OPTICAL AND DIMENSIONAL CHANGES WHICH ACCOMPANY THE FREEZING AND MELTING OF HEVEA RUBBER.

By W. Harold Smith and Charles Proffer Saylor

ABSTRACT

The opacity of "frozen" rubber results from crystallization of the rubber hydrocarbons. At temperatures between $-15°$ and $-35°$ C rubber is known to freeze in a few hours. The rubber of *Hevea brasiliensis* and its sol and gel fractions were frozen at about $-25°$ C and maintained at that temperature for periods of 2 weeks to 3 months. Microtome sections were prepared and examined at controlled temperatures under a polarizing microscope.

When unstrained rubber was studied in this way, each section appeared to be composed entirely of irregular, strongly birefringent, crystalline particles, exhibiting no systematic orientation with respect to each other. The crystalline rubber usually melted between $+5°$ and $+16°$ C, a range which was similar to that observed previously with discrete crystals of rubber which had been prepared from solution. With the frozen specimens, however, the temperatures through which melting occurred were not the same in different pieces of frozen rubber, even when they had been prepared from the same material and frozen simultaneously. The crystals in adjacent microtome sections cut from any piece of frozen rubber melted alike, but crystals in sections from widely separated parts of the same piece sometimes exhibited real differences.

When rubber was frozen while strained, crystalline groups tended to be oriented with their high refractive indices parallel to axes of elongation. A curious consequence of this was observed in strips of rubber which were stretched and then frozen. As freezing progressed, the continuing orientation of rubber molecules caused the strips to elongate about 4 percent beyond the length previously attained by the stretching. The melting temperatures of strained, frozen rubber did not greatly differ from those of unstrained rubber, although they may have been slightly lower.

When rubber was frozen under pressure, the melting points of its crystals were higher than those determined without pressure, melting not being complete below 33° C. Vulcanized rubber did not crystallize at the temperatures used to produce crystals in unvulcanized rubber, but when a lightly vulcanized rubber was stretched before being subjected to low temperatures, notable amounts of freezing occurred.

CONTENTS

I. INTRODUCTION

At suitable low temperatures, unvulcanized rubber loses its elasticity and becomes hard and opaque. Similar changes frequently occur in baled rubber, which has been tightly compressed before shipment. It is said to be frozen or "boardy." The phenomenon has been studied by many investigators who have determined changes of volume [1] [1], softening temperatures [2], the effects of increasing time of storage at low temperatures [2], the influence of pressure during freezing [3, 4], and changes in heat capacity and entropy [5]. These effects have generally been ascribed to a form of crystallization, and X-ray diffraction powder patterns indicate that crystals are present in frozen rubber [6].

When total rubber is stretched, there are changes of volume and of heat content such as attend crystallization. With X-rays a crystal fiber pattern is obtained. It and the powder pattern obtained with frozen, compact rubber have been shown to indicate similar spacings and are assumed to be caused by the same type of crystal, [7] the differences being ascribed to conditions of orientation.

Dilute solutions of rubber hydrocarbon in ethyl ether yield small crystals of the hydrocarbon when they are subjected to temperatures between $-35°$ and $-60°$ C for several hours. [2] The optical properties and melting points of these crystals and their X-ray diffraction patterns [7] indicate their identity with the crystals in stretched and frozen rubber. Under the best conditions the crystals appear in spherulitic groupings, the individual needles in each spherulite having optical properties that closely approach those of a uniaxial crystal with negative elongation. [3] The crystals of sol rubber which we obtained, [4] melted between 9.5° and 11.0° C. Crystals of gel rubber [4] melted between $-2°$ and 14° C, but the melting ranges within this interval were not the same for all samples. Numerous observations have repeatedly confirmed the data. About 90 percent of the rubber in solution may be obtained as birefringent material at $-65°$ C. Temperatures between $-40°$ and $-50°$ C have been preferred, however, because better crystals are obtained in that range.

Thus crystalline rubber has been prepared in fundamentally different ways—by sustained low temperature, by stretching, [5] by compression, and by separation from solution at low temperatures. It

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The methods of purifying and of fractionating rubber hydrocarbon used in this work and of obtaining discrete crystals from solution have been discussed in this Journal, BS J. Research **10**, 479 (1933) RP544; **13,** 453 (1934) RP719.

[3] It is not improbable that the crystals are in fact biaxial, although, under the difficult conditions of observation, differences between β and γ, normal to the long axis of the needles, have not been detected.

[4] In the dark, in the absence of oxygen, rubber hydrocarbon can be separated into fractions which are soluble and insoluble in ethyl ether, Ether was used as a medium of separation in earlier work. A separation has been made with petroleum ether, chloroform, and with other solvents by different investigators. Whether the same molecular species exist in the two fractions when different solvents are used is not known. In accordance with common usage, the fractions separated with ether are here called sol and gel. The use of these terms does not imply that the sol does not form true solutions. The gel when dissolved may not have the same molecular structure as in latex or as in unmilled crude rubber. Presumably it is insoluble because it has a higher molecular weight than the sol, or a different structure. It is separated from the sol by its insolubility in the presence of light, and in the presence of natural antioxidants which normally protect crude Hevea rubber from oxidation. Light accelerates solvent action. When it is absent the gel remains undissolved for months. Of the structure of undissolved gel little is known. It may have weak crosslinkages connecting molecules which are similar to those in the sol. If that structure exists, the linkages are readily destroyed by light and air. It may possess strong cohesive forces, which are related to the existence of molecules of very long chains. By the breaking of the chains into smaller units these forces would decrease and the hydrocarbon become soluble.

