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X-RAY DIFFRACTION PATTERNS OF SOL, GEL, AND TOTAL RUBBER WHEN STRETCHED, AND WHEN CRYSTALLIZED BY FREEZING AND FROM SOLUTIONS

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ABSTRACT

Total, sol, and gel rubber were prepared under conditions which were selected to avoid oxidation and structural changes. Total rubber when stretched and exposed to an X-ray beam produced the characteristic crystal fiber pattern. Stretched sol rubber produced no evidence whatever of this pattern even at 1,000 percent elongation. With stretched gel rubber, the pattern was formed above 100 percent elongation, and at 200 percent was sharp and intense. A large interplanar spacing of 54 A, found in the unstretched gel, was absent in the sol. The patterns obtained with stretched gel, with frozen sol, gel, and total rubber, and with gel crystals produced from an ethereal solution were measured and analyzed. The crystals produced by all of these methods are similar. The measurements agree excellently with those reported recently by Lotmar and Meyer, and by Barnes.

CONTENTS

I. INTRODUCTION

When unstretched rubber is examined by X-rays, it produces a blurred ring, the halo which is typical of the amorphous or liquid state. Its behavior when stretched was first reported by Katz,[3] who observed interference spots at 80 percent elongation. Their intensity increased with increasing elongation and at 400 percent a definite fiber diagram was observed. Consequently, rubber, when extended, was considered to be crystalline, and the Joule effect to result from an actual formation of crystals. When Katz heated stretched rubber, the interference spots vanished. Vulcanized rubber produced inter-

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[3] J. R. Katz, Kolloid Z. **36**, 300; **37**, 19 (1925).

ferences, but the spots were weaker than those obtained with unvulcanized rubber. The identity period along the direction of stretch was 8 A and the dimensions assigned to the unit cell were 8×6.5×6.5 A, with a volume of 338 A^3.

The behavior of stretched rubber between 80 and 1,000 percent elongations was investigated by Hauser and Mark,[4] who made a more accurate study of the positions and intensities of the interferences. The positions of the interferences were found to be independent of the degree of stretching, but their intensities increased proportionally with it. The position of the amorphous ring remained unchanged during extension, but its intensity decreased with continued elongation. Therefore, an amorphous or liquid phase in unstretched rubber was supposed to be changed to a crystalline phase when it was stretched. The positions of the interferences, which depend on the dimensions of the unit cell, did not change with continued stretch and consequently a definite space lattice was indicated. Other evidence showed that new crystalline units were constantly produced during elongation, and that the major axis of the crystalline phase was oriented parallel to the direction of stretch. The interferences in stretched rubber disappeared at 60° C. When rubber was maintained in an extended condition for some time, the interference spots vanished. If rubber was milled or swollen by solvents before stretching, the interference spots did not appear. An orthorhombic configuration was assigned to the unit cell, but the possibility of a monoclinic structure was admitted. Its dimensions, 8.0×8.6×7.68 A, correspond to a cell volume of 529 A^3. There were 4.12 molecules of C_5H_8 per unit cell.

The interferences obtained by Mark and von Susich[5] were better defined, and better measurements were possible. A rhombic cell was assumed and the dimensions given to it were 8.3×8.1×12.3 A ±0.1 A. The volume of the unit cell was reported to be 830 ± 30 A^3, with 7.1 molecules and not 8, presumably because of poor density values. With the Weissenberg apparatus, Mark and von Susich proved that the indices (111) and (200) of Hauser and Mark are really (100) and (010). They observed that very thin specimens of rubber showed fibering and also three-dimensional orientation. So a distribution of carbon atoms was proposed which aims to reconcile the orientation of the primary valence chains in the direction of stretch, atomic spacings for single and double-linked carbon atoms, and the observed intensities. By topochemical reactions, they attempted to convert stretched rubber into derivatives retaining the structure, but X-ray patterns of the derivatives indicated an amorphous condition.

