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FORMS OF RUBBER AS INDICATED BY TEMPERATURE-VOLUME RELATIONSHIP

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ABSTRACT

Temperature-volume measurements were made from -85 to $+85$ C on rubber hydrocarbon and 3 soft rubber-sulphur compounds, using dilatometers of a low thermal expansion glass with alcohol, acetone, water, and mercury as confining liquids. Measurements of linear expansion were made on one specimen of rubber hydrocarbon from -190 to 0 C.

These measurements indicate that unvulcanized rubber may exist in at least 4 forms. The familiar form, designated as amorphous I, undergoes slow transition at 6 to 16 C to a form called crystalline I which is the stable modification between -72 and $+6$ C. At 0 C the transition takes place more rapidly, requiring about 10 days, and is accompanied by a change of volume of 2.65 percent. At about -72 C both the crystalline I and the metastable amorphous I forms undergo transitions, with large decreases in coefficients of expansion, to crystalline II and amorphous II forms, respectively. Vulcanized rubber, in the unstretched state, exhibited only the amorphous I and the amorphous II forms, the compounds containing 2, 4, and 6 percent of combined sulphur undergoing transition at -72 , -62 , and -53 C, respectively.

The volume coefficient of expansion of rubber in the amorphous I form, from -72 to $+85$ C, is given by the relation,

$$\frac{dv}{dt} = 0.00067 + 0.0000007 (t - 25)$$

where t is the temperature in degrees C. The volume coefficient for the crystalline I form between -72 and $+6$ C is approximately 0.00053. Between -72 and -85 C both the amorphous II and the crystalline II forms have approximately the same volume coefficient, 0.00020. The average linear coefficients between -190 and -72 C are 0.000060 for the amorphous II form and 0.000054 for the crystalline II form.

The results of the present investigation afford a basis for correlating and interpreting data obtained by the author and other investigators on the heat capacity, electrical properties, and behavior of rubber on stretching.

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I. INTRODUCTION

This paper describes measurements of the change of volume of rubber with change of temperature, which have been used as a means for determining the forms in which rubber may exist and ascertaining the conditions under which transition from one form to another may occur.

This work is part of a study of the basic thermodynamic properties of rubber which is being conducted at the cryogenic laboratory of the National Bureau of Standards. In this study, an attempt was first made to measure the heat capacity of rubber over a wide range of temperature, but under some circumstances anomalies due to change in phase were encountered which took place so slowly that it was impracticable to follow them through by calorimetric methods. These anomalies have been studied by the measurement of the changes in volume or coefficient of expansion associated with them, it being possible to follow changes in volume over as long a period of time as desired. At temperatures at which rubber is relatively stiff and rigid, measurements of length have been used as an adjunct to the volume measurements.

Measurements of the temperature-volume relations of rubber have been made by several previous investigators who have recognized the existence of rubber in different forms. The contribution of the present investigation lies in the fact that it reports a somewhat more comprehensive and systematic study than has been made previously. The findings are largely in accord with those of the other workers, as will be brought out in a subsequent section of the paper.

The results of the measurements indicate that between -190 and $+85$ C unvulcanized rubber may exist in at least 4 forms. Similar measurements on vulcanized rubber demonstrate the existence of 2 analogous forms, while the behavior on stretching points to the possibility that the other 2 analogous forms may exist in stretched rubber. The temperatures of transition have been determined approximately, and observations have been made on the rates of transition under various circumstances. Thus a foundation has been laid on the basis of which the calorimetric investigations referred to above can be conducted with facility.

The anomalies which have been observed in the temperature-volume measurements of the unstretched rubber find a close counterpart in preliminary measurements of heat capacity by the author, and also in data published by other investigators. Indications of anomalies corresponding to those found in the temperature-volume

studies described in this paper were also found in studies of the electrical and of the mechanical properties of rubber.

II. TYPES OF RUBBER INVESTIGATED

The samples on which measurements were made included crude rubber in the form of smoked sheet, rubber hydrocarbon, and compounds of the latter with sulphur. Rubber hydrocarbon was prepared by the digestion of latex with steam at about 190 C and the subsequent extraction of the resins and the products of hydrolysis with alcohol and water.¹ Where the term rubber hydrocarbon is used without qualification in this paper, this product is understood. The vulcanized samples contained 2, 4, and 6 percent of sulphur, and were prepared from rubber hydrocarbon and sulphur. They were vulcanized so as to bring all but a few hundredths of a percent of the sulphur into combination with the rubber.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

The measurements of the change in volume of rubber were made by enclosing samples with suitable confining liquids in dilatometers and observing the changes in height of the liquid in calibrated capillary tubes when the dilatometers and contents were subjected to different temperatures. The dilatometers were made of a laboratory glass having a low coefficient of expansion. The measurements of the change of length were made with the fused quartz tube apparatus described by Hidnert and Sweeney.²

1. DESCRIPTION OF DILATOMETERS

The dilatometers were patterned after liquid-in-glass thermometers and consisted of bulbs sealed to capillary tubes as shown in figure 1. In making them, the capillaries were first sealed to tubes about 2 cm in diameter, leaving the end opposite the capillary open. Weighed samples of rubber were then placed inside the tubes and the ends quickly sealed, taking care not to scorch the rubber. The dilatometers containing the samples were weighed, filled to a mark on the capillary with a confining liquid at a given temperature, and again weighed. The volumes of the dilatometers were found from the weights and densities of the samples and confining liquids at a given temperature. Volumes of the dilatometers at other temperatures were computed using the volume of coefficient of expansion for the glass used.³

Three sizes of capillaries were used, ranging from about 40 to 90 cm in length and having diameters approximately 0.6, 1.8, and 2.5 mm, respectively. They were

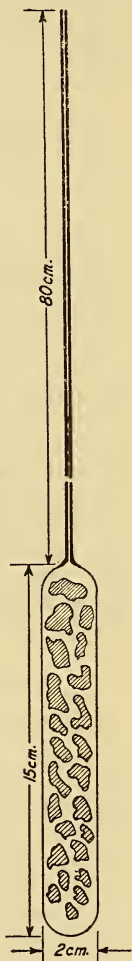


FIGURE 1.—Dilatometer used for determination of temperature-volume relations of rubber and confining liquids.

¹ BS. J. Research 8, 751(1932);RP449.

² BS. J. Research 1, 771(1928);RP29.

³ Buffington and Latimer, J. Am. Chem. Soc. 48, 2305(1926).

calibrated in the usual way by measuring the length of a mercury thread of known weight. In the circumstances under which they were used they covered temperature ranges of about 8, 40, and 120 degrees centigrade, respectively. The capillaries of the smaller diameters were used for the measurement of the coefficient of expansion over small intervals of temperature, while the larger were used to make series of observations continuously over a wide range. The smaller capillaries, of course, gave the more precise values.

Density measurements which were required in the course of the investigation were made with a pycnometer of the type described by Ashton, Houston, and Saylor⁴ which was found suitable for use not only at or above room temperature, but also at low temperatures.