[5] By the application of the term "crystalline" to stretched rubber, nothing is implied except that the atoms assume some form of orderly, spatial arrangement which produces optical effects and X-ray patterns which do not differ in general characteristics from those produced by ordinary types of crystals.
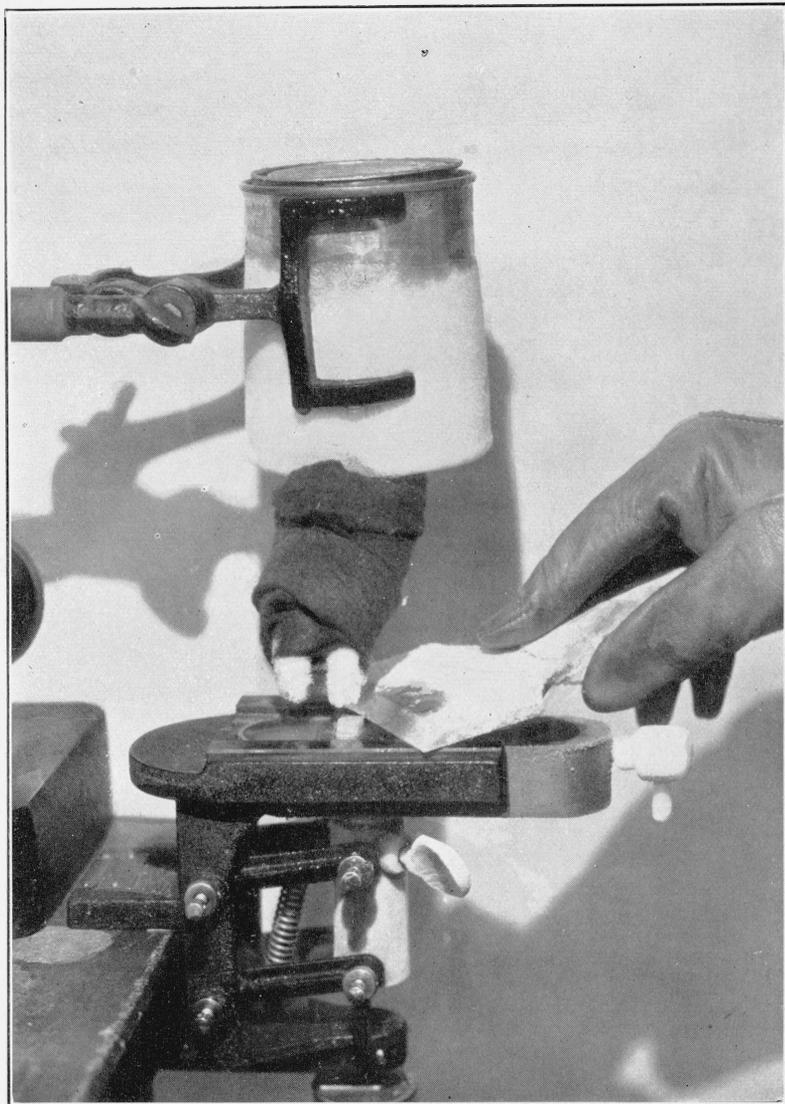
FIGURE 1.—*Apparatus for slicing frozen rubber hydrocarbon.*

The sample, held in the jaws of the microtome, is surrounded by cold acetone in which are chunks of solid carbon dioxide. From the tin can two streams of carbon dioxide vapor descend upon the surface of the sample and the slice after it is cut. The chisel-form knife is used on account of its rigidity.
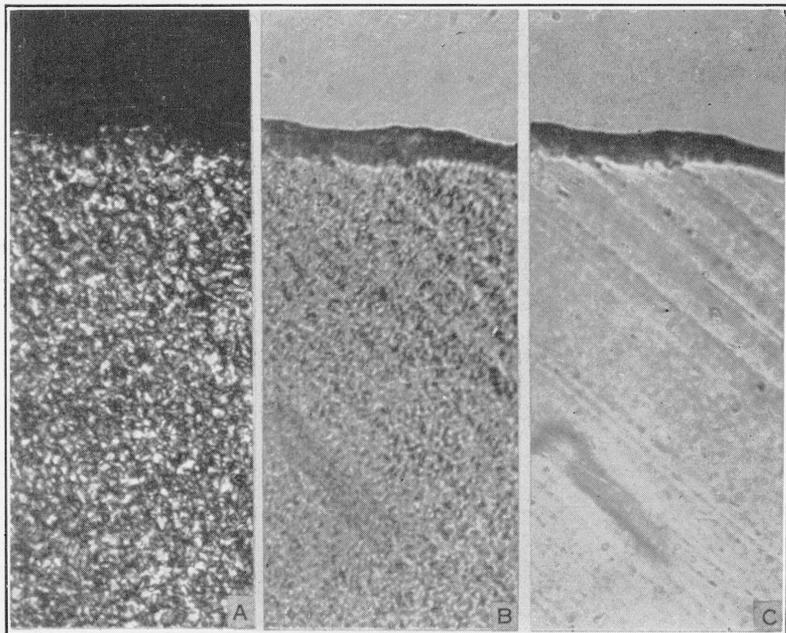
FIGURE 3.—*Photomicrographs of sliced total rubber hydrocarbon.*

