored, which was approximately 25° C. As may be seen from the curve, this index corresponds to a solubility of about 1.2 percent. This is somewhat higher than the value 0.85 percent, which is obtained by extrapolation from measurements of the solubility of sulphur in rubber by Morris.[3]

3. MIXTURES OF RUBBER AND PHENYL-β-NAPHTHYLAMINE

Measurements of the refractive index were made on samples which contained from 1 to 8 percent of phenyl-β-naphthylamine and yielded results quite similar to those obtained with the rubber-sulphur stocks. The index of the freshly prepared stocks in which no crystallization had taken place is given by the equation,

$$n_D^{25}=1.5188+0.0015P,$$

where P is the percentage of phenyl-β-naphthylamine. This equation agrees with the observations with a maximum deviation of 0.0003 and an average deviation of 0.0001. When the samples were remeasured after 14 months, those which had contained from 2 to 8 percent of the solute all showed values of n_D^{25}, between 1.5204 and 1.5208, with an average of 1.5206. Taking this as the index of a saturated solution, the solubility of phenyl-β-naphthylamine in rubber is about 1.2 percent. By extrapolation from the measurements by Morris, referred to above, the value 0.7 percent was obtained.

V. REFRACTIVE INDEX OF VULCANIZED RUBBER

Measurements of refractive index were made on vulcanized rubber to determine the relation of the index to the percentage of combined sulphur and the temperature. The samples used were prepared from purified rubber and sulphur in connection with an investigation of the electrical properties.[4] The conditions of vulcanization were such that very nearly all of the sulphur was brought into combination with the rubber. The range of composition on which measurements are here reported extends from 0 to 19 percent of sulphur, or from unvulcanized rubber to semihard rubber. The effect of temperature was investigated for some of the samples, and the range covered was from about 10 to 75° C.

1. EFFECT OF COMBINED SULPHUR AT 25° C

The refractive indices of rubber-sulphur compounds are presented graphically in figure 3, in which the index is plotted against the percentage of combined sulphur. The index bears a linear relation to the sulphur content up to 16 percent. The only higher point shown is at 19 percent of sulphur and falls below the line for a reason which will be discussed in the next section of this paper. Few of the measurements were made at exactly 25° C. In some instances the refractive indices at 25° C were read from a curve which related the indices to temperature. Most of the measurements, however, were made at temperatures which differed from 25° by only 1 or 2° C, and were reduced to this standard temperature by the use of the temperature coefficient discussed in a later paragraph. The relation shown in

[3] Ind. Eng. Chem. **24,** 584 (1932).
[4] Scott, McPherson, and Curtis, BS J.Research **11,** 173 (1933) RP585.

figure 3 between the refractive index at 25° C and the percentage of sulphur is described by the equation,

$$n_D^{25} = 1.5190 + 0.00370\ S_c$$

where S_c is the combined sulphur expressed in percentage. In a report[5] describing preliminary measurements the index was expressed as a linear function of the sulphur content in terms of atoms of sulphur per C_5H_8, but the present results indicate a more nearly linear relation when the sulphur is given in percentage by weight.

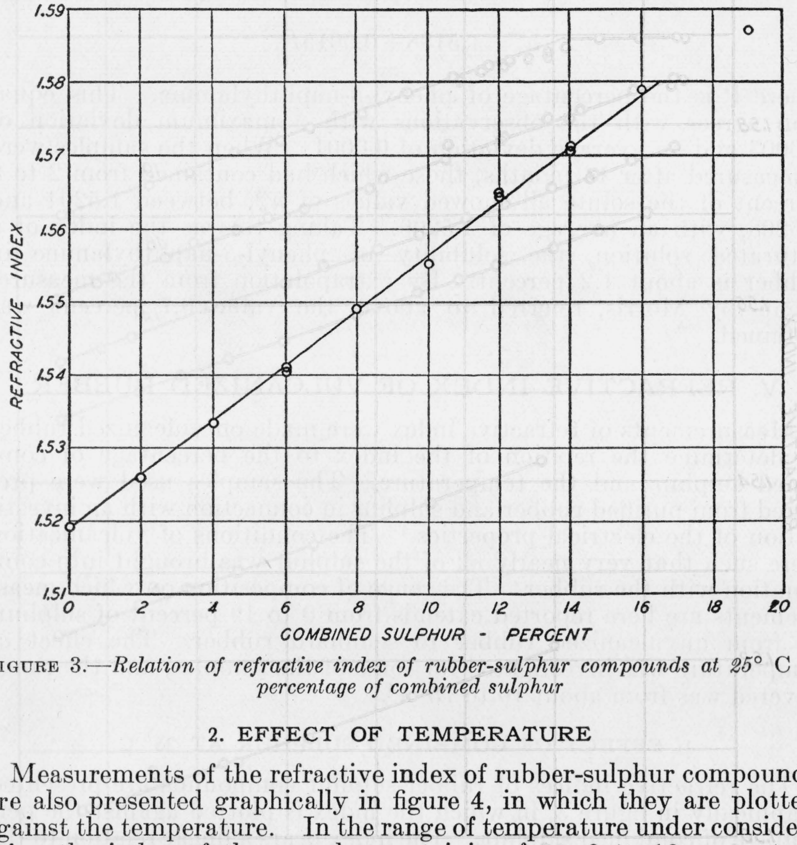

FIGURE 3.—*Relation of refractive index of rubber-sulphur compounds at 25° C to percentage of combined sulphur*

2. EFFECT OF TEMPERATURE

Measurements of the refractive index of rubber-sulphur compounds are also presented graphically in figure 4, in which they are plotted against the temperature. In the range of temperature under consideration the index of the samples containing from 0 to 16 percent of sulphur decreased linearly with increasing temperature. The change in index per degree centigrade was from 0.000345 to 0.00036, with an average value of 0.00035. This is in reasonable agreement with the change in index, 0.00036 per degree centigrade, reported in a previous investigation by one of the authors.[6] Kirchhof[7] has measured the refractive indices of a number of samples of crude rubber at different temperatures. His observations indicate a change in index of from 0.00034 to 0.00042 per degree centigrade, with an average of 0.00039.