2. CONFINING LIQUIDS

Water, alcohol, acetone, and mercury were employed as confining liquids in the temperature ranges for which they were respectively suitable. The alcohol was used in three different concentrations. Most of the measurements were made with a product which was taken from the laboratory supply and contained 89 percent of ethanol and 11 percent of water by weight. But to eliminate the possibility that the water content of this product may have influenced the results at low temperatures, measurements were also made with 92.5 percent alcohol and with absolute alcohol as confining liquids. The acetone was of the chemically pure grade and was not further dehydrated or specially purified before use. The density and the volume coefficient of expansion were determined for the particular samples of alcohol and acetone that were employed. The density and the coefficient of expansion of mercury and of water were taken from the International Critical Tables.⁵

3. MEASUREMENT AND CONTROL OF TEMPERATURE

The temperature range covered in this investigation was from about -85 to $+85$ C with the dilatometers, and from -190 to 0 C in the case of length measurements. Measurements of temperature were made by means of calibrated copper-constantan thermocouples, the electromotive force of which was read on a Wenner potentiometer⁶ having a precision of better than one microvolt. This is equivalent to a precision of at least 0.04 C. The measuring junction of the thermocouple was mounted in the bath with the dilatometers, and in the rubber sample itself for the length measurements.

The dilatometers were maintained at the desired temperatures by means of liquid baths in dewar flasks. Above the temperature of 0 C, water was used; below this acetone or a eutectic mixture of carbon tetrachloride and chloroform was employed and was cooled with carbon dioxide snow. Temperatures somewhat below those given by the carbon dioxide snow alone were obtained by the additions of small quantities of liquid air.

⁴ BS J. Research **11**,233(1933):RP587. This pycnometer is a modification of the one used by Richards, Hall, and Mair, J. Am. Chem. Soc. **50**,3308(1928).

⁵ International Critical Tables, First Edition, McGraw-Hill Book Co., New York, **II**,457, and **III**,24.

⁶ Rev. Sci. Instruments **3**,109(1932). Also Phys. Rev. **31**,94(1910).

Slow rates of heating were usually obtained at temperatures below those of the room by allowing the baths to warm spontaneously. With efficient dewar flasks a period of 2 or 3 days was required to reach approximately room temperature from -85°C ; by using unsilvered dewar flasks more rapid warming was obtained.

The samples for the length measurements were maintained at about -190°C by means of a bath of liquid air. No observations were recorded between -190 and -95°C . Above the latter temperature an acetone bath was used.

4. COMPUTATION OF COEFFICIENT OF EXPANSION

The method of computing the coefficient of expansion of rubber from the readings of the dilatometer is shown by the following example. A dilatometer containing rubber and alcohol gave a linear change of 8.10 cm per degree centigrade in the height of liquid in the capillary for the range from -4 to $+4^{\circ}\text{C}$. The volume of the dilatometer including one-half of the capillary was 29.462 ml at a temperature of 0°C , found as indicated above. Calibration of the capillary showed 1 cm of the length to be equivalent to 0.003177 ml. The change in volume, therefore, was 0.02573 ml per degree centigrade at a temperature of 0°C for the rubber and alcohol together, or 0.000874 vol/vol/ $^{\circ}\text{C}$.

The change in volume of the alcohol was 0.00108 vol/vol/ $^{\circ}\text{C}$ at a temperature of 0°C as determined by measurements in a similar dilatometer.

In the dilatometer containing rubber, the sample weighed 13.032 g and occupied a volume of 14.150 ml at a temperature of 0°C taking the density to be 0.921⁷ at that temperature. By difference, then, the volume of the alcohol at 0°C was 15.312, or the volume fraction of the alcohol 0.520.

The following equation results:

$$(0.520 \times 0.00108) + (1 - 0.520)x = 0.000874$$

which, when solved, gives

$$x = 0.00065.$$

This, then, is taken as the coefficient of expansion of rubber at a temperature of 0°C .

IV. RESULTS WITH UNVULCANIZED RUBBER

The results which were obtained in the studies on unvulcanized rubber indicate that it may exist in different forms. For simplicity and clarity in presentation, a general statement regarding these forms will be made first and this will be followed by a description of the observations and experiments.

1. FORMS OF UNVULCANIZED RUBBER

The temperature-volume measurements on unvulcanized rubber exhibited two types of anomalies. One of these was the well-known freezing of rubber. This was accompanied by a change of volume of about 2.7 percent and was found to occur in the temperature range 6 to 16°C . The transition was half complete at about 11°C and is

⁷ See footnote 1, p. 413.

considered for discussion as the 11 C transition. As will be discussed in a subsequent section, the results of other workers show that frozen rubber is crystalline, and it will be so considered throughout this paper,⁸ while the ordinary form of rubber will be regarded as amorphous. The crystallization of rubber on cooling is a relatively slow process so it was found possible to deal with the amorphous phase of rubber as well as the crystalline phase at temperatures below 11 C.

The second type of anomaly was observed at about -72 C. When either the amorphous or the crystalline rubber was subjected to temperatures below this, a marked change in the coefficient of expansion was observed, the coefficient below this temperature being only about one-third as great as that above it.

The relation between the relative volumes of these different forms of rubber is shown graphically in figure 2. In this figure the relative

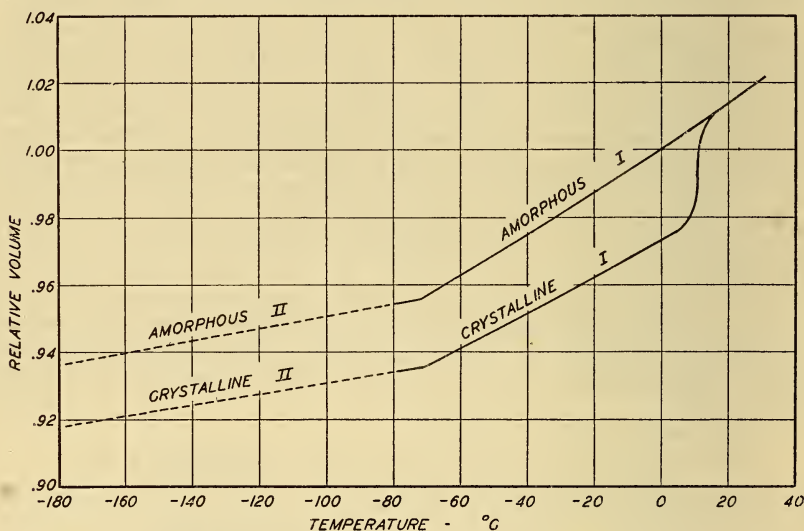


FIGURE 2.—Relation between volume of rubber hydrocarbon and temperature.