A, view near the edge of a slice of frozen rubber. Temperature about 0° C. Crossed nicols. ×250. All brightness in the field is caused by the birefringence of crystal grains; *B*, same conditions except that polarizer has been removed. Random orientation of birefringent particles causes boundary effects by which crystal grains are seen superimposed upon faint streaks caused by the microtome blade; and *C*, sample at about 15° C. Polarizer removed. Crystals have melted and the grain boundaries between them have disappeared. Streaks caused by the microtome blade are relatively prominent. Between crossed nicols the entire field is black.

has not been clear whether, in each case, the crystals represented the same solid phase. Since we had previously used the polarizing microscope to determine the behavior of crystalline rubber grown from solution, we decided to extend the observations to frozen and stretched rubbers. By making microtome sections of frozen rubber, and its frozen sol and gel fractions, it was possible to determine some optical properties; and by observing the disappearance of birefrigence as temperatures rose, to determine melting points by a technic similar to that which had been used with crystals grown from solution.

II. PREPARING, SECTIONING, AND EXAMINING FROZEN RUBBER

The greater part of the work described in this communication was performed upon rubber hydrocarbon purified and separated into ether-soluble and ether-insoluble fractions by the methods previously described. The total purified but unseparated hydrocarbon, or its fractions, in the form of chunks 0.5 to 1 cm on a side, were subjected to a temperature of $-25°$ C for periods of 2 weeks to 3 months. At that temperature oxidation is suppressed. At the end of such periods the pieces had acquired the hardness and turbidity that is associated with the frozen state.

To obtain sections, the chunks of rubber were held directly between the jaws of a Spencer table microtome and slices made with a chisel-form microtome blade. In the first experiments the sectioning was performed out-of-doors on days when the temperature was $-10°$ C or lower. Such days were not common, however, and there was evidence that even these temperatures were not adequately low. In consequence, the accessories illustrated in figure 1 were adopted and operations transferred to the laboratory. The steel pin which normally supports the clamp was replaced by a pin of vulcanized fiber. The trough was cemented to the bottom of the clamp. It was filled with acetone and maintained at approximately $-70°$ C by adding small pieces of solid carbon dioxide. The can, filled with solid carbon dioxide, had two outlet tubes through which the cold vapors of carbon dioxide emerged, one being directly above the specimen and the other above the position at which the knife stopped after the section had been cut. The microtome blade and all accessory apparatus, brushes, tweezers, etc., were kept surrounded by solid carbon dioxide until the moment when they were to be used.

When all was in readiness, the sample previously held in a Dewar flask with cold acetone was transferred to the clamp. There it was largely immersed in cold acetone and was directly under the stream of cold carbon dioxide. A dozen or more slices were made to prepare a suitable surface and then the critical sections were made—as thin as the behavior of the sample would permit—each section being washed with a brush into the acetone as soon as it was cut. The heat capacity of the knife was such that its temperature did not rise appreciably during the cutting. Occasionally when slicing was difficult, it was thought expedient to interrupt the proceedings and rechill the knife. These sections and the acetone in which they were immersed were then poured into another vessel in which the low temperature could more easily be maintained until needed.

For microscopic study, sections were selected that were as uniform and undistorted as possible. One of them would be grasped with a pair of tweezers and by a quick movement transferred to a vessel containing an aqueous solution of calcium chloride at about −20° C to remove acetone. From this it was transferred to a similar solution in another vessel, placed upon a microscope cover glass, and then covered with another cover glass. The two cover glasses were grasped by the edge with another pair of tweezers and transferred to the wire support of the cold stage illustrated in figure 2.[6] Here the sections were studied under the microscope.
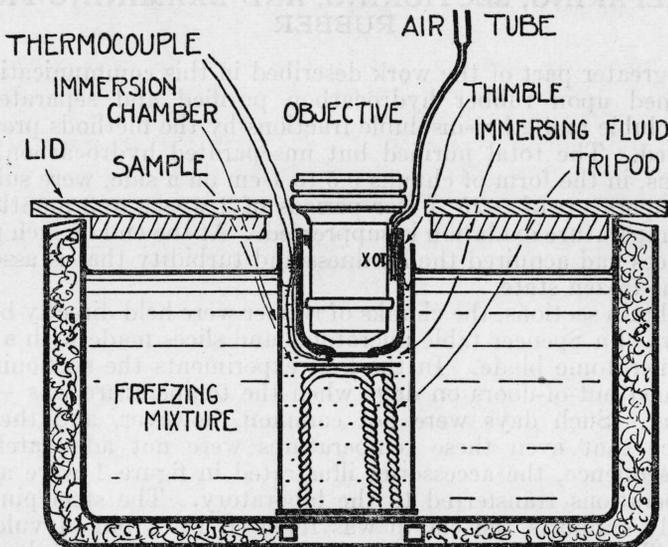

