U.S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP719

Part of Journal of Research of the National Bureau of Standards, Volume 13, October 1934

ETHER-INSOLUBLE OR GEL RUBBER HYDROCARBON, ITS SOLUTION, CRYSTALLIZATION, AND PROPERTIES

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ABSTRACT

A method was previously described for purifying the hydrocarbon in Hevea latex and separating it into two fractions by extraction with ethyl ether. The present paper deals with the insoluble (commonly called the gel) fraction, of which about one-fourth of the total hydrocarbon is composed. Presumably the gel is insoluble in ether because of a complex structure and high molecular weight. When traces of oxygen are present, it becomes soluble in suitable organic liquids. The dissolved gel was crystallized from a dilute solution at low temperatures, and the crystals were examined. The refractive indices, $\epsilon=1.535$ at $-5°$ C, and $\omega=1.583$ at $-5°$ C, are very close to the values previously found for crystals of ether-soluble hydrocarbon. Melting temperatures, which lie somewhere between $-5°$ C and $+14°$ C, depend upon the history of the sample and indicate that the crystals are solid solutions, probably of many closely related components. As witnessed by micromanipulation below their melting temperature, the gel crystals contrast sharply in elasticity with the crystals of sol rubber. The former appear to be elastic, the latter are plastic. Also, after the loss of birefringence indicates that the crystals are melted, the gel is more resistant to deformation than the sol. Crystals of ether-soluble rubber have been vulcanized below their melting point by means of sulphur chloride. The shape of the crystals remains unchanged, but birefringence, the optical evidence of crystallinity, disappears, and their resistance to deformation is increased.

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I. PREPARATION AND CRYSTALLIZATION OF GEL RUBBER HYDROCARBON

By W. Harold Smith

1. PREPARATION OF THE GEL

A method of purifying and crystallizing ether-soluble rubber hydrocarbon was described in an earlier paper in this journal.[1] The same

[1] BS J. Research 10, 479(1933); RP544. In the earlier paper the portions into which rubber is separated by ethyl ether were called the ether-soluble and the ether-insoluble fractions. To conform to common usage, the fractions will also be called sol and gel, and these terms refer specifically to fractions which have been purified and separated as described in the earlier paper. The use of these terms does not imply that the sol does not dissolve to form a true solution at the temperature and concentration which prevail during crystallization. They are used as names and do not necessarily refer to the sol and gel states of matter as defined by colloid chemistry.

procedure for purifying the hydrocarbon and separating it into two fractions was followed in the preparation of the insoluble or gel fraction, the properties of which are the subject of this paper. The method of purification was not merely another procedure for removing the impurities from rubber hydrocarbon, but, as stated in the earlier paper, it also "sought to maintain unchanged the structure of rubber hydrocarbon and to permit a sharp separation of the ether-soluble and insoluble fractions."

The latex which has been used was, in part, obtained from Harry L. Fisher of the United States Rubber Co. Through the courtesy of the U.S. Department of Agriculture, latex has also been obtained direct from the plantation on the north shore of Haiti. Before the trees were tapped, the area surrounding the intended incision was carefully cleaned. After tapping commenced, the trees were tapped once each day, the latex from the first two tappings was rejected, and that obtained on the third day was put into clean glass bottles, which were filled completely after the addition of a little ammonia as stabilizer. The latex was immediately shipped to this Bureau and stored at a temperature maintained between 0 and 2° C.

Briefly, the rubber hydrocarbon was prepared as follows. Latex of *Hevea brasiliensis* was dialyzed and the protein removed by tryptic digestion in the presence of natural antioxidants, which had been extracted from crude rubber and which were added to the latex at intervals. The purified hydrocarbon was separated into two fractions by thorough continuous extraction with ethyl ether in an apparatus constructed entirely of glass and similar to that described by Pummerer, Andriessen, and Gündel.[2] Oxygen in the apparatus was displaced by a continuous stream of nitrogen of 99.8 to 99.9 percent purity. The nitrogen was under slight pressure, and to facilitate the exclusion of air all joints were covered with a film of glycerol. The rigid exclusion of oxygen is necessary because the presence of even a minute amount of it causes the gel to dissolve slowly and makes a sharp separation impossible. It is advantageous to have an antioxidant in the solution during the extraction, and either the natural antioxidants or phenyl-β-naphthylamine was used. With these precautions against oxidation, it was possible to separate the rubber into the two fractions rather sharply.