Below the transition at 11 C the amorphous form is metastable and the crystalline form is stable. The dotted portions of the curves were computed from length measurements.

volume of rubber is plotted as a function of the temperature, taking the volume of rubber as unity in the familiar amorphous form at a temperature of 0 C. As a matter of convenience the various forms of rubber are here designated: The ordinary amorphous form above -72 C is called amorphous rubber I; below -72 C, amorphous rubber II. The crystalline forms are likewise called crystalline rubber I and crystalline rubber II as shown in the figure.

The curves indicate that rubber exists in the amorphous I form at room temperature but that below the transition at 11 C it may either remain in the amorphous I form or undergo transition to the crystalline I form depending on the time and temperature. The crystalline form has the smaller specific volume and is the stable form below about 11 C. The amorphous form is metastable below this tempera-

⁸ The product here called the crystalline form of rubber should not be confused with rubber crystals referred to in a recent publication by W. H. Smith, Charles Proffer Saylor, and Henry J. Wing, *BS J Research* 10,479(1933);RP544. The former is an agglomerate of crystals with a melting range of about 10 degrees centigrade, while the latter is made up of distinct, individual crystals having relatively sharp melt ing points.

ture. At about -72°C the crystalline I form undergoes transition to the crystalline II form which is apparently the stable form at low temperatures. At approximately the same transition temperature the amorphous I form changes to the amorphous II form which, although it is evidently metastable, has not been observed to undergo transition to the crystalline II form.

2. MEASUREMENTS OF CHANGES OF VOLUME OF RUBBER

The solid line curves in figure 2 represent measurements which were made on rubber hydrocarbon using the 89 percent alcohol as the confining liquid. The exploration of the temperature range from -80 to $+40^{\circ}\text{C}$ was made with use of a dilatometer having a capillary tube of such capacity that the entire range was covered without the addition or removal of confining liquid. The dotted portions of the curves were computed from length measurements to be described later in the paper. Observations in other ranges were made with dilatometers having small capillaries so that more precise measurements could be made on the coefficients of expansion and on the change in volume. Individual points are not shown for the curves in figure 2 because the amounts by which they deviate from the curves are not appreciable for the scale used. The precision of the measurements is illustrated by figure 3, curve D, in which the portions of the curves showing the transitions from the I forms to the II forms are drawn on a larger scale.

Measurements with acetone, with 92.5 percent alcohol, and with absolute alcohol as confining liquids are also shown in figure 3. The curves with the three concentrations of alcohol all point to a transition at about -72°C , but the curve obtained with acetone gives no indication of a transition. Evidence from changes in length and in other properties with temperature indicates that the results with alcohol, rather than with acetone, represent the true state of affairs. It is possible that the discrepancy is due to the swelling action of acetone on rubber, but further experimental work is required before a definite explanation can be offered.

Measurements on crude rubber gave results closely similar to the above results on rubber hydrocarbon. The freezing occurred in the same temperature range, 6 to 16 $^{\circ}\text{C}$. The I-II transitions of both the amorphous and crystalline rubber occurred at about -72°C . The numerical values of the volume change on crystallization and the coefficient of expansion differed slightly from those for the rubber hydrocarbon as will be indicated in section 5.

3. RATE OF CRYSTALLIZATION OF RUBBER

Observations were made on the rate of crystallization of rubber as indicated by volume measurements at several temperatures, particularly at 0°C . When rubber was cooled from $+40$ to -72 at a fairly uniform rate in 4 or 5 hours, the volume decreased in a nearly linear manner with the temperature as is shown in the upper curve in figure 2. When it was allowed to warm at the same rate or more rapidly, the volume increased in the same manner. When the rubber was cooled to -72°C as before and allowed to warm at a slower rate, such that 2 or 3 days or more were required to reach room temperature, the volume-temperature relation described this same curve up

to about -25 C. But at some temperature near -25 C, which differed from one experiment to another, the rubber began to decrease in volume with increasing temperature, and continued its decrease until the volume corresponded to that indicated by the lower curve in the figure.

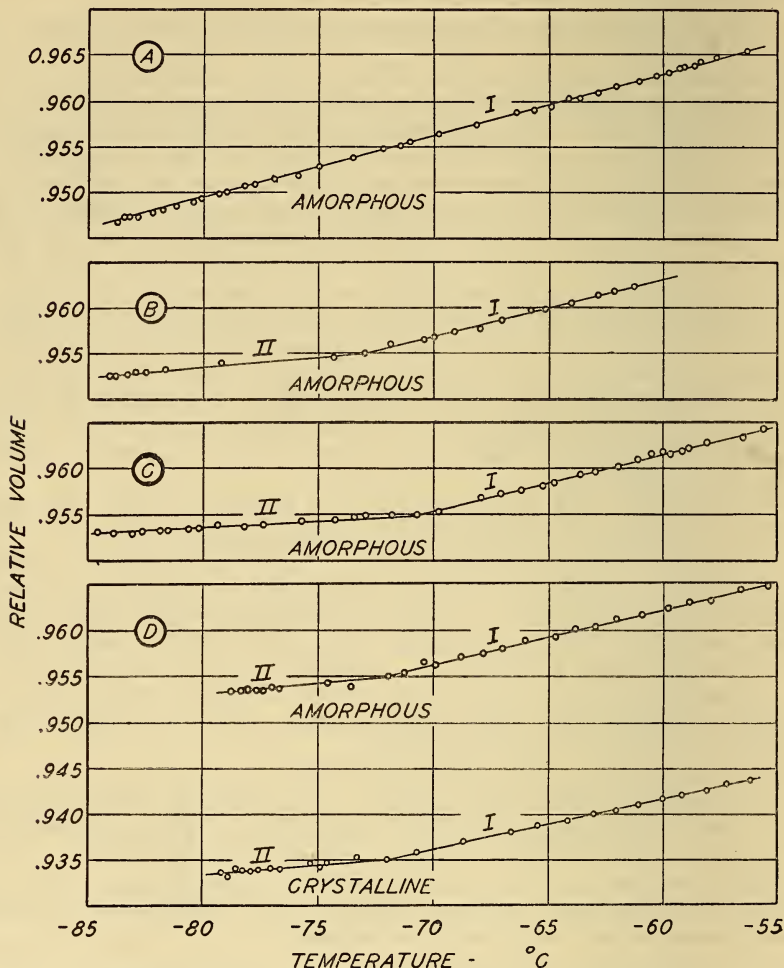


FIGURE 3.—Relation between volume of rubber hydrocarbon and temperature with different confining liquids in the dilatometers.

A, acetone; B, absolute alcohol; C, 92.5 percent alcohol; D, 89 percent alcohol. D is a large-scale drawing of a portion of figure 2.

When crystallization was taking place with rising temperature there was a negative coefficient of expansion, and when effected in a calorimeter there was a marked evolution of heat. When the volume decreased to that indicated by the lower curve, the temperature-volume relation was described by that curve. On further heating, the rubber underwent the 11 C transition and returned to its original volume.