FIGURE 2.—*The simple cold stage.*

Two crystallizing dishes of slightly different sizes were chosen. Except for windows at the center of the bottom, the space between the dishes has been stuffed with rock-wool and the surfaces of the dishes silvered. The dishes are filled with a freezing mixture. Above the windows rests the immersion chamber made from a glass tube to the lower end of which is cemented a glass plate. This contains immersing fluid and a tripod of bent wire upon which the sample rests. The microscope objective dips into the immersing fluid, but is protected by a thimble made from a piece of constricted glass tubing, to the ground lower end of which is cemented a small cover glass. The thermocouple is held in place by being tied with thread to the thimble. The air tube of drawn copper tubing conducts a very slow stream of well-dried air into the space between the objective and the thimble and prevents the formation of frost. The entire apparatus rests upon the stage of a petrographic microscope.

In general, sections were easily cut. They could never be made as thin as desired because of a tendency to crumple, and a few specimens were so hard that successful cutting was difficult, but in most instances it was much like cutting across the end grain of a soft wood. It was vitally important, however, that the temperature be kept very low at all times. Otherwise, the outside of the sample would regain its rubberiness and sectioning become impossible. A warning was conveyed when the fresh slice adhered to the edge of the frozen block.

Sections made by the foregoing process were generally about 50µ thick. When viewed between crossed nicols they had a fine granular appearance, the individual granules being equidimensional and varying in diameter between approximately 5µ and 20µ. A photomicrograph is reproduced in figure 3 (A). It is plain, therefore, that despite

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[6] This stage and its equipment have been described in J. Research NBS **13**, 453 (1934) RP719.

the effort to secure sections as thin as possible, their thickness still
was several times the diameter of a particle. In consequence, com-
plete extinction of any part was uncommon. Instead, the granules
had high-order polarization colors, the order in each granule changing
with the synchronous rotation of the crossed nicols, as the vibration
direction of the first and last particles on any optical path became
parallel to the axes of the nicols. Boundaries between adjacent
granules were darkened by refraction effects. The entire preparation,
by being a complex mixture of small granules of high-order colors and
occasional granules in the position of extinction, all separated by dark
borders, produced between crossed nicols a general effect of grayness.

When the analyzer was removed, strong refraction effects at the
borders persisted, but the interference colors in each granule dis-
appeared. The section still looked very granular, but no noteworthy
changes occurred during rotation of the polarizer.

Thus, both under crossed nicols and with the analyzer removed,
the slices had properties consistent with a section composed of many
small crystals, strongly birefringent.

III. MELTING BEHAVIOR OF SECTIONS OF FROZEN
RUBBER

1. UNVULCANIZED SPECIMENS

In general, at temperatures well below the melting point of their
crystals, sections which had been prepared from unstrained compact
rubber crystallized at sustained low temperatures, exhibited no other
birefringence than the heterogeneous birefringence of numerous con-
tiguous granules. At places, however, where the microtome knife
had entered a pore in the rubber, then at the edges, or where the
section had crumpled slightly, there was an oriented birefringence
that had a definite relation to the direction of cutting. This bire-
fringence was similar to that which was previously noted [7] with crystals
of sol rubber grown from a solution. Such crystals yielded plastically
and acquired a new and strong birefringence when they were deformed
under the microscope.

In the present work, it was noted that this phenomenon could be
greatly reduced if slicing was performed at very low temperatures.
The earlier experiments in the sectioning of frozen rubber, undertaken
on cold days, out-of-doors, showed the effect rather prominently. In
the later work indoors at lower temperatures, well below the melting
point of the crystals, the rubber did not yield plastically and there
was no oriented birefringence. Defects in the cutting edge tended to
cause flow and hence new anisotropy. Such effects, however, were
not common and did not affect the granular crystallinity.

After the appearance of a slice had been well observed, residual
pieces of ice were removed from the freezing mixture, and by passing
an electric current through a coiled resistance wire immersed in the
bath, the temperature was caused to rise slowly. It was always
difficult to determine the precise temperature at which melting of the
crystals commenced. Since, except for changes in birefringence, there
was no evidence of the melting process until melting was nearly over,
and since the birefringence itself had complex causes, it was necessary
to observe minutely the first changes of the interference colors.
Nevertheless, it is certain that in nearly all cases some melting occurred

7 See footnote 2.

at temperatures slightly below the first changes that were noted. During melting, as long as the interference colors were those of superimposed birefracting granules and, therefore, composed of interference colors of high order, the changes were difficult to observe and analyze, but as melting neared its end, the polarization colors became much brighter, the transparency of the slice increased rapidly, and refraction effects at the interfaces between granules decreased. Finally, all birefringence related to the granules disappeared and genuine melting of the crystalline rubber was considered complete. Photomicrographs of a melting sequence are reproduced in figure 3. At this point some feeble birefringence that was related to the physical history of the sample persisted. The manner in which slices curled and wrinkled after the disappearance of granular birefringence indicated the persistence of strains. Distortions of the rubber, by the act of forming the original piece or of sectioning, showed as a general feeble birefringence. Often this did not disappear until well above the melting point (judged by loss of crystallinity) or until there was increasing mobility of the rubber, which is ordinarily so viscous that individual molecules are slow to change their relative positions.