The manner in which oxygen causes the insoluble gel fraction to become soluble is not understood. Oxygen adsorbed by the rubber, or a trace of an oxygen addition product of rubber such as that formed by auto-oxidation, or a trace of acid formed by oxidation may peptize the gel in suitable organic solvents. In a typical experiment with 50 g of total rubber the extraction was continued beyond the point at which it is normally considered to be complete. One week of continuous extraction was required. The final extract was removed, a fresh supply of ether, which had been previously saturated with nitrogen, was added to the rubber, and the extraction was continued for 72 hours longer. The extract contained 20 mg of rubber, or 0.04 percent of the original sample. The swollen gel rubber which remained after extraction was desolvated with acetone, and residual ether and acetone were removed in vacuo. If it was necessary to preserve the gel fraction for an interval, it was cut into suitable small

[2] Ber. Deut. Chem. Ges. **60B**, 1583(1928).

pieces and allowed to remain for 24 hours in an acetone solution of the natural antioxidants or of phenyl-β-naphthylamine. The acetone was removed in vacuo, and the gel was placed in a desiccator which was evacuated and filled with nitrogen several times. Before the gel was put to any use, the antioxidants were removed by extraction with acetone.

In the extraction of numerous samples of latex, about the same proportion of gel, 25 percent of the original hydrocarbon, was always obtained. Other observers have reported very divergent proportions, ranging from 0 to 70 percent, in rubber of various kinds extracted with different solvents.

The quantitative determination of sol and gel in the total rubber by extraction with ether must be conducted in the absence of oxygen. A small Soxhlet extractor, suitably modified to allow a continuous stream of nitrogen to pass through it during the extraction, was used. The upper outlet of the extractor, above the condenser, was connected to a flask through which an auxiliary stream of nitrogen was constantly passed and the outlet of the flask consisted of a mercury bubble trap. To avoid prolonged extraction, samples weighing about 1 gram were used. They were first extracted with acetone to remove antioxidants and the weight of the sample was corrected for acetone-soluble material. After the excess acetone was siphoned from the rubber, ether was added to remove residual acetone and immediately siphoned away. Sufficient ether was added to cover the rubber, the flask was cleaned and filled with ether, the apparatus assembled, and nitrogen was passed through it. The rubber was allowed to swell to a maximum before the extraction with ether was started. During the extraction, fragments of the swollen gel tended to become detached and to be swept out with the extracted material. The rubber was therefore placed in a container of no. 100 platinum gauze of sufficient size to permit the rubber to swell to its maximum volume. The approximate time necessary to extract the soluble fraction was determined on a separate sample by weighing successive extracts. The last traces of soluble material were removed with difficulty from the swollen gel. When the extraction was complete the ether was removed from each fraction in vacuo and the residues were dried in vacuo to constant weight. Each fraction was corrected for ash.

The mean of six determinations, which were obtained after some familiarity with the details of the method was acquired, indicated a sol content of 75.3 ± 0.8 percent and a gel content of 24.2 ± 0.7 percent. Probably a little gel was dissolved during the extraction and the results represent only an approach to the true value.

2. SOME PROPERTIES OF SOL AND GEL

Some investigators who purified rubber by methods other than the one which is used in this work, noted differences in the soluble and insoluble fractions. The fractions of rubber, as separated in this investigation, show marked differences. The sol can be stretched or otherwise deformed more than the gel and by smaller forces, and it can be readily masticated on a rubber mill. The gel is tough, resistant to mastication, and may be described as gristly. No quantitative study of the physical properties of the unvulcanized fractions has yet been made.

A sol-gel reversible transformation has been attributed to rubber on the assumption that a single chemical compound is concerned. The data which follow on the melting points of crystals obtained from the gel after it has become soluble in ether indicate that the soluble gel is not the same hydrocarbon that is in the ether-soluble fraction of total rubber hydrocarbon. Consequently the gel and sol, as these terms are here used, are not merely different phases of the same molecular species.

Porritt [3] observed that gel was formed in a rubber solution which was sealed in glass and exposed to sunlight. When the container was opened the gel became soluble. A similar effect in a solution of ether-soluble rubber has been noted by the author. (See footnote 1.) There is no evidence that the gel formed in the sealed tube is identical with that left after the original extraction of the rubber with ether. The conversion of the sol to a gel has not yet been investigated by an examination of the crystals.