Crystallization of rubber seemed to take place most readily at temperatures between -35 and -15 C and was usually complete in a few hours. At the lower part of this range the transition became slower, and at still lower temperatures it did not take place. Samples which were kept below -50 C for 3 weeks gave no indication of transition. One sample which had been cooled to the triple point of hydrogen, -259 C, in a calorimeter, on warming underwent transition at about -35 C indicating that crystallization had not taken place at the lower temperature.

The rate of transition at a temperature of 0 C was measured using dilatometers with alcohol, acetone, mercury, and water, respectively, as confining liquids. The measurements made on rubber hydrocarbon with alcohol as a confining liquid are shown in figure 4 in which the relative volume of rubber is plotted as a function of the time. The curve is S-shaped, which is characteristic of transitions of this type. The change in volume is apparently complete in about

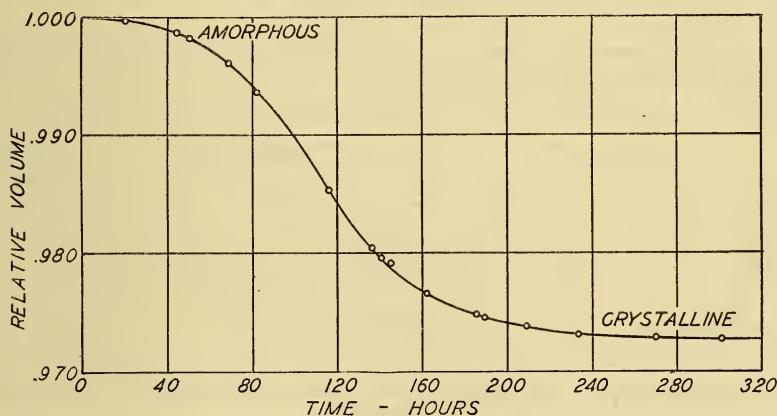


FIGURE 4.—Decrease in volume with time as rubber hydrocarbon changes from amorphous I to crystalline I form at a temperature of 0 C.

10 days. This is in quite close agreement with the results of other investigators as will be discussed in section VII. Similar curves were obtained for rubber hydrocarbon with other confining liquids, and also with crude rubber using alcohol as a confining liquid. But when ammonia-preserved rubber latex was kept at a temperature of 0 C for a month no change in volume was observed.

The reverse transition—that is, the one from the crystalline I form to the amorphous I form of rubber—seemed to take place without appreciable delay. Measurements on the rate of transition were made with different rates of warming without significant variation in results. Samples of crude rubber which had been in the crystalline state for several weeks were quickly withdrawn from the ice bath and were placed in water at about 25 C. The stiffness and opacity disappeared within the time required for the samples to reach temperature equilibrium. When crystalline samples were warmed to about 10 C in the dilatometers and cooled again, the temperature-volume relation described exactly the lower curve without lag.

4. CHANGE OF VOLUME OF RUBBER ON CRYSTALLIZATION

The magnitude of the volume change which accompanies the transition of rubber from the amorphous to the crystalline form is indicated by the results previously set forth in figures 2 and 4. The measurements of the change in volume which were made with the different confining liquids at a temperature of 0 C gave somewhat different results for the change in volume depending upon the liquid used. The results are given in table 1. For purified rubber the change was from 2.43 percent with mercury to 2.81 percent with acetone, the average being 2.65 percent. The variation was considerably greater than the probable experimental error and may have been due to the action of the confining liquids on the rubber.

The volume change with crude rubber was 2.20 percent, alcohol being used as the confining liquid. Assuming that crude rubber is 93 percent hydrocarbon, this is equivalent to a volume change of 2.37 percent for the hydrocarbon content.

TABLE 1.—Decrease in volume in the transition from amorphous to crystalline rubber at a temperature of 0 C when observed in the presence of different confining liquids

Material	Confining liquid	Decrease in volume
		<i>Percent</i>
Rubber hydrocarbon.....	Alcohol, 89 percent.....	2.65
Do.....	Acetone.....	2.81
Do.....	Mercury.....	2.43
Do.....	Water.....	2.70
Average.....		2.65
Smoked sheet rubber.....	Alcohol, 89 percent.....	2.20

5. COEFFICIENT OF EXPANSION OF DIFFERENT FORMS OF RUBBER

Determinations of the volume coefficient of expansion of rubber hydrocarbon in different forms were made in dilatometers provided with small capillary tubes. These tubes were about 75 cm in length and were of such bore that consecutive measurements could be made over a temperature range of about 8 degrees centigrade. To make measurements at other temperatures it was necessary to add or remove confining liquid. The measurements of temperatures below that of the room were made while the dilatometers and their contents were warming slowly, and measurements at higher temperatures while the dilatometers were cooling slowly. The rates of heating and cooling were of the order of 2 degrees centigrade per hour. The bath was stirred constantly so that for practical purposes the contents of the dilatometers may be regarded as being at bath temperatures at all times.

The results are shown in figure 5, in which the volume coefficient of expansion is plotted as a function of the temperature. The coefficients of both the amorphous I and the crystalline I forms bear a nearly linear relation to the temperature, decreasing slightly with decreasing temperature. The coefficient for the crystalline form was not so accurately determined but was found to be about 15 percent lower than that of the amorphous form.

The volume coefficients of expansion for the amorphous I form of rubber between the limits of +85 and -72 C can be calculated from the equation,

$$\frac{dv}{dt} = 0.00067 + 0.0000007(t - 25)$$

or its volume may be found from the equation,

$$V_t = V_{25}[1 + 0.00067(t - 25) + 0.0000004(t - 25)^2]$$

in which $\frac{dv}{dt}$ is the rate of change of volume with temperature, t is the temperature in degrees centigrade, V_t is the volume at the temperature, t , and V_{25} is the volume at 25 C.

At about a temperature of -72 C the coefficients of expansion of each form undergo a marked change, below which both forms have

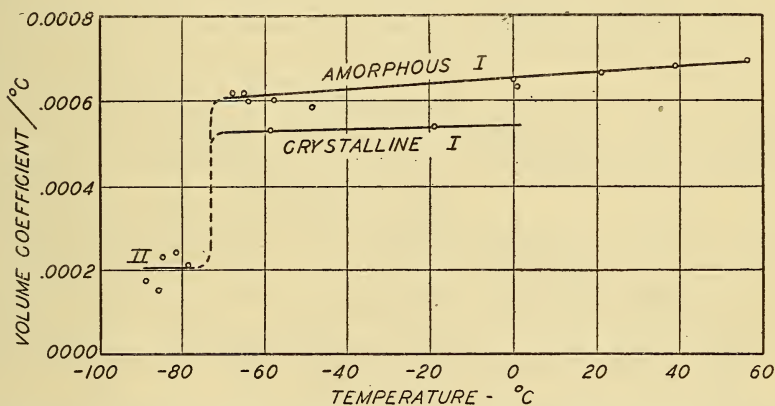


FIGURE 5.—Relation between coefficients of expansion of different forms of rubber hydrocarbon and temperature.

values of approximately 0.00020. This latter value was not determined with as great accuracy from volume measurements since they were carried to only about -85 C. The measurements which have thus far been made do not suffice to indicate whether the amorphous I-amorphous II and the crystalline I-crystalline II transitions take place at the same or at slightly different temperatures. No lag was noticed in the transitions between the lower temperature forms and the amorphous I or crystalline I forms.