In columns 2 and 3 of table 1 is presented a summary of the melting ranges of ether-soluble, ether-insoluble, and total rubber hydrocarbons as determined upon slices made from frozen compact samples.

The temperature ranges within which the frozen specimens melted are far from the same. The upper and lower limits vary, as well as the ranges of temperatures, and the data offer nothing which distinguishes total, sol, and gel rubber. Some specimens began to melt at 4.5° and others at 14°. In one specimen, melting was complete at 8.5° and in another at 15.6°. The temperatures do not agree precisely with those found for unstrained crystals of rubber as grown from ether solutions, principally in the particular that the ranges are greater and the reproducibility is less.

TABLE 1.—*Temperatures between which melting occurred*

Specimens sliced outdoors at about −10° C	Specimens sliced indoors at about −60° C	Specimens on cover glasses
SOL		
°C +9.8 to +12.1 (44.5)[a]	°C +12.1 to +15.3 (40.7) +6.0 to +8.5 +5.7 to +13.7	°C +12.1 to +15.0. +14.0 to +15.6.
GEL		
+5.7 to +15.3 (>20) +5.7 to +13.8 (>21.7)	+10.6 to +15.8 (18.8) −5.5 to +13.1 +4.5 to +14.5	+6.5 to +13. +5.7 to +15.3. +14.0 to +15.1. +13.5 to +14.9. +11.1 to +12.2.
TOTAL		
+8.8 to +15.3 (37.3)	+11.6 to +14.4 (17.3) +9.5 to +13.5 +4.5 to +10.5	

[a] Temperatures in parentheses are those at which birefringence of strain disappeared. The birefringences of strain and crystallinity originate in dissimilar causes and, in most cases, are easily differentiated under the microscope.

There were irregularities in the melting ranges of different specimens of frozen rubber, although they were prepared from the same material and were frozen simultaneously. Adjacent microtome sections, cut from any specimen of frozen rubber melted alike, but sections from widely separated parts sometimes exhibited real differences. In one experiment an oblong piece of purified total rubber was cut in two parts which were approximately of equal size, and cubical. The two parts were placed in separate bottles and frozen side by side. Samples were sliced from the sides which had been formed when the specimen was cut (B and C in table 2), and from the sides opposite to them (A and D in table 2). The data given in table 2 were obtained.

TABLE 2.—*Melting ranges of samples sliced from an oblong block*

Sample	First changes	Region of maximum change	Last persistence of granular birefringence
	°C	°C	°C
A	5.0	6.2 to 8.1	9.8
B	4.0	4.5 to 6.9	7.7
C	4.0	4.5 to 6.8	7.6
D	4.1	4.4 to 7.0	7.8
A (repeat)	5.3	5.7 to 8.1	9.0

2. SPECIMENS PARTIALLY VULCANIZED BY PEACHEY PROCESS

To compare the behavior at low temperatures of unvulcanized and vulcanized rubber, a specimen was surface-cured by the Peachey process. In this method active sulfur is produced at room temperature by the interaction of sulfur dioxide and hydrogen sulfide. The specimen was kept at $-25°$ C for several weeks, sectioned, and a photomicrograph between crossed nicols was made. (See fig. 4.) The inner or unvulcanized rubber has crystallized; the outer layers of vulcanized rubber are unchanged except at the edges, which are birefringent, the effect, it was at first supposed, of free sulfur. The edges however, lost their birefringence at temperatures slightly lower than those at which this occurred in the middle of the specimen. The surface therefore, consisted of unvulcanized rubber and not free sulfur. During the vulcanization process, sulfur dioxide probably diffused from the surface before hydrogen sulfide was applied.

IV. MELTING BEHAVIOR OF THIN FILMS OF FROZEN RUBBER

As an alternative method of observing the optical properties that appear with the freezing of rubber hydrocarbon, solutions of the forms of the hydrocarbon in ethyl ether (see footnote 4) were allowed to evaporate upon circular microscope cover glasses. By this means, very thin films were produced. As with the bulk samples, freezing was brought about at a temperature of about $-25°$ C during 2 weeks, after which the originally transparent films were noticeably murky. They were immersed in a solution of aqueous calcium chloride at about $-25°$ C, transferred to the cold-stage apparatus and examined between crossed nicols. The general appearance of these samples is represented by the finely grained portions of figure 5 and was very similar to that of most of the frozen and sliced samples.

When samples frozen from films deposited upon cover glasses were allowed to melt, their behavior was the same as that of sliced rubber, except that there were no birefringences caused by strain that persisted above the temperature of true melting. The melting points of these samples are given in column 4 of table 1. They do not differ significantly from those determined from sections of the bulk specimens.