On the basis of a single experiment, Ott[6] assigned a volume of 259 A^3 to the largest possible cell. Using the values of Bragg for the radius of carbon, 0.77 A, and of hydrogen, 0.73 A, and assuming close packing, the volume of C_5H_8 was computed to be 43.1×10^{-24} ml or 43.1 A^3. On these assumptions, the maximum number of C_5H_8 groups in Ott's cell is six.

A recent paper by Lotmar and Meyer[7] reports accurate measurements of the structure of crystallized rubber. The unit cell was

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[4] E. A. Hauser and H. Mark, Kolloidchem. Beihefte **22**, 63 (1926).

[5] H. Mark and G. von Susich, Kolloid Z. **46**, 11 (1928).

[6] E. Ott, Naturwissenschaften **14**, 320 (1926).

[7] W. Lotmar and K. H. Meyer, Monatsh. **69**, 115 (1936).

derived by the graphical method of Sauter, is monoclinic, and has the following axes:

$a=8.54\pm0.05$ A
$b=8.20\pm0.05$ A (fiber axis)
$c=12.65\pm0.05$ A
$\beta=83°20'$
Volume of unit cell=880 A^3, approximately.

They report 7.6 molecules per unit cell and this value is based on the highest value of density, 0.965, reported in the literature.[8] Eight molecules are assumed to be present. By an elimination of possible space groups, there remains the probable one, C^5_{2h}, and the chains are presumed to have the symmetry of a twofold screw axis. The crystallite is said to be a molecular racemate of right and left spiral molecules.

Subsequent to the work of Lotmar and Meyer, Barnes [9] examined two samples of frozen crude rubber, one of which had remained frozen for 22 years, and the other for at least 11 and probably for 30 years. They lost their opacity at approximately 41° C. The measurements of Barnes agree excellently with those reported by Lotmar and Meyer for stretched rubber. Identical patterns were obtained from each specimen.

Crystal interferences in frozen, unstretched smoked sheet were found by Hauser and Rosbaud.[10] They were indicated by Debye-Scherrer rings. Later, von Susich [11] constructed a melting curve from the behavior of patterns of frozen rubber at different temperatures. With unstretched rubber, the powder pattern disappeared completely at approximately 35° C, and with stretched rubber at about 90° C. Above 90° C the pattern was that of an amorphous material. Indices were assigned to four rings in the frozen-rubber pattern, but no spacings or calculations were mentioned.

In the present investigation the work of Lotmar and Meyer is checked with stretched gel rubber, which yields a sharper and more intense diffractive pattern than is obtained with the total rubber. The powder patterns of frozen sol, gel, and total rubbers are compared as to their interplanar spacing and the intensity of their interferences, and an examination is made of the sol and gel fractions crystallized from an ethereal solution at low temperature.

II. MATERIALS AND METHODS

The rubber hydrocarbon used in this investigation was obtained from the latex of *Hevea brasiliensis*, the source of the principal rubber of commerce. It was prepared at the National Bureau of Standards from latex supplied by the United States Department of Agriculture, and was studied by X-rays at the University of Illinois.

The preparation of pure sol, gel, and total rubber hydrocarbons, and the formation of discrete crystals of sol and gel rubber from solution, have been discussed in previous issues of this journal.[12] Similar

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[8] H. Mark and G. von Susich, footnote 5.
[9] William H. Barnes, Can. J. Research 15, 156 (1937).
[10] E. A. Hauser and P. Rosbaud, Kautschuk 3, 17 (1927).
[11] G. von Susich, Naturwissenschaften 18, 915 (1930).
[12] W. Harold Smith, Charles Proffer Saylor, and Henry J. Wing, BS J. Research 10, 479 (1933) RP 544. W. Harold Smith and Charles Proffer Saylor, J. Research NBS 13, 453 (1934) RP719.

material was used in this investigation. The rubber was purified and separated into sol and gel fractions under conditions which aimed to preserve its structure and to avoid the effects of light and of oxygen. Oxidation of the rubber was minimized by allowing it to remain in contact with the natural antioxidants which are in crude Hevea rubber, until the final stage of purification. At low temperatures the hydrocarbons in massive rubber crystallize without a solvent. Specimens of "frozen" sol and gel were prepared by maintaining the samples at −25° C for 30 days. Other specimens of crystalline sol and gel rubber were prepared at low temperatures from ethereal solutions of the fractions.