6. LINEAR EXPANSION OF RUBBER

Measurements of the linear expansion of rubber were made⁹ to afford an independent check on the results of volume measurements, and to extend the observations to temperatures below those at which the ordinary confining liquids could be used. The specimen employed was in the form of a rod about 11 cm in length and 1.5 cm in

⁹ The author wishes to thank Dr. Peter Hidnert of this Bureau for cooperation in making these measurements.

diameter. Measurements of the change in length were made with a dial gage graduated to 0.01 mm, using the quartz tube apparatus referred to above. Observations were made on the sample first in the amorphous form and then after it had been converted to the crystalline form. The results of the measurements are shown in figure 6 in terms of relative length plotted as a function of the temperature.

The observations on the sample in the amorphous form extended from the temperature of liquid air, or about -190°C , to about -72°C , above which temperature the sample decreased in length and gave indication that it was undergoing deformation under the pressure exerted by the measuring mechanism. In the crystalline form, however, it was found possible to observe the expansion from -190 to 0°C . No plastic deformation occurred, since at the end of the run the sample resumed its original length when replaced in liquid air.

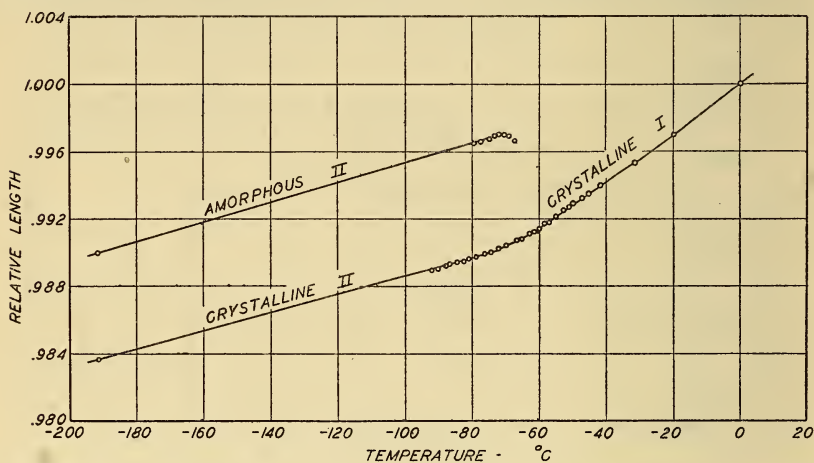


FIGURE 6.—Relation between length of specimen of rubber hydrocarbon and temperature.

Measurements on the amorphous II form were discontinued at about -70°C because of softening of the sample.

Relative positions of the curves for the amorphous and the crystalline forms in the figure were not found by direct observation but were computed from the change of volume on crystallization as measured with the dilatometer.

The curve for the crystalline form gives an indication of a transition in the neighborhood of -70°C , thus substantiating the results obtained with the dilatometers in which alcohol was used as a confining liquid.

The average linear coefficient of expansion for the amorphous II form between -190 and -72°C was 0.000060, while that for the crystalline II form was 0.000054. The volume coefficients which may be derived from these linear coefficients, assuming the rubber to be isotropic, are 0.00018, and 0.00016, respectively. These values are consistent with the value 0.00020 obtained from the dilatometer measurements between -85 and -72°C . They are slightly lower since they refer to a lower mean temperature. In the case of nearly

all substances the coefficient of expansion decreases with decreasing temperature.

The average linear coefficient of expansion for the crystalline I form from -72 to 0 C was 0.00014 ; this corresponds to a volume coefficient of 0.00042 , which is somewhat lower than the value 0.00053 obtained with the dilatometer. No definite explanation can be offered for this discrepancy but it is possible that the pressure exerted by the measuring mechanism prevented equal expansion in all directions.

V. RESULTS WITH VULCANIZED RUBBER

Temperature-volume measurements were made on vulcanized rubber from -85 to $+85$ C and showed only one anomaly, which was comparable to the transition occurring at -72 C with the unvulcanized rubber. This anomaly was a change in coefficient of expansion, and with different compounds occurred at temperatures determined by the percentage of combined sulphur. Analogous to the nomenclature for unvulcanized rubber, the ordinary vulcanized rubber is called the amorphous I form and that having the low coefficient of expansion the amorphous II form.

The measurements on the vulcanized samples were made with dilatometers having capillary tubes of such capacity that a range of about 40 degrees centigrade could be covered by a continuous series of observations. The results are, therefore, somewhat less precise than those obtained with unvulcanized rubber.

The relative volumes of the samples are shown in figure 7 as a function of the temperature. In the case of each of the three compositions the relation to temperature is linear and is characterized by an abrupt change of slope. For the sample containing 2 percent of combined sulphur this change occurs at about -72 C; for 4 percent it occurs at about -62 C; and for 6 percent at about -53 C. The data are not sufficiently precise to give exact values for the coefficient of expansion. Within experimental error the coefficients of expansion above the transition points are the same and are about 0.00065 ; below the transitions they are all about 0.00022 .

VI. DISCUSSION

The crystallization of rubber is essentially the same as the crystallization of any organic substance of high molecular weight. It is a relatively slow process and is speeded up by a certain degree of supercooling. Cooling quickly to a temperature considerably below the transition point, however, inhibits crystallization, presumably for the reason that the viscosity of the rubber becomes so great that the molecular orientation cannot take place to any appreciable extent. This is comparable to the supercooling and formation of glassy modifications by many substances.

In contrast to the behavior of unvulcanized rubber, vulcanized rubber, unless external force is applied, undergoes no volume change which might be attributed to crystallization at any temperature in the range covered by the investigation. This may be explained by assuming that in unvulcanized rubber the molecules have a sufficient degree of mobility to permit the formation of crystals, while in vul-

canized rubber the molecules are linked together with sulphur or are so held by other forces that orientation to the extent necessary for the crystallization cannot take place spontaneously. There is, however, ample evidence that the application of external force may produce crystallization. The formation of X-ray diffraction patterns in stretched rubber is one type of evidence, while the change in volume of