In several samples of sol rubber prepared as films upon cover glasses, there were groups of striking spherulitic clusters. A photomicrograph is reproduced in figure 5. Since it was thought that this might indicate a partial recrystallization of the fine-grained portions, the sample was kept for 2 months at −25° C and examined, and then for 1 month at 0° C, with the hope that recrystallization would be accelerated. Another photomicrograph was made at the end of the 3 months. Since no differences could be observed in prints made before and after that period, it was evident that no growth had occurred. When the sample was allowed to melt, the rubber film was found to be much thinner at the region of the spherulites. The departure from a uniformly granular appearance, therefore, was caused by fewer nuclei which had formed per unit of area, and because the extent of each crystal in the plane of the film had been correspondingly larger.

The similar properties of frozen rubber in slices and of frozen thin films deposited from solution on cover glasses established the following points: No important changes in the material were caused by slicing. Solution of total, sol, and gel rubber hydrocarbon had not modified the manner of their freezing or the characteristics of the frozen material.

V. EFFECT OF STRESS ON THE FREEZING OF RUBBER

1. COMPRESSION

There is a form of boardy rubber which is observed at times in bales of crude rubber that have been tightly compressed before shipment. This is of interest because it usually persists in the frozen state at ordinary room temperatures or slightly above them, and in this respect is similar to rubber which was frozen for 8 years by van Rossem, and which melted at 37° to 38° C. No crystalline rubber with such melting characteristics has been observed in this laboratory, but the following experiment was performed with the object of producing it. A specimen of gel rubber was used, since in earlier work it had been shown that gel rubber is more resistant to an impressed force than sol. It was placed between two aluminum plates, about 6 mm thick, which were forced together as closely as possible by wing bolts, and immediately subjected to a temperature of −25° C. After 6 months, the specimen was sliced parallel to the axis of compression and examined. The slice had a marked directional birefringence with much extinction when the nicols were parallel and perpendicular to the compression axis. The direction of the highest index of refraction was normal to the direction of compression. Superimposed upon this directed birefringence there was a granular birefringence that tended to be parallel to it. By compression, the rubber molecules were oriented to positions which were approximately maintained during crystallization.

Both forms of birefringence disappeared in the temperature range 10.6° to 11.1° C. A birefringence, which, from its position, was no doubt related to the stresses of cutting, slowly disappeared with rising temperature but persisted up to 57.5° C.
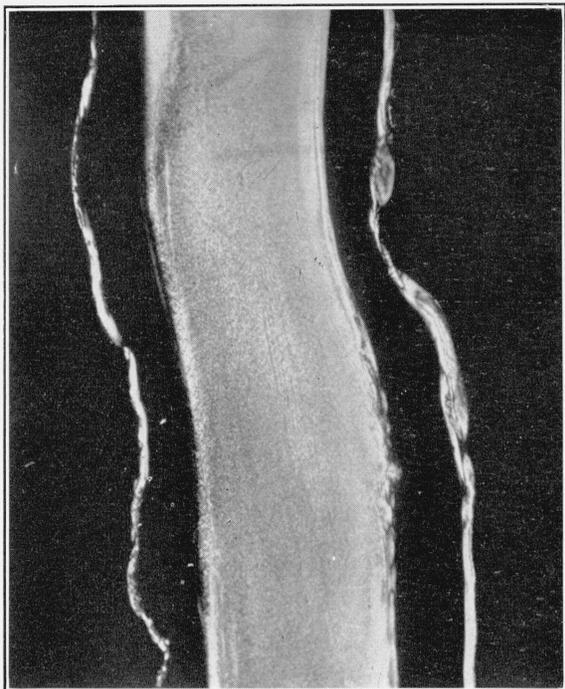
FIGURE 4.—*Strip of total rubber, vulcanized, frozen and sliced.*

Crossed nicols. ×25.

A strip of rubber was vulcanized by the Peachey process, and then frozen. In the center where the vulcanizing gases failed to penetrate, the rubber has crystallized in the usual way. In two zones on each side of the center zone, where vulcanization was most complete, there has been no crystallization. In thin films along the surface from which it is supposed that the sulfur dioxide diffused before application of hydrogen sulfide, vulcanization has not been sufficiently complete to prevent freezing.
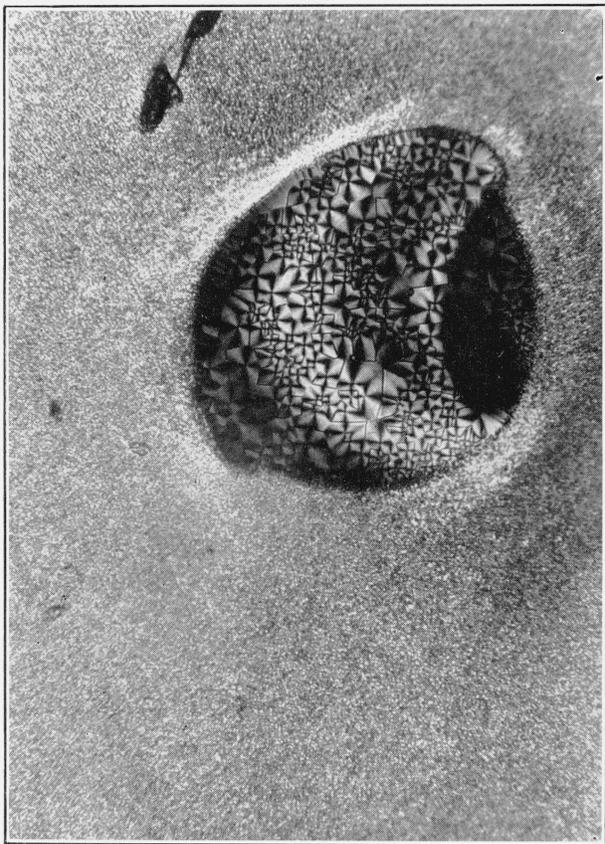
FIGURE 5.—*Sol rubber deposited on cover glass and frozen.*

Crossed nicols.   ×75.