The production of a diffraction pattern by stretched rubber, and the changes which occur when unstretched rubber is frozen and when it separates from an ethereal solution at low temperatures as discrete particles have been repeatedly termed crystallization, and that word will be used in this paper.

In the application of the ordinary X-ray diffraction equipment and technique there is no resolution of interferences which correspond to the very long interplanar spacings which frequently exist in natural materials. Hence, special apparatus and methods have been developed in the X-ray laboratory of the University of Illinois, in which a magnetic field is used to deflect the scattered electrons which ordinarily fog the film. Definite and reproducible evidence has been obtained of very large spacings in collagen, gelatin, keratin, and other materials, including gel rubber.

For the work with stretched gel rubber an ordinary flat-film camera was used. The distance from specimen to film was 5 cm. For the work with frozen sol, gel, and total rubbers, and rubber crystals deposited from solution, special apparatus and technique were again required to obtain the diffraction patterns at temperatures below the melting point of the crystals.

The crystallized rubber specimens were examined by two specially constructed types of cameras. One was a cylindrical camera, shown in figure 1, in which a low-temperature specimen holder, pictured in figure 2, was inserted in place of the wedge sample holder used for powder specimens. The entire holder was cooled by the exhaust from a liquid-air reservoir, and the cold air passed out alongside the specimen. The sides of the cylindrical camera were closed to prevent condensation of moisture on the specimen. The air in the camera was readily precooled by placing solid carbon dioxide within it. The other low-temperature camera is shown in figure 3, and had the advantage of a longer distance from specimen to film for the accurate determination of the longer spacings. It consisted simply of a funnel, in the apex of which was situated the pinhole and specimen, the latter held in place with aluminum washers. Cooling was accomplished by means of solid carbon dioxide and acetone. The open end of the funnel was fastened to a wooden frame which held a flat film. The collimator (not shown in the drawing) which defined the beam of X-rays, and which touched the camera, was constructed of wood to prevent the condensation of moisture upon it and to avoid the conduction of heat to the specimen.

In all X-ray investigations of rubber we have employed the copper K radiation from a Philips Metalix tube operating at 26 kv and 22 ma.