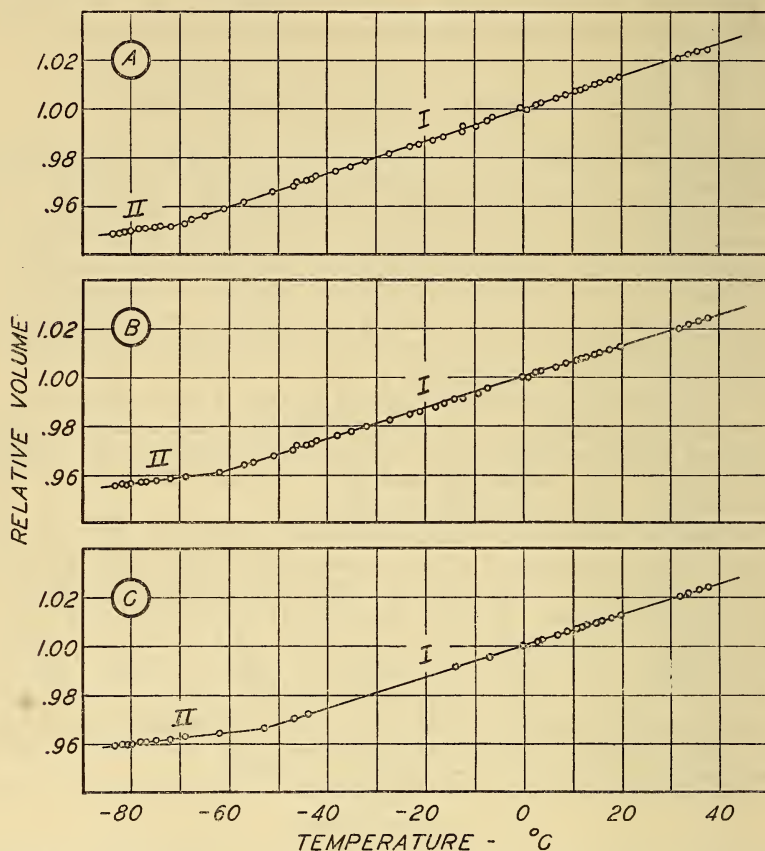


FIGURE 7.—Relation between volume of rubber-sulphur compounds and temperature.

Curve A refers to a compound with 2 percent sulphur, curve B to a compound with 4 percent, and curve C to a compound with 6 percent. I and II refer to the amorphous I and amorphous II forms, respectively.

rubber after stretching is another. This matter will be discussed further in a subsequent section of this paper.

The low temperature transitions which are observed to occur in both forms of the unvulcanized rubber and in the amorphous form of the vulcanized rubber are of the type considered by Ehrenfest¹⁰ as transitions of the second order. In these transitions ΔS and ΔV are zero at constant temperature, but $\Delta \frac{dS}{dT}$ and $\Delta \frac{dV}{dT}$ are not zero; S being the entropy, V the volume, and T the temperature.

¹⁰ Koninklijke Akad. Wetenschappen Amsterdam 36, 153(1933).

Transitions of the second order are considered to arise from changes which take place within the molecule, such as excitation by rotation or vibration, in contrast to transitions of the first order which are associated with molecular phenomena, such as crystallization or changes of crystal structure. From this standpoint it is reasonable that the transitions from form I to form II for both the amorphous and the crystalline rubber should occur in the same temperature range, since the two forms are probably the same as regards the internal structure of the molecules.

The transitions from form I to II for the vulcanized rubber were observed to occur at temperatures which are determined by the percentage of sulphur in combination with the rubber. This is in accord with the well-established principle of organic chemistry that the addition of an atom or radical to a long chain molecule affects the properties not merely of the atom or groups to which the addition is made but also of remote parts of the molecule. Consequently, it is reasonable that the temperature at which the transition occurs should be changed by the addition of even a relatively small proportion of sulphur.

The crystallization of unvulcanized rubber is not sharp but takes place over the range 6 to 16 C. This fact indicates that the material dealt with is not a single definite molecular species but is a mixture of two or more kinds of molecules. The data here presented, however, are not adequate to warrant any speculation as to the number of types of molecules involved.

The present investigation does not afford a complete description of the forms of rubber because it does not include the well-known form of frozen rubber which undergoes transition to the amorphous form at about 35 C. The investigation of this form of rubber is in progress but the indications are that a long time, perhaps years, may be required for an adequate study since the transformation from the amorphous form to this crystalline form is very slow.

VII. COMPARISON WITH OTHER INVESTIGATIONS

The results of the present investigation serve to clarify and coordinate a variety of different observations that have been made regarding the influence of temperature on the properties of rubber. The measurements here reported for the transitions and for volume changes associated with the transitions are in agreement with some of the determinations by previous investigators which are summarized in table 2. The existence of rubber in different forms has a direct bearing on phenomena as diverse as the behavior of rubber on stretching and the change of electrical properties with temperature.

TABLE 2.—Comparison of the data of different investigators on the crystallization of rubber

Investigators	Type of measurement	Kind of rubber	Temperature of melting	Volume change
Bunschoten	Density	Raw	About 35 C after storage for several years in the frozen condition.	2.0 percent at 35 C.
Ruhemann and Simon.	Volume change in dilatometer.	Smoked sheet	About 8 C	Qualitative observations only.
van Rossem and Lotichius.	Hardness	Latex sheets	2 to 15 C	
Do	Density	do	do	2.5 percent at 0 C.
Do	do	do	About 35 C after storage for several years in the frozen condition.	3.1 percent at 35 C.
Carson	Manual examination	Milled crude	Below room temperature after storage for several months at 0 C; between room temperature and 50 C after similar storage under pressure.	
Smith, Saylor, and Wing.	Observations on crystals under polarizing microscope.	Pure ether-soluble fraction.	8 to 11 C depending on conditions of measurement.	
Gibbons, Gerke, and Tingey.	"T-50" test	Smoked sheet	16 C	
Present author	Heat capacity	Rubber hydrocarbon.	6 to 16 C	
Do	Volume change in dilatometer.	Rubber hydrocarbon and smoked sheet.	do	2.65 percent at 0 C.

1. FREEZING OF RUBBER

The work of previous investigators points to the existence of two forms of frozen rubber; one, the form melting at about 35 C, and the other, a form which may be identified with the one here designated as crystalline I. van Rossem and Lotichius¹¹ obtained the first of these by keeping rubber at a low temperature for several years, and the second by keeping rubber at a temperature of 4 C for about 10 days, or at -10 C for 3 or 4 days. The conditions under which the latter product was obtained were comparable to those found in the present investigation for producing the crystalline I form. The temperature range of transition to the amorphous form was 2 to 15 C which is roughly the same as the range 6 to 16 C found for the crystalline I form.

Carson¹² observed both types of freezing in crude rubber which had been kept in storage for 9 months. Samples which had been under an applied pressure were found to thaw at a temperature between that of room and 50 C, while the samples to which no pressure had been applied thawed at a temperature below that of room. The first of these may be identified with the form melting at about 35 C, and the second with the crystalline I form.