Fine grained portions represents the usual appearance of such samples.   The marked spherulitic tendency has occurred in a region where the film of rubber was thinner so that fewer crystal nuclei formed per unit of area.

Another slice was cut from the frozen material, at a direction 90 degrees from that at which the first slice was made. In this slice, also, the direction of highest index of refraction was normal to the direction of compression. There was no evidence in either slice of granular, crystalline rubber which persisted above room temperature.

Between aluminum plates the effects were more largely those of distortion than compression. To restrict conditions so that the effects would be primarily those of compression, the following experiment was conducted. A sample of total rubber about 1 cm³ in volume was placed in a hole 1 cm square in a steel block. Steel pistons which closely fitted the cavity were placed above and below the specimen, and the whole was compressed to about 1,000 atmospheres between the jaws of a 6-inch screw clamp. After remaining at −25° C for 2 weeks the specimen was examined. A cubical block of rubber had been formed. It was very hard and exceedingly difficult to slice. Incipient melting was observed at 6.9° C, but the birefringence of the crystalline rubber had not all disappeared until 33° to 34° C. was reached. It was difficult to determine the temperature more exactly as there was sufficient birefringence of strain to obscure that of the granules. This birefringence persisted to 41.3° C. The result is in accord with observations by others [2] of the melting of crude rubber frozen for several years without compression or for several weeks under it.

2. EXTENSION

All available evidence indicates that the molecules of rubber are very long. In the course of some observations which were made to test the orientation of birefringent colors by directed strain, a curious effect was observed that probably had its origin in this excessive magnitude of one dimension [8]. For this work strips of crude rubber about 5 mm wide and 2 mm thick were used. They were stretched different amounts and nailed to a board. The elongations varied between 20 percent and the point at which rubber greatly resists further extension. The stretched samples were placed in a cabinet at −25° C. During a few hours, they increased in length about 4 percent, with the exception of specimens stretched to the point at which further extension was greatly resisted. With them the secondary extension was feeble. The strips rose to form an arc between the points of attachment. The secondary extension was observed with smoked sheet, pale crepe, milled pale crepe, and with smoked sheet that had been swelled slightly by benzene, to remove strains or orientation caused by processing and from which the benzene was subsequently evaporated. The elongation does not occur with unstretched rubber. Stretched vulcanized rubber bands increased in length slightly when kept for several days at −25° C. This is interpreted as an instance in which stretching has fostered the freezing even of a vulcanized rubber. Samples of the product from the reaction between dichloroethyl ether and sodium polysulfide, a Thiokol, also exhibited a secondary extension after 2 weeks at −25° C, whether tested in the unvulcanized or the vulcanized condition.

The piece of smoked sheet that had been swelled with benzene, and from which the benzene had evaporated before the stretching and freezing experiment, was allowed to remain at −25° C for 2 weeks. It was then sliced, and the sections observed microscopically. They were smooth and very strongly birefringent, the direction of highest

index being parallel to the axis of elongation. The multitude of bire-fringent granules usually observed with the sections of frozen rubber was not present. When the temperature was allowed to rise, slight changes in the degree of double refractions were first observed at −2° C. At +3° C melting (judged by changes in birefringence) was proceeding rapidly, and at +6° C, after a marked deformation caused by the retraction of the stretched piece, it was complete.

The secondary elongation of stretched rubber may occur at approxi-mately 0° C and does not require freezing temperatures as low as −25° C. It always disappears, however, on warming to about 10° C and the rubber resumes its previously stretched condition. This indicates that the elongation is associated with crystallization. The following explanation is suggested.

When stretched or compressed, rubber is forced to flow, its molecules are oriented parallel to the direction of elongation, and when freezing begins a crystal axis is already established. As crystallization pro-ceeds, molecules enter the spacing, the rubber hardens, and presently when a tendency to elongate is asserted, the stresses that produced stretching are neutralized. Then, as more molecules move into the crystalline arrangement, the spacings at right angles to the stretch become less, the long directions of the molecules become more strictly parallel to the axis of stretch, and the strip elongates. Stretched rubber contracts when heated, the well-known Gough-Joule effect. The density of rubber which is chilled while stretched is higher than that of rubber which is chilled without stretching [9, 10] and since the chilling of the stretched rubber is accompanied by an elongation, it is necessarily accompanied by a lateral contraction and a decrease of volume.