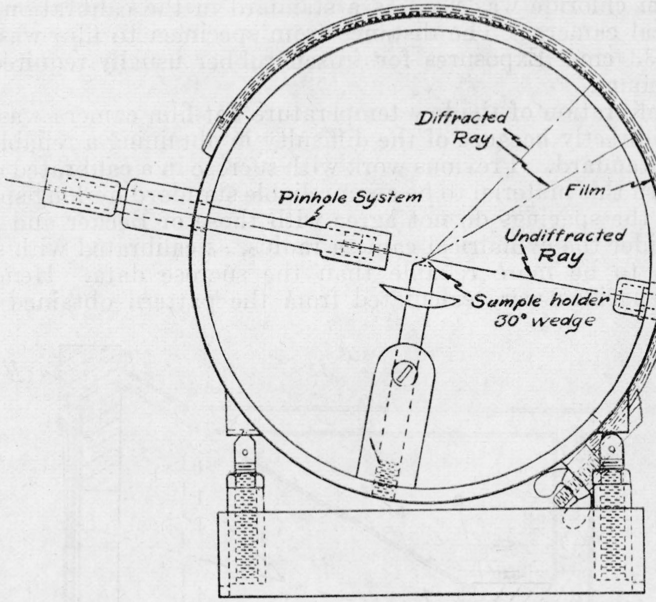

FIGURE 1.—*Cylindrical camera.*

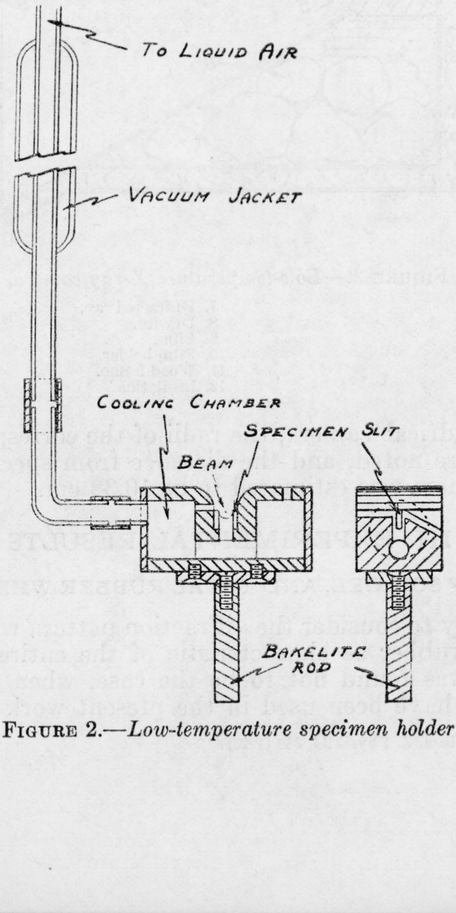

FIGURE 2.—*Low-temperature specimen holder.*

Sodium chloride was used as a standard in the calibration of the cylindrical camera. The distance from specimen to film was found to be 6.33 cm. Exposures for frozen rubber usually required from 5 to 10 hours.

The calibration of the low temperature flat-film camera was determined indirectly because of the difficulty in obtaining a reliable long-spacing standard. Previous work with sucrose in a calibrated camera had shown this material to be an unreliable standard for long spacings. At least the spacings do not agree with those of Becker and Rose.[13] We consider the cylindrical camera radius, as calibrated with sodium chloride, to be more reliable than the sucrose data. Hence, the sucrose spacings were calculated from the pattern obtained in the calibrated, cylindrical camera, the radii of the corresponding lines on the flat film were noted, and the distance from specimen to film of the flat-film camera was estimated to be 10.32 cm.

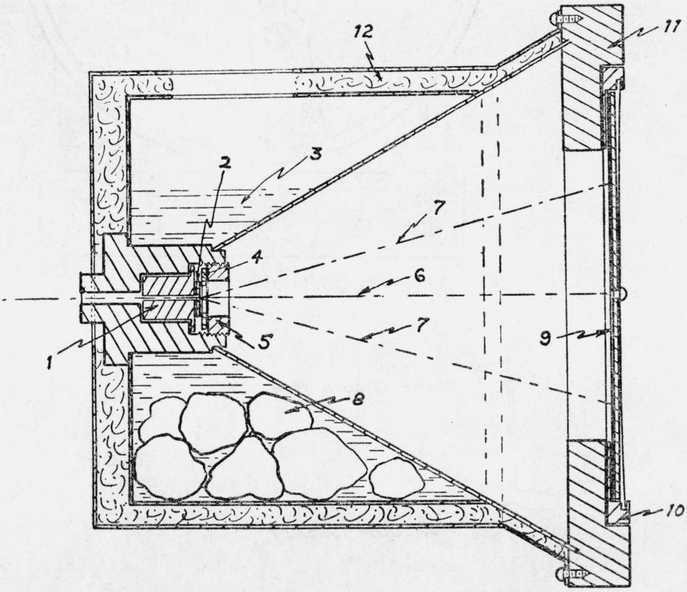

FIGURE 3.—*Low-temperature X-ray camera.*

1. Pinhole.
2. Specimen.
3. Acetone.
4. Aluminum washer.
5. Threaded washer.
6. Undiffracted ray.
7. Diffracted ray.
8. Dry ice.
9. Film.
10. Film holder.
11. Wood frame.
12. Insulation.