3. DISSOLVING AND CRYSTALLIZING THE GEL

The gel was dissolved in an organic solvent by permitting the entry of a little air and, depending upon the amount of air used, temperature, and other conditions, the time required completely to dissolve the gel could be varied from a few weeks to several months. Ethyl ether, ethylbenzene, or toluene was generally used because it remains liquid under the conditions of crystallization. Inorganic constituents of the latex, which concentrate in the gel when the soluble fraction is extracted, remain undissolved by the organic solvent.

It is evident from the preceding discussion that the gel fraction is separated from the sol by its insolubility in ethyl ether and that subsequently it is dissolved in ethyl ether. Organic compounds of high molecular weight tend to be less soluble in the inert solvents than their simpler homologs. The solution of the gel probably contains the products of disaggregation of a more complex structure which exists in the insoluble gel.

Suitable conditions for the growth of crystal nuclei of ether-soluble rubber hydrocarbon and the establishment of their crystal habit were discussed in the earlier paper. (See footnote 1.) The same technic was used to obtain crystals of the dissolved gel fraction. When hydrocarbon solvents were used, they were customarily diluted with anhydrous ethyl ether before crystallization of the rubber, as this medium has greater fluidity and therefore insures greater mobility of the nuclei than hydrocarbon solvents alone. One volume of a hydrocarbon solution of rubber diluted with four volumes of ethyl ether is suitable, but these proportions may be varied considerably. For studies of the optical properties and melting point, the dissolved gel hydrocarbon was crystallized from ethyl ether or a mixture of ethylbenzene and ethyl ether.

The particles which appeared in the solution at low temperature were birefringent under crossed nicols, and nodules formed on the walls of the container when proper supersaturation existed in the solution, a behavior similar to that observed with ether-soluble rubber hydrocarbon. Between 90 and 95 percent of the rubber in the solution separated as crystals.

[3] India Rubber J. 60, 1161(1920).

The optical properties of the crystals were studied with deposits made in the special cell which was described in the earlier paper. (See footnote 1.) The following technic was developed to permit the study of several crystalline deposits obtained simultaneously from a single solution. A vertical glass support was provided with glass brackets to hold a succession of cover glasses and the support was placed in a 12-in. test tube which contained the solution of gel rubber. Two cover glasses were placed on each bracket to prevent the deposition of crystals on the under side of the upper cover glass—the one which was subsequently observed. After crystallization was accomplished, the ethereal solution was removed at low temperature through a siphon and the crystals were washed with acetone at a temperature below the melting points of the crystals, which was then similarly removed. After washing with cold acetone several times, a cold solution of calcium chloride was poured into the tube. A cover glass was quickly removed from the rack when required and placed in a cold solution of calcium chloride under the objective of a microscope.

A supplementary method of obtaining crystalline rubber has been observed. If a lump of pure sol rubber, or of gel rubber which previously has been made soluble, is placed in cold ether and the temperature maintained at −55 to −60° C, crystals are produced. The solubility under these conditions is sufficient to permit a continuous deposition of crystalline hydrocarbon. This technic is commonly used by the crystallographer and it may offer a means of producing crystalline rubber in greater quantity than can be readily obtained from previously prepared solutions. Aside from establishing the crystallinity of the deposits by their appearance when viewed between crossed nicols, no detailed study of their optical properties was made.

The effect of a trace of trichloroacetic acid or of a mineral acid in a solution of total rubber is well known to rubber chemists. The viscosity of the solution is lowered and a profound change occurs in the structure of the rubber. Sunlight accelerates these changes. Gel rubber hydrocarbon was dissolved in ethylbenzene which contained 0.05 percent of trichloroacetic acid. When it was completely dissolved the acid was removed, and the rubber hydrocarbon in a solution of suitable concentration was subjected to the conditions for obtaining crystals. A deposit was obtained which was found to be crystalline when viewed between crossed nicols. The initial products of disaggregation can therefore be crystallized.