When rubber is stretched or compressed there appears to be a move-ment of whole, or parts of, molecules by compulsion. When a strain orients the molecules so that they are approximately parallel to each other, the movement permits an adjustment of positions so that the rigid spacings necessary for an X-ray diffraction fiber pattern are possible. When stretched, the highest refractive index and, when compressed, the lowest index is parallel to the direction of the applied force. An increased index is an indication either of changed spacing or of the orientation of molecules so that their long directions are parallel to the increased index. In the case of rubber, it is evident that the latter phenomenon predominates.

The conditions of melting of stressed and frozen rubber are briefly summarized in table 3.

TABLE 3.—*Temperature of melting of specimens frozen under stress*

Kind of rubber	Mode of applying stress	Conditions of freezing	Temperature of melting
			°C
Gel	Compressed between aluminum plates	6 months at −25° C	10.6 to 11.1.
Total	1,000 atm applied with piston	2 weeks at −25° C	6.9 to 33 or 34.
Crude	Stretched 20 percent (secondary increase in length occurred).	2 weeks at −25° C	3 to 6.ᵃ

ᵃ Some indications of incipient melting appeared as low as −2° C.

VI. CRYSTALLINITY OF FROZEN AND STRETCHED RUBBER

The granular birefringence of a frozen specimen makes it appear that crystallization has gone far toward completion, but determinations of the density of frozen rubber, as reported in the literature, indicate that rubber when frozen for comparatively short periods of several weeks may be incompletely crystallized. This fact may be related to the varying melting points of frozen specimens prepared under similar conditions. The density of amorphous rubber is approximately 0.92, whereas that of frozen, unstretched rubber has been reported by several investigators as about 0.95. When stretched and frozen, that is, under conditions which are more favorable to the growth of crystals than when rubber is frozen unstretched, the density increases, and the highest value reported for rubber so treated 0.965, was obtained by Kirchhof [9] and was duplicated by Lotmar and Meyer [10]. These authors have calculated from X-ray data that the density of completely crystallized rubber should be 1.02, if there are eight isoprene groups in the monoclinic unit cell. Assuming that 1.02 represents the density of rubber which is completely crystallized, the approximate amount crystallized in frozen rubber would be 30 percent and in stretched frozen rubber 45 percent.

When a block of rubber crystallizes the medium in which crystallization occurs is, of course, the rubber itself. The ease with which crystallization is initiated is surprising, in view of the low fluidity of this medium. It is probably quickly retarded because chilling must lower appreciably the mobility of molecules, which are admitted to be large. Then too, the mobility necessary for the intimate alignment of molecules in a crystal lattice must be quickly diminished as parts of very long molecules enter into crystalline structures and ultimately impede all further movement. For these reasons, it was hoped that crystallization from a solution of ethyl ether, a medium more mobile than rubber, would induce the maximum number of molecular species to become crystalline. This has not been the case, since when this method is used there is no evidence of crystals which exist unchanged at 25° C or higher. (See footnote 2.) Our present knowledge of the crystallinity of rubber appears to be far from complete, and deductions drawn from it, therefore, seem subject to reserve.

No doubt exists about the crystallinity of many complex organic compounds, albumin and some vitamins, for example, but there is a curious reluctance by many scientific authors to concede the crystallinity of rubber. The word crystal is frequently used in quotation marks when rubber is discussed, or it is indicated that its use is justified because others have employed it. However, rubber assumes a crystalline state with great facility. This is accomplished merely by stretching it, and its crystallinity is confirmed by the X-ray diffraction patterns of stretched and frozen rubber, which indicate the same structure in each. Studies by Thiessen and Wittstadt [11] indicate that crystallization during stretching is influenced by pressure, and that it may be reconciled with the normal process of crystallization which is accompanied by the formation and growth of nuclei.

The superficial characteristic of a crystal, that which attracts the eye, is external symmetry, the regularity and planarity of the bounding surfaces. This external symmetry is only an indication, however,

of a more fundamental symmetry according to which its atoms and molecules are arranged. Crystallinity is defined most rationally in terms of those properties which bring about the symmetry of surfaces. A certain minimum number of atoms or molecules grouped together in a definite pattern is a unit cell. It is the smallest part of a crystal that can contain all spacings and orientations that characterize the crystal, as a whole. In an ideal or perfect crystal every part would consist of elements like the unit cell, all strictly parallel to each other and displaced with respect to each other by distances that are precise multiples of the length of a side. From this there results an anisotropy of physical properties. The orderly arrangement causes the diffracted energy of X-rays to follow, by interference, definite paths. With these criteria, crystallized rubber is in complete accord. It has been repeatedly demonstrated that rubber when crystalline produces a characteristic diffraction pattern, which cannot be caused by liquid crystals, as these do not form X-ray crystal patterns.

Usually the unit cell of a crystal contains several molecules. In some substances there are repeated atomic groupings within the molecule. Since these groupings may respond to X-rays as though they were molecules which compose a unit cell, it may happen that the unit cell is much smaller than a single molecule. In rubber the molecule varies in size, but is long and by some evidence, usually over 500 times as large as the unit cell. Consequently, a rubber molecule may possibly be crystalline in one part and amorphous in another. Perhaps it may simultaneously belong to several different crystalline particles and several groups of amorphous matter. Certainly the crystallinity of rubber is of an unusual type and differs profoundly from that of a substance like sodium chloride. But each yields a characteristic X-ray diffraction pattern.

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