III. EXPERIMENTAL RESULTS

1. BEHAVIOR OF SOL, GEL, AND TOTAL RUBBER WHEN STRETCHED

It is customary to consider the diffraction pattern which is obtained with stretched rubber as characteristic of the entire rubber hydrocarbon. This was found not to be the case, when the sol and gel fractions which have been used in the present work were examined

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[13] K. Becker, and H. Rose, Z. Physik **14**, 369 (1923).

separately. The original observations were reported briefly by Clark, Warren, and Smith,[14] and since that report they have been confirmed.

When stretched, at room temperature, the purified total rubber hydrocarbon behaved exactly like any specimen of whole rubber, and produced a similar crystal fiber diffraction pattern.

The sol rubber fraction produced no evidence whatever of the characteristic crystal fiber pattern when stretched, even at 1,000 percent elongation. The liquid halo was retained at all elongations, but it became *broader* in proportion to the increased percentage of stretch. This may be caused by decreasing particle size. The same results were observed in the presence or absence of antioxidants.

When elongated 100 percent or more, the gel fraction produced the characteristic crystal fiber pattern. At 200 percent elongation the pattern was quite sharp and intense. The liquid halo remained unchanged in width but decreased in intensity as the crystal interferences increased in intensity. When, however, antioxidants were removed and the gel rubber was exposed to air for some time in the unvulcanized condition, it was difficult to find crystal interferences, even at 400 percent elongation.

Samples of sol and gel rubber were vulcanized by the Peachey process. In this method, active sulphur is formed at room temperatures by the reaction between hydrogen sulphide and sulphur dioxide. Vulcanized sol rubber began to show faint evidence of crystal interferences when stretched more than 400 percent, which showed that sulphur had produced a profound structural effect. Vulcanized gel rubber produced a fiber pattern, but not at elongations less than 250 percent.

Differences in the physical properties of sol and gel rubber are indicated by their stress-strain behavior, when vulcanized.[15] The unvulcanized gel fraction, when milled, is the more difficult to "break down" or plasticize. The gel has much greater stiffness and more perfect elasticity; the sol is softer, more extensible, and when deformed takes a permanent set.[16] The sol fraction is the more mobile of the two. For that reason, crystals which may be formed when sol rubber is stretched probably melt quickly and a diffraction pattern cannot be obtained. If successive strips of it were stretched, immediately before they were passed through an X-ray beam, evidence of crystallinity might be produced.

Pummerer [17] separated total rubber into sol and gel by a modification of Feuchter's [18] diffusion method, which differs from that used in the present study. Each of the fractions which he obtained produced a diffraction pattern when stretched. Subsequently, Hauser [19] observed that rubber when extended very slowly, that is, isothermally, produced no interference.

2. LARGE INTERPLANAR SPACING IN GEL RUBBER

When unstretched gel rubber is examined with the equipment for detecting and measuring the very long interplanar spacings, there appears a ring of small diameter with arcs which indicate fibering.

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[14] Geo. L. Clark, W. J. Warren, and W. Harold Smith, Science **79**, 433 (1934).

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

[16] See footnote 12.

[17] R. Pummerer, Kautschuk **2**, 85 (1926).

[18] H. Feuchter, Kolloidchem. Beihefte **20**, 434 (1925).

[19] M. Hunemörder and P. Rosbaud, Kautschuk **3**, 228 (1927).