4. COMPOSITION OF THE GEL CRYSTALS

Crystalline hydrocarbon obtained from the dissolved gel fraction was analyzed by Henry J. Wing to determine the ratio of hydrogen to carbon. The apparatus described in Research Paper RP544 was used and the ratio was established by the criteria discussed in that paper. It was necessary to heat carefully when removing traces of solvent from the rubber. To effect this, the sample was placed in a small glass chamber and heated to 100° C by a glycerol bath. A low pressure was maintained by a mercury vapor pump. It was observed that the ether-insoluble material obtained by crystallization was more susceptible to decomposition, as indicated by discoloration and an odor of oxidation products, than ether-soluble rubber obtained similarly. Attempts to prepare suitable material for combustion often

failed. However, three determinations were made in which the technic was satisfactory. The ratios of hydrogen to carbon were 0.1346, 0.1346, and 0.1347, respectively and corresponded to that required by a compound of formula C_5H_8, on the assumption that the compound does not have more than 100 carbon atoms in the molecule.[4]

It will be observed in the section on the solubility and melting points of the crystals obtained from dissolved gel, that there is continuous melting of the crystals over certain ranges of increasing temperature. This suggests the possible presence of a solid solution. If a solid solution exists in the ether-insoluble fraction before it becomes soluble, the solid solution might consist either of rubber polymers of C_5H_8 of varying complexity; or it might consist wholly or in part of molecular species in which the ratio of hydrogen to carbon differs slightly from C_5H_8. The evidence favors the former condition. Should the latter exist, the variation in the composition of the crystals must be very small and it is doubtful whether analyses by combustion can disclose it.

II. MICROSCOPICAL STUDY OF THE DISSOLVED AND CRYSTALLIZED GEL

By Charles Proffer Saylor

1. HABIT AND APPEARANCE

The same apparatus [5] as previously described was employed to observe the growth of the crystals and to learn their habit. This apparatus consists essentially of a petrographic microscope, the tube of which is used in an inverted position, a special dewar flask so constructed that it has plane windows at the bottom, a cell which has plane windows at top and bottom, and tubes for emptying and filling. The cell holds about a milliliter of fluid. In addition to these, there are various structural parts and devices which provide illumination and temperature control. For further details, reference is made to the earlier article.

We frequently watched the crystals in the process of forming by filling the cell with a solution of the gel,[6] keeping it at −50° C for about 1 hour, cooling to −70° C for a few minutes, and then transferring it to the dewar flask for microscopical examination at low temperatures. Here for several hours it was maintained at approximately −50° C. Finally, when the cell was observed between crossed nicols, bright birefringent particles began to appear. They remained suspended in the fluid and moved with the convection currents, until, growing in size and number, they clustered and settled. Finally, with some amorphous material, they covered the bottom of the cell. The crystalline masses formed in this way were not satisfactory for general observation or the determination of properties. For the purpose of shortening the time necessary to produce crystals, the amount of supercooling had been large. Too many nuclei formed, the individual crystals were too small, and the complexity of the groups obscured their component parts.

[4] BS J.Research **10**, 492(1933);RP544.
[5] Reference 1, p.484–5.
[6] Smith prepared all of the solutions and most of the crystals whose properties are reported in this section.

Better crystals resulted when the apparatus and cycle of temperatures employed for the ether-soluble fraction (reference 1, p. 483–4) were again used. In this procedure the milder supercooling (to −65° C instead of −70° C) and the greater freedom from convection currents seem to cause formation of fewer nuclei and therefore fewer and better crystals. Even when this method was closely followed, the crystalline clumps were much less reproducible than were those obtained from the ether-soluble rubber hydrocarbon. Most frequently the nodules were badly ordered groups of birefringent particles, the individual shapes of which could not be discerned. This appearance is represented in figure 1(A). Occasionally, when only a very small part of the rubber in solution had crystallized over a long period, branching groups of needles were obtained. Sometimes there were spherical clusters formed from numerous needles radiating from a center. These, which were rarely obtained, had the same appearance as the crystals of ether-soluble hydrocarbon which were previously illustrated.[7]