Recently Smith¹³ and coworkers, at this Bureau, measured the properties of crystals of the pure ether-soluble fraction of rubber hydrocarbon. Their product was designated as true crystals to distinguish it from frozen rubber in which the individual crystals are not discrete. The true crystals melted sharply at temperatures which varied from 8 to 11 C with the conditions under which the determina-

¹¹ Kautschuk 5,2(1929). Also Rubber Chem. Tech.2,378(1929). Cf. India Rubber J.67,69(1924).¹² Ind. Eng. Chem. 23,691(1931). Also Rubber Chem. Tech.4,417(1931).¹³ See footnote 8 for reference.

tions were made. These temperatures lie within the range found in the present investigation for the crystalline I—amorphous I transition, and it is probable that the product represents a single molecular species which is one of the constituents of the rubber used by the present and other investigators.

The volume change on crystallization was investigated by Bunschoten¹⁴ who found a change of 2.0 percent for the transition at 35 C. van Rossem and Lotichius, however, found a change of about 3.1 percent for this transition at 35 C, and a change of about 2.5 percent for the transition from the amorphous I to the crystalline I form at a temperature of 0 C. The latter determination is in fair agreement with the average value, 2.65 percent, found in the present investigation.

Ruhemann and Simon¹⁵ made some observations on the behavior of crude rubber in a dilatometer with mercury as a confining liquid. The curve which they obtained for the temperature-volume relation was but semi-quantitative, and showed a deviation from a straight line from about -25 to $+10$ C for which they offered no explanation. From the present results, however, it appears that when the sample was cooled to a low temperature it remained in the amorphous form at the lower temperatures, but when it was warmed slowly partial transition to the crystalline phase took place through the range -25 to $+10$ C with a resulting deviation from a straight line in the temperature-volume curve. At about 10 C the sample returned to its original amorphous condition, and the temperature-volume relation was again represented by a straight line.

Katz and Bing¹⁶ studied the X-ray diffraction patterns of frozen rubber and concluded that it was crystalline, the crystals being in random orientation rather than in definite alignment as in stretched rubber.

Pummerer and Von Susich¹⁷ sought, by means of X-ray diffraction studies, for evidence of crystallization in rubber that had been kept at -190 C for 8 days, but found none. This negative result is easily understood from the results of the present investigation which show that crystallization takes place readily only in the range from about $+11$ to -35 C, while at much lower temperatures the rate becomes so slow as to be inappreciable.

Unpublished work by the present author on the measurement of heat capacities of rubber indicates a transition of the first order in the vicinity of 10 C which is consistent with other findings of the present investigation. Ruhemann and Simon,¹⁸ however, found a large latent heat effect at a temperature of 0 C. No interpretation for this latter observation can be offered at the present time.

2. CRYSTALLIZATION OF RUBBER BY STRETCHING

Several lines of evidence indicate that the crystallization of rubber which is brought about by stretching is closely allied to, if not identical with, the crystallization produced by freezing. Katz and Bing found, as was mentioned above, that the X-ray diffraction patterns of frozen rubber and of stretched rubber were identical except that the crystals

¹⁴ Meded. Rikjsvoorlichtingsdienst behoeve rubberhandel rubbernijverheid, Delft, [3],37(1921).

¹⁵ Z. phys. Chem. 138A,1(1928).

¹⁶ Z. angewandte Chem. 38,439(1925).

¹⁷ Kautschuk 7,117(1931). Also Rubber Chem. Tech. 5,245(1932).

¹⁸ See footnote 15.

in the frozen rubber were in random orientation. Davey and his coworkers¹⁹ showed that a small interval of time elapses between the extension of a sample of rubber and the appearance of an X-ray diffraction pattern. A similar time lag was recently observed in connection with the decrease in volume of rubber on stretching.²⁰ Measurement of the change in volume was found to afford a simple means for following the progress of crystallization. Under some circumstances a considerable part of the volume change occurred within a few seconds after the stretching, while under other circumstances a similar change required hours. This is further evidence that the rubber molecules do not form a crystal lattice in the process of stretching, but that crystallization is a subsequent and distinct process.

The melting of unvulcanized rubber which has been crystallized by stretching occurs in the same range of temperature as that of rubber crystallized by cooling. This is indicated by a comparison of the results of the "T-50" test described by Gibbons, Gerke, and Tingey²¹ with measurements made in the present investigation. In the T-50 test rubber which has been stretched and cooled quickly is released and allowed to warm, observations being made on the temperature at which the rubber retracts to 50 percent of the original elongation. The above-mentioned investigators found a retraction temperature of 16 C for smoked sheet which had been stretched to 700 percent elongation. This corresponds to the higher temperature of the melting range, 6 to 16 C, reported in a previous section of this paper. This agreement is as would be expected since the restoring forces in stretched crystalline rubber would become operative only after much of the crystal structure had disappeared.

Measurements of the change in volume of rubber under conditions comparable to the T-50 test afford further evidence that the crystallization produced by stretching is comparable to that brought about by cooling alone. The results of one experiment²² in this connection are shown in figure 8. In this experiment rubber rings cut from lightly-milled pale crepe were stretched to an elongation of about 350 percent, and cooled at once to a temperature of about 1 C at which they were kept for 19 hours. The volume decreased rapidly at first, and then more slowly. The magnitude of the change which took place is indicated by the curve AB. The rings were then released and allowed to warm slowly, and the increase in volume observed, the results being given by curve BCD. Although released, the rubber remained in its elongated form until a temperature of about 10.5 C was reached at which contraction in length began. At 12 C it had contracted to 50 percent of its elongation in the stretched condition, but recovery was not complete until a temperature of 24 C had been reached. The rubber samples were again cooled to a temperature of 1 C and measurements made as indicated by curve DA to complete the cycle.

The volume change on crystallization here observed was only 1.86 percent as compared with 2.20 percent for the crystallization of smoked sheet rubber by cooling alone. In another experiment, however, a volume change of 2.54 percent was observed when rubber produced

¹⁹ Ind. Eng. Chem. 24,54(1932). Also Ind. Eng. Chem. 26,543(1934).

²⁰ Technical News Bulletin of the Bureau of Standards, 6, January 1934.

²¹ Ind. Eng. Chem., Anal. Ed. 5,279(1933).

²² A. T. McPherson, unpublished work.

by the evaporation of latex was stretched to an elongation of 500 percent and kept at a temperature of 1 C for 8 hours. The point of inflection of curve BD is at 11 C which is in agreement with the mid-point of the melting range found for rubber crystallized by cooling alone.