(See fig. 4.) It corresponds to a spacing of 54 A, or a multiple of this value, instead of 58 A, as previously reported.[20] When gel rubber is stretched, these arcs condense into very sharp equatorial spots, corresponding to this periodicity. There is a lateral separation of molecules or crystallites of 54 A, or perhaps a multiple of it, which persists in stretched gel rubber with the fibering. An examination of sol rubber indicated that no such spacing was present. It was reinvestigated under conditions which were carefully controlled, but no evidence of large spacing interference was produced by the sol phase.

3. DIFFRACTION PATTERNS OF STRETCHED GEL RUBBER

The gel rubber, when stretched nearly to the breaking point, produced an intense diffraction pattern which was sharper than that obtained with total rubber. The diffraction data are given in tables 1 and 2. In these tables, and in those to follow, d is the distance between the set of planes, making an angle θ with the incident beam. R is radius of the diffraction spot or ring as measured on a flat film. L is the distance on the film from the diffraction line to the central spot when the cylindrical camera is used. When symbols are used to indicate relative intensities, they have the following conventional designations: *s*, strong; *m*, medium; *w*, weak; and *v*, very weak.

TABLE 1.—*X-ray-diffraction data for stretched gel rubber; see figure 5*

Flat-film camera. Distance from specimen to film 5 cm.

Pattern	Equator			First layer line			Second layer line		
	R	θ	d	R	θ	d	R	θ	d
	cm		A	cm		A	cm		A
R57	1.26	7°4.34′	6.24				1.98	10°48.1′	4.102
	1.925	10°31.41′	4.21						
R61	1.258	7°3.68′	6.253	1.60	8°52.34′	4.983	2.435	12°59′	3.421
	1.925	10°31.7′	4.207	2.20	11°52.5′	3.735			
	2.738	14°21.17′	3.100	2.44	13°0.4′	3.41			
R62	1.26	7°4.33′	6.243	1.62	8°58.56′	4.926	1.99	10°51.1′	4.082
	1.94	10°36.19′	4.177	2.215	11°56.8′	3.714	2.47?		
	2.755	14°25.64′	3.084	2.44	13°0.375′	3.412			

TABLE 2.—*X-ray diffraction data for stretched gel rubber; see figure 6*

Flat-film camera. Distance from specimen to film 5.09 cm. Pattern *R64* (with NaCl).

Equator			First layer line			Second layer line		
R (cm)	θ	d	R (cm)	θ	d	R (cm)	θ	d
		A			A			A
1.27	7°0.3′	6.30	0.87	4°51′	9.09	2.00	10°44′	4.13
1.95	10°29′	4.23	1.63	8°53′	4.98	2.46	12°54′	3.45
2.76	14°14′	3.13	2.22	11°47′	3.76			
			2.47	12°57′	3.43			

The data in table 2 are assumed to be more reliable than the data in table 1, because the distance from specimen to film was more ac-

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[20] Geo. L. Clark, Rubber Age 38. 79 (1935).

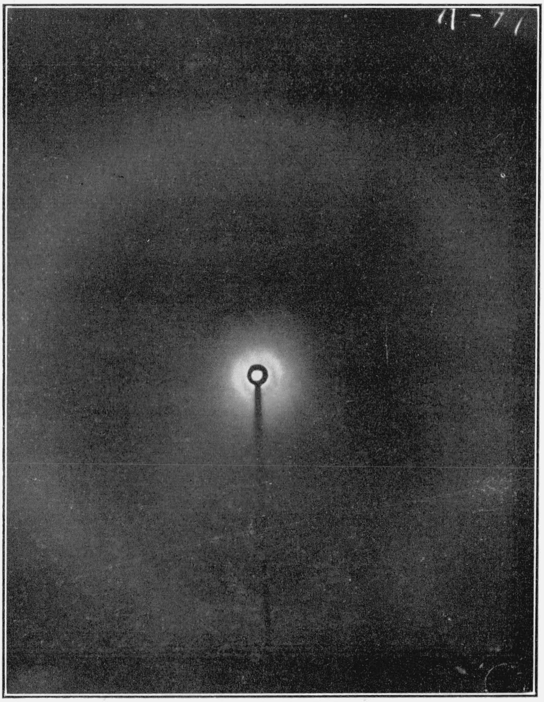

Figure 4.—*Long spacing in unstretched gel.*

Room temperature. Exposure 18½ hours.