2. OPTICAL PROPERTIES

A preparation in which the slender crystals radiated from a center was used for the determination of refractive indices. Needles projecting slightly from the group were used for the actual determination because they permitted greater accuracy. The liquids which matched their indices appeared satisfactory for the main body of the clumps, but the sensitivity was greater with the projecting needles on account of their isolation. The refractive indices at −5° C for light vibrating parallel and normal to the long directions of the needles were found by immersion, the method of central illumination serving as a criterion of the relation between the indices of the crystals and the immersing liquid. The immersion liquids were concentrated aqueous solutions of potassium mercuric iodide, diluted with acetone progressively until the indices of the crystals were matched. An Abbe refractometer was used to determine the indices of the immersion liquids at −5° C. As in the previous paper, and with the same reservations, the index for light vibrating parallel to the long direction of crystals has been designated as ϵ. The values

$$\epsilon = 1.533 \text{ at } -5° \text{ C}$$
$$\omega = 1.583 \text{ at } -5° \text{ C}$$

were so close to those previously reported for the crystals of ether-soluble hydrocarbon

$$\epsilon = 1.535 \text{ at } -5° \text{ C}$$
$$\omega = 1.583 \text{ at } -5° \text{ C}$$

as to lie well within the probable error of the determination. The close similarity in the optical properties of the crystals obtained from solutions of the ether-soluble and the gel portions of the rubber does not necessarily indicate identity. Members of the normal paraffins, the normal saturated higher fatty acids, and many other series show similarly close refractivities. Other properties indicate that the two fractions of rubber differ in molecular composition, but it is probable that the molecules are similarly oriented in the crystals of both and that both belong to the same homologous series.

[7] See figure 4, reference 1.

3. SOLUBILITY AND MELTING POINT

When crystals of gel rubber in contact either with the ethylbenzene-ether mother liquor, or with ether that has replaced it, are observed as the temperature slowly rises from −50° C, no change is seen until a temperature between −40 and −30° C is reached. Then through a few degrees the crystals swell with loss of birefringence, and the swollen jelly dissolves at a temperature a degree or so higher. The hydrocarbon has been so changed by or during its solution in ethylbenzene that the form which would not dissolve during continuous extraction with ether for weeks at ordinary temperatures now dissolves quickly at −35° C.

To determine the melting point of the crystals of dissolved gel rubber, many successive preparations were made. The solvent was rinsed out with numerous changes of acetone, and the melting process observed either while the crystals were immersed in acetone or after the acetone had been replaced by ethyl alcohol or a strong aqueous solution of calcium chloride. Melting was determined by the disappearance of birefringence as the temperature was permitted to rise. The melting points as found were entirely discordant. The lack of uniformity persisted when samples were prepared with scrupulous care to make them identical and when the conditions of melting were as nearly as possible the same. For this reason it was necessary to examine larger numbers of samples than was convenient with two cells of the form described. Further, it was desirable to compare the possible effect of environment upon the melting point by employing samples known to be identical, preferably by the use of several portions crystallized simultaneously from the same solution. To do this crystals were grown upon stacks of microscope cover glasses in the way described on page 457 and studied with the simple form of microscope cold stage, illustrated in figure 2.

Using this apparatus, in which the temperature rose as the liquid phase in the freezing mixture became diluted, the melting points of different portions from the same crystallization were found to check within a few tenths of a degree. This variation in the recorded temperatures may be explained by difficulties in accurately observing the beginning and end of the slow melting process. The clusters of needles are complex, which makes it difficult to know exactly when melting begins and when it is entirely ended. The elements of a cluster melt independently. They are protected from one another by the surrounding liquid and by their own resistance to movement after melting. It is possible to observe, therefore, a range of melting not merely for the entire cluster but even for some of the individual crystals of which it is composed. By examining cover glasses upon which crystals had been deposited simultaneously from the same solution, it was found that the crystals of dissolved gel rubber melt at a little lower temperature when they are immersed in acetone than when covered with an aqueous solution of calcium chloride, but that the melting interval is greater when they are immersed in the aqueous solution. Ethyl alcohol produces intermediate results. It appears from this that although acetone and alcohol are not rubber solvents, small amounts of them are dissolved by the gel rubber at temperatures above its melting point. The melting point observed when the crystals are covered by the aqueous solution must therefore be looked upon as the best value.