The temperature at which rubber becomes brittle when cooled and bent quickly has been investigated by Kohman and Peek²³ who have found that the temperature is definite, and within limits is practically independent of the dimensions of the sample or the angle of bending. The temperature found for pale crepe was -58 C and for smoked sheet -57 C. These temperatures bear no apparent relation to any

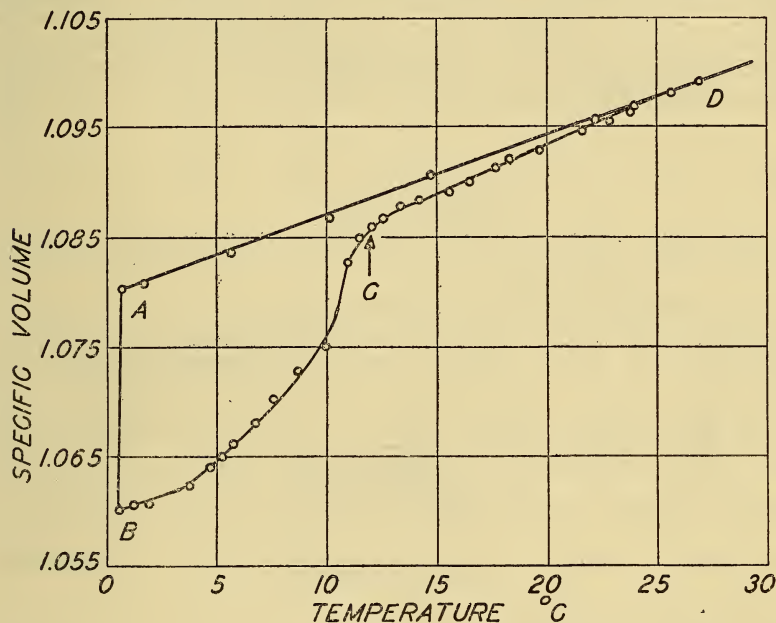


FIGURE 8.—Temperature-volume relations of stretched and unstretched rubber.

At A rubber is stretched; from A to B transition from amorphous to crystalline form occurs; at B rubber is released; between B and D rubber is allowed to warm, retraction being one-half complete at C; from D to A rubber is cooled to complete cycle.

of the changes in form which have been observed in the present investigation.

3. TRANSITIONS OF THE SECOND ORDER IN RUBBER

Ruhemann and Simon²⁴ found that unvulcanized rubber underwent a change in heat capacity at about -70 C. No latent heat effect was observed in connection with this transition, hence it is not a transition of the first order. Unpublished heat capacity measurements by the present author confirm the observations of Ruhemann and Simon as to the nature of this transition and the approximate temperature at which it occurs.

²³ Ind. Eng. Chem. 20, 81(1928).

²⁴ See footnote 15.

Kimura and Namikawa²⁵ studied the specific gravity of rubber-sulphur compounds at different temperatures and found that these compounds underwent changes in coefficient of expansion at temperatures which were determined by the percentage of sulphur. The temperatures of transition observed for the compounds containing 2, 4, and 6 percent of sulphur, respectively, in the present investigation are in agreement with values taken from a curve published by them.

4. ELECTRICAL PROPERTIES OF RUBBER

Evidence for the changes in the form of rubber can be deduced from the results of a recent investigation on the electrical properties of rubber.²⁶ In this investigation it was found that the dielectric constant of the unvulcanized rubber was independent of the frequency at which the measurement was made. This being the case, the measurements of dielectric constants at all frequencies reported in the above-

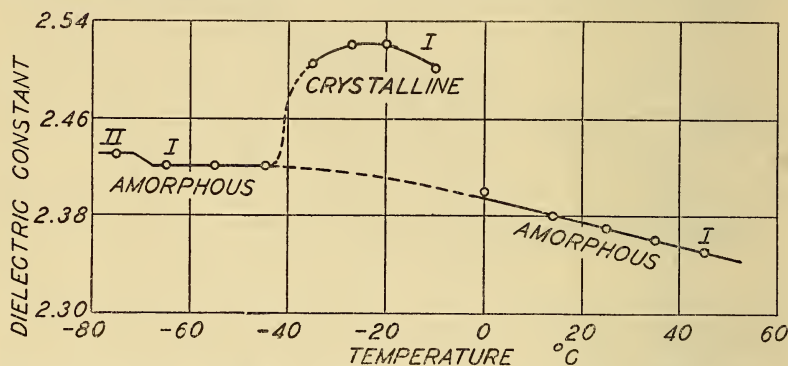


FIGURE 9.—Relation between dielectric constant of rubber hydrocarbon and temperature.

The data are from the paper referred to in footnote 26. The forms of rubber shown are those indicated by the present investigation.

mentioned investigation have been averaged and the results are shown in figure 9 for temperatures from -75 to $+50$ C. The prominent feature of the curve in this figure is the group of high values for dielectric constant between the temperatures of -35 and -10 C. These are about 0.1 unit above a smooth curve drawn through points for other temperatures, and on the basis of the present investigation may be attributed to the crystallization of rubber. The samples on which these measurements were made were first cooled to -75 C. and observations then taken at intervals of about 10° C while the temperature was slowly rising.²⁷ Between -45 and -35 C crystallization evidently took place and the values from -35 to -10 C pertain to the crystalline rather than to the amorphous form of rubber. One effect of the crystallization would be to change the dimensions of the specimens and make the observed dielectric constant values too high by about 0.05 unit. Taking a correction for this into consideration, the dielectric constant of the crystalline form of rubber is about 0.05 unit higher than that of the amorphous form.

²⁵ J. Soc. Chem. Ind. (Japan), Supplemental Binding 32, 196B(1929).

²⁶ A. H. Scott, A. T. McPherson, and Harvey L. Curtis, BS J. Research 11, 173 (1933), RP585.

²⁷ Private communication from the authors.

This series of observations was discontinued at -10 C and a new series was made from 0 C to higher temperatures in which the samples were first cooled from room temperature to 0 C in about 1 day. Probably a little crystallization took place, causing the value for the dielectric constant at 0 C to be a little greater than that represented by the smooth curve.

Careful examination of the dielectric constant data in the low temperature range indicates by the change in slope of the curve a slight but definite anomaly between -75 and -65 C. Dielectric constant

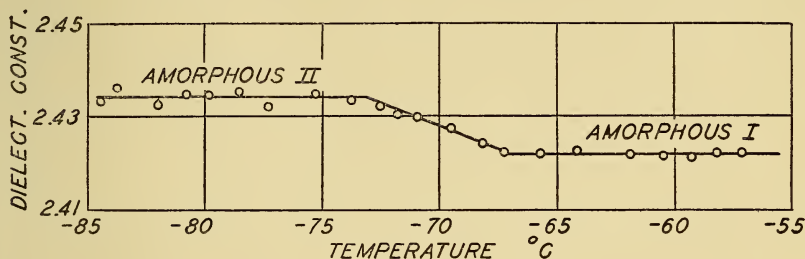


FIGURE 10.—Relation between dielectric constant of rubber hydrocarbon and temperature showing transition between amorphous I and amorphous II forms.

measurements were repeated at intervals of about a degree from -80 to -60 C.²⁸ The results of these measurements which are given in figure 10 show a transition between -73 and -67 C. This transition may be identified with the one in which form I of the amorphous rubber changes to form II.

The values for the dielectric constant given in the figure were corrected for temperature using the coefficient of expansion 0.00022 below -72 C and 0.00060 above this temperature.

WASHINGTON, July 24, 1934.

²⁸ A. H. Scott and A. D. Cummings, unpublished work.