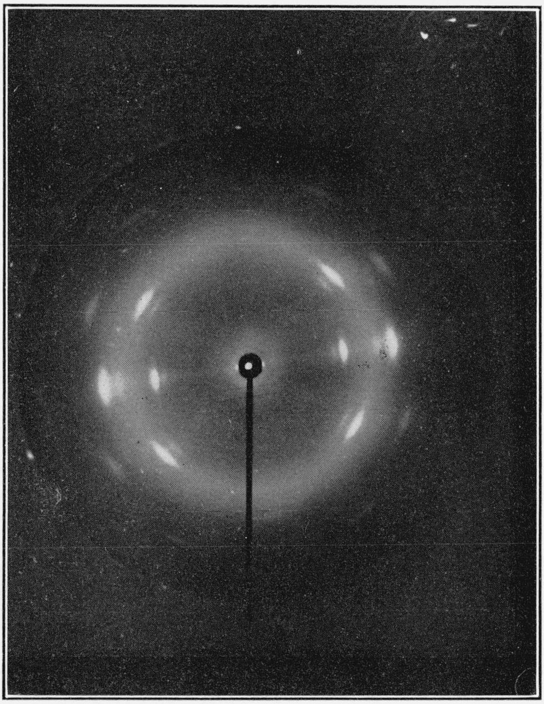

FIGURE 5.—*Pattern R57.*

Gel without sodium chloride. Stretched about 500 percent. Fiber axis normal to beam. Room temperature. Exposure 6 hours.

curately determined in this case by covering the sample with finely powdered sodium chloride. The results are in very good agreement with those of Lotmar and Meyer, as shown later in table 5. In view of the broad interferences in the pattern used by Lotmar and Meyer, it is surprising that the agreement is so good.

4. DIFFRACTION PATTERNS OF FROZEN SOL, GEL, AND TOTAL RUBBERS

In the present investigation, sol, gel, and total rubbers are examined individually, to compare the spacings and the intensities of interferences in their powder patterns, and also to compare the spacings of frozen rubber with those of stretched rubber at room temperature. Two types of patterns were taken of each kind of frozen rubber, one with the cylindrical camera and the other with the flat-film box camera. The data are recorded in tables 3 and 4 and the diffraction patterns reproduced in figures 7 and 8. Uncertain interferences were not measured, as indicated by blank spaces in table 3.

TABLE 3.—*X-ray diffraction data for frozen sol, gel, and total rubbers; see figure 7*

Cylindrical camera. Distance from specimen to film 6.33 cm.

Sol—pattern *R29*			Gel—pattern *R28*			Total—pattern *R34*		
L (cm)	θ	*d*	*L* (cm)	θ	*d*	*L* (cm)	θ	*d*
	Degrees	A		*Degrees*	A		*Degrees*	A
1.44β	6.52	6.12	1.42β	6.43	6.20	1.43β	6.47	6.16
1.58	*s*7.15	6.17	1.57	*s*7.11	6.21	1.57	*s*7.11	6.21
1.77	*m*8.01	5.52	1.76	7.97	5.54	1.76	7.97	5.54
1.97	*s*8.92	4.96	1.96	*s*8.87	4.99	1.96	*s*8.87	4.99
2.12β	9.58	4.17	2.10β	9.51	4.20	2.11β	9.55	4.19
2.36	*vs*10.68	4.15	2.34	*vs*10.59	4.18	2.34	*vs*10.59	4.18
2.65	*ms*11.99	3.70	2.62	*ms*11.86	3.74	2.64	*ms*11.95	3.71
2.86	*m*12.95	3.43	2.82	*m*12.76	3.48	2.82	*m*12.76	3.48
3.21	*mw*14.53	3.07	3.26	*mw*14.76	3.02	3.28	*mw*14.85	3.00
3.56	*w*16.11	2.77	3.49	*w*15.80	2.82			
						3.67	*vw*16.61	2.69
3.86	*w*17.47	2.56	3.86	*w*17.47	2.56	3.91	*mw*17.70	2.53
4.16	*vw*18.83	2.38						
						4.36	*m*19.73	2.28
4.52	*vw*20.46	2.20	4.47	*w*20.23	2.22			
4.84	*m*21.91	2.06	4.81	*m*21.77	2.07	4.78	*mw*21.63	2.08
5.14	*w*23.27	1.95				5.09	*w*23.04	1.96
						5.48	*w*24.80	1.83