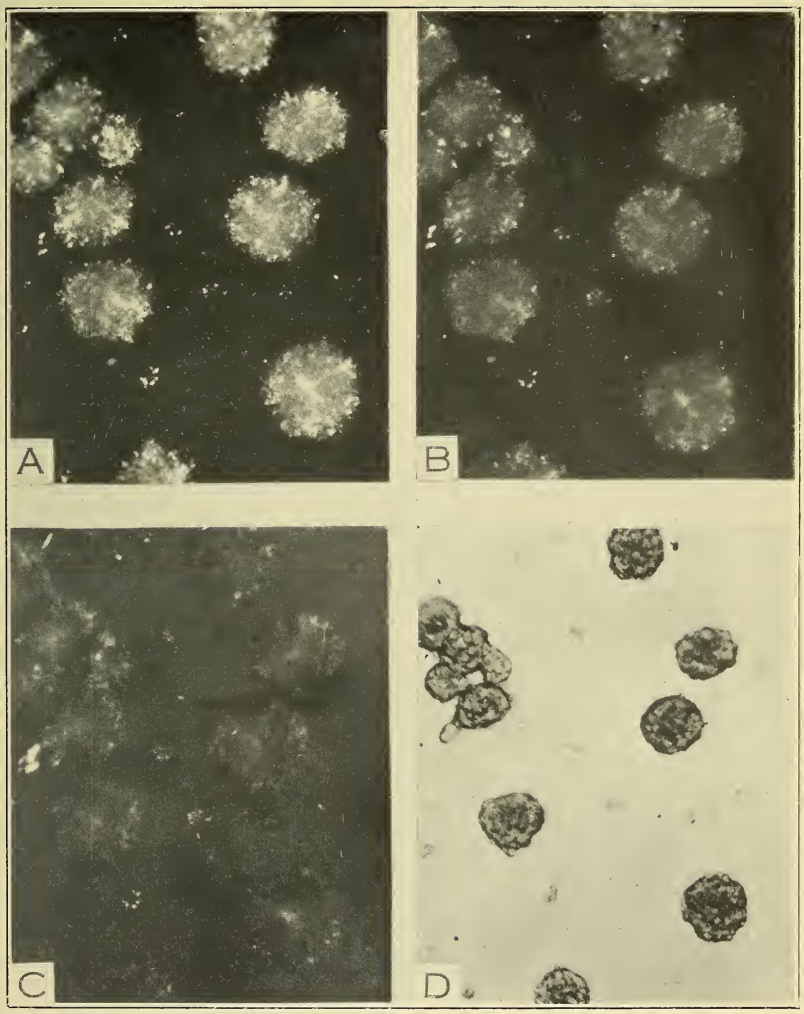

FIGURE 1.—*Photomicrographs showing melting of one sample of gel rubber crystals.*

A, Crossed nicols × 200. The mother-liquor has been replaced with acetone and the temperature allowed to rise, but the appearance of the field is not detectably changed. The brightness of the groups is caused by the optical anisotropy of the many crystals which compose them. Temperature, −6.2° C.

B, Crossed nicols × 200. The temperature has risen about four degrees. A large part of the brightness has disappeared, indicating that considerable melting has already occurred. Temperature, −1.9° C.

C, Crossed nicols × 200. Melting is nearly complete. Temperature, −0.4° C.

D, Parallel nicols × 200. After melting, surface tension has shrunken the clusters, but the large part of their structure which remains will continue indefinitely. Temperature, +0.4° C.

When the cells were used they were well drained between applications of liquids. After withdrawing the mother liquor, the crystals were twice treated with acetone, in which they were allowed to steep for several minutes at least. They then received two treatments with aqueous calcium chloride. When the cover glasses were used, they were washed in a stream of cold acetone, steeped in acetone, washed once in aqueous calcium chloride and transferred to another portion of calcium chloride solution for the melting point determination. The melting point of a preparation treated in this way was the same as the melting point of crystals grown simultaneously from the same solution but with which the steeping in acetone had lasted more than 24 hours. This procedure differs from that described in