[5] BS Tech. News Bul. 194, p. 66 (June 1933).
[6] A. T. McPherson, BS J. Research 8, 751 (1932) RP449.
[7] Kautschuk 8, 137 (1932); also Rubber Chem. Tech. 6, 92 (1933).

When the relation between refractive index and temperature is combined with the relation between refractive index and sulphur content, the following expression is obtained,

$$n_D^t = 1.5190 + 0.00370S_c - 0.00035\ (t-25)$$

where S_c is the percentage of combined sulphur, and t, the temperature in degrees centigrade. The maximum deviation of observa-

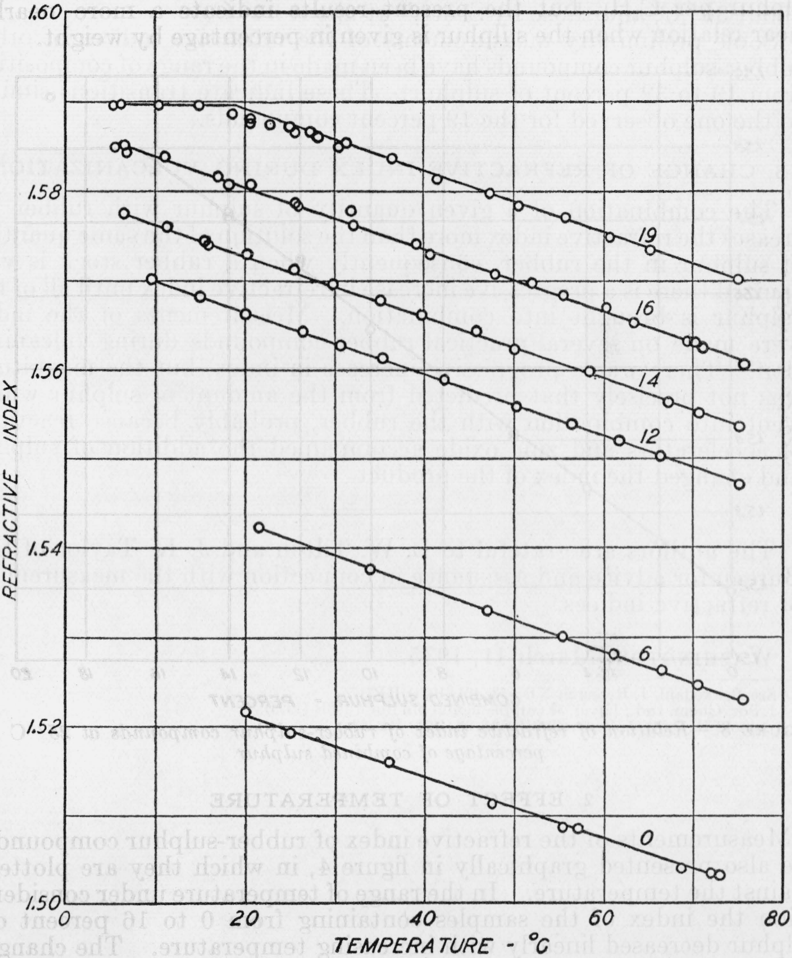

FIGURE 4.—*Relation of refractive index of rubber-sulphur compounds to temperature.*

The figures on the different curves denote the percentages of combined sulphur.

tions at different temperatures from values computed by this equation was 0.0015 and the average deviation was 0.0006.

The curve in figure 4, which relates the refractive index of the compound containing 19 percent of sulphur to the temperature, shows a change in slope at approximately 17° C. This point represents the intersection of two straight lines drawn through the points above and below the transition, respectively. As indicated by the observations, however, the transition is not sharp but gradual, and this is probably the reason why the index at 25° C does not fall quite in line with the indices of compounds containing lower percentages of sulphur. The transition is probably of the type designated by Ehrenfest as a transition of the second order.[8] Such a transition is indicated in the same region of temperature for a compound containing 19 percent of sulphur, by temperature-volume measurements. The temperature-volume measurements by Kimura and Namikawa[9] indicate a transition at about 30° C, and those by Scott,[10] at about 34° C.

Some preliminary measurements of the refractive indices of other rubber-sulphur compounds have been made in the range of composition from 19 to 32 percent of sulphur. These indicate transitions similar to the one observed for the 19 percent compounds.

3. CHANGE OF REFRACTIVE INDEX DURING VULCANIZATION

The combination of a given quantity of sulphur with rubber increases the refractive index more than the solution of the same quantity of sulphur in the rubber, consequently when a rubber stock is vulcanized there is a progressive increase in refractive index until all of the sulphur is brought into combination. Measurements of the index were made on several practical rubber compounds during vulcanization. There was a progressive increase in index, but the magnitude was not precisely that predicted from the amount of sulphur which went into combination with the rubber, probably because reactions of accelerators and zinc oxide accompanied the addition of sulphur and changed the index of the product.

The authors are grateful to L. W. Tilton and J. K. Taylor of this Bureau for advice and assistance in connection with the measurement of refractive indices.

WASHINGTON, March 11, 1935.

[8] See Bekkedahl, J. Research NBS **13**, 424 (1934) RP717.
[9] J. Soc. Chem. Ind., Japan, **32** (supplemental binding), 196B (1929).
[10] Arnold H. Scott, J. Research NBS **14**, 99 (1935) RP760.