TABLE 4.—*X-ray diffraction data for frozen sol, gel, and total rubbers; see figure 8*

Flat-film camera. Distance from specimen to film 10.32 cm.

Sol—pattern *R20*			Gel—pattern *R22*			Total—pattern *R24*		
R (cm)	θ	*d*	*R* (cm)	θ	*d*	*R* (cm)	θ	*d*
		A			A			A
2.36β	6°26′	6.19	2.38	6°30′	6.13	2.36	6°26′	6.19
2.63	7°9′	6.18	2.65	7°12′	6.13	2.63	7°9′	6.18
2.98	8°3′	5.49	2.99	8°5′	5.47	2.97	8°2′	5.50
3.32	8°55′	4.96	3.34	8°58′	4.94	3.32	8°55′	4.96
3.61β	9°38′	4.15	3.64	9°43′	4.12	3.62	9°40′	4.14
3.85	10°14′	4.33	3.88	10°18′	4.30	3.86	10°15′	4.32
4.05	10°43′	4.14	4.08	10°47′	4.11	4.06	10°44′	4.13
4.59	11°59′	3.70	4.62	12°4′	3.68	4.59	11°59′	3.70

Within experimental error, the sol, gel, and total rubbers produce similar patterns. The spacings in sol rubber obtained with the cylindrical camera are uniformly smaller than the others by approximately 0.04 A, but the difference probably is not significant. The flat-film camera shows the gel spacings to be uniformly smaller than the others, which may be a temperature effect, since no special precaution was taken to insure a constant temperature. Some interplanar spacings, including the important 020 interference of the frozen rubber, could not be distinguished in patterns *R28*, *R29*, and *R34*, but were satisfactorily resolved by the flat-film camera, which uses a longer distance from specimen to film.

An analysis of the (200) line with a microphotometer gives a slight indication of a doublet character.

For each type of rubber, in order to prove that the "powder" pattern of frozen rubber was characteristic of rubber, a pattern was also obtained after warming up to room temperature. In all cases the crystal interferences disappeared completely, leaving only the halos obtained from ordinary unstretched rubber. These patterns are shown in figure 9.

5. COMPARISON BETWEEN STRETCHED RUBBER AND FROZEN RUBBER, AND THE ASSIGNMENT OF CRYSTAL INDICES

The diffraction data on stretched and frozen rubber are arranged for comparison in table 5. The assignment of indices is based on the rubber structure given by Lotmar and Meyer. Values of d have been calculated from their sin θ/λ values for stretched rubber, and are also recorded in the table for comparison.

The lower value for the (002) spacing in frozen rubber, 6.18 instead of 6.30 in stretched rubber, is undoubtedly beyond experimental error and represents a significant difference which may be an effect of temperature. However, stretched rubber cooled to the same temperature as frozen rubber displays no change in its normal (002) spacing. Except for small differences in the (002) and (200) spacings, the principal interferences of frozen and stretched rubber confirm the structure of Lotmar and Meyer. Likewise the intensities compare favorably.