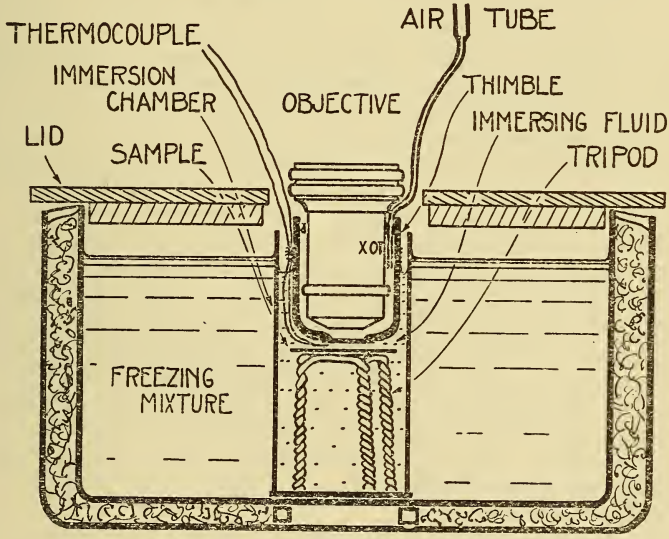

FIGURE 2.—*The simple cold stage.*

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

the paper on ether-soluble rubber hydrocarbon, but the results by the two methods are consonant as indicated by the melting point of 9.7 to 10.3° C found for sol crystals immersed in aqueous calcium chloride.

Even when the aqueous solution was used to surround the crystals, wide spreads were found between different preparations of crystals.[8] Sometimes melting began as low as −1.5° C and at other times not below +9.6° C. In a few experiments melting ended at +5.5° C and in others was not complete below +13.8° C. There were ranges as great as 8° C and as small as 1.2° C. The 1.2° C melting range

[8] The number of melting point determinations is too great and the significance of the variations too doubtful to justify including at this place a chronicle of them all.

was exhibited by crystals prepared in the following manner. They were grown in the cell from an ethylbenzene-ether solution. The mother-liquor was removed, the crystals were washed once with very cold ether and dissolved in more ether. From this solution crystals were again grown, the yield being small. The cell was emptied of liquid and filled twice with cold acetone and twice with a cold solution of aqueous calcium chloride. The temperature was allowed to rise and melting was observed from +4.4 to +5.6° C. Apparently fractionation was produced by the second crystallization from ether. Within the range exhibited by any preparation, the bright spots caused by the birefringence of the individual crystals disappeared sporadically, sometimes with great suddenness. In each cluster the melting was usually continuous, a crystal here and a crystal there losing birefringence without any seeming association. Individual particles sometimes continued to melt over an interval of a degree or more. Neither the melting range of the cluster nor the difference between the melting points of the crystalline particles can be explained by the assumption of delayed equilibrium or of different thermodynamic or chemical environment in the several parts of the clusters. Particles immediately adjacent to one another, separated by less than a hundredth of a millimeter, melted at temperatures differing by 5 or 6°. During the months necessary to dissolve one sample of gel,[9] crystals made from successive extracts tended to melt at progressively higher temperatures, but the character of the melting (as indicated by length of range and the independence of one another with which the individual particles melted) was the same for all and did not differ from that observed when an entire sample of gel had been dissolved in a single solution. Large irregularities in melting range, which seem to depend only upon the accidents of nucleus formation, persisted and occurred whether the gel had been dissolved in ethylbenzene or in ether. This entire behavior contrasts sharply with that of ether-soluble rubber hydrocarbon, which, when well controlled, always melted at about 10° C.

The way in which dissolved gel rubber crystals melt makes it plain that we are dealing here with no single compound. The gel rubber appears to have dissolved as a result of partial depolymerization. The separate crystals which make the clusters have different molecular compositions and are themselves almost certainly solid solutions of several different polymers. It is obviously desirable that such a mixture be separated into its constituents by fractional crystallization.

4. ELASTICITY

The simple cold stage illustrated in figure 2 made it possible to determine for the sol at least whether the crystals possess the peculiar elasticity of rubber. A striking difference between the properties of the sol and gel fractions was revealed.

Crystals of dissolved gel rubber were grown on microscope cover glasses. One of these was placed in the cold stage under aqueous calcium chloride. The rubber was present as the entangled network of crystalline needles and rods which is often obtained with the gel. While observing the crystals between crossed nicols they were manipulated with a wire. There was no plastic deformation. Instead the

[9] See p. 456.

network seemed to yield elastically. The amount and nature of the birefringence did not change, so far as could be noticed. The crystals appeared to be elastic to some degree, but it could not be fully established whether they possessed true rubber-like elasticity. The preparation was allowed to melt and the cover glass taken from the apparatus. The deposit of rubber was pressed into a ball. It had the usual physical properties of gel rubber, considerable stiffness, less extensibility than sol rubber, but also more perfect elasticity.

On the other hand, when a wire was drawn across a preparation of sol crystals, they were found to be plastic. After deformation they had strong birefringence and a new direction of extinction. A clear cover glass was pressed upon the crystalline deposit. The clusters flattened and did not recover when the pressure was released. After some crystals were melted the same experiment with the wire was tried. The rubber could not be plastically deformed, but instead the wire loosened the globules from the cover glass and pushed them aside. The cover glass was taken from the apparatus and washed with water and acetone. The deposit of rubber was rolled into a lump between the fingers. The lump possessed the customary physical characteristics of sol rubber, great extensibility but a rather large permanent set.

5. COMPARISONS OF SOL AND DISSOLVED GEL RUBBER .

It was made clear on page 455 that gel rubber cannot be dissolved in ethyl ether unless some of the precautions against oxidation are abandoned. Under these conditions the ether-insoluble form becomes in some ways more like the ether-soluble rubber. The irregularity of the melting points found for the dissolved gel crystals is consistent with a partial decomposition of very large molecules in the presence of traces of oxygen—a phenomenon over which accurate laboratory control is probably impossible. The dissolved gel seems to consist of many different kinds of molecules. Most of them may still be the same as they were before. To these it may owe its peculiar type of elasticity. It may even contain some of the same molecules as predominate in the sol portion. As contrasted with the dissolved gel, the sol form seems to have suffered no decomposition. When suitable precautions against oxidation are taken, the size of the molecules is not improbably the same as it was in the rubber tree. For this reason, the appearance of the crystals tends to be about the same every time, and the same melting point is always observed.

That the gel rubber is still very different from the sol form, even after an oxygen-fostered disaggregation permits it to dissolve in ethylbenzene or in ether, is indicated by the different elastic behavior after the rubber crystals are melted. When sol rubber melts under a liquid, each nodule quickly forms a sphere with small inclusions of the surrounding liquid.[10] When the space surrounding the nodules is evacuated there form clear droplets adhering to the glass. On the other hand, when the crystals of dissolved gel rubber melt, as judged by loss of birefringence, their original shape is held almost unchanged to a temperature of 30° C or higher. There is slight deformation, but it is

[10] It must be remembered that the power of surface forces to cause deformation is much greater with substances on a microscopic scale.

not progressive and the shape is the same 24 hours later as it is after 10 minutes. The viscosity is great and the granular structure shown in figure 1 (D) is preserved. This difference between the two portions is consistent with all other data [11]—the gel has much greater stiffness and more perfect elasticity; the sol is softer, more extensible, and when deformed takes a permanent set.

By chemical action, these properties of both the sol and the gel can be changed. Thus, the crystals of dissolved gel rubber do not exhibit the more perfect elasticity after melting if they have been grown from a solution prepared by more strenuous treatment. If the gel has been dissolved by treatment with trichloroacetic acid, and crystals prepared from the solution are allowed to melt under aqueous calcium chloride solution, the clusters of crystals flow into rounded globules. This chemical action makes the gel behave more like the sol.

On the other hand, vulcanization makes the sol behave more like the gel. Sol crystals were prepared in one of the cells. The solvent was removed by washing with acetone at low temperature and all the acetone that could be siphoned was removed by that method. Always maintaining the temperature below the melting point of the crystals, a little sulphur chloride vapor was allowed to enter the cell. Much sulphur was deposited. The sulphur was dissolved with carbon disulphide at low temperature, the carbon disulphide removed with acetone, and the preparation observed with the microscope. The rubber was no longer birefringent but the original shapes of the crystalline spherulites persisted. They were pseudomorphs after the original crystals, but by combination with sulphur they had lost the molecular orientation peculiar to crystalline phases. When they were heated to 40° C there was no further change, showing that vulcanization had increased their stiffness.

The authors have appreciated the technical advice of E. W. Washburn, the late chief of the Bureau's Chemistry Division, throughout this investigation. We are indebted to Harry L. Fisher of the U.S. Rubber Company and Loren G. Polhamus of the U.S. Department of Agriculture, who supplied the latex used in this investigation.

WASHINGTON, August 21, 1934.

[11] W. Harold Smith and William L. Holt, BS J.Research **13**, 465 (1934);RP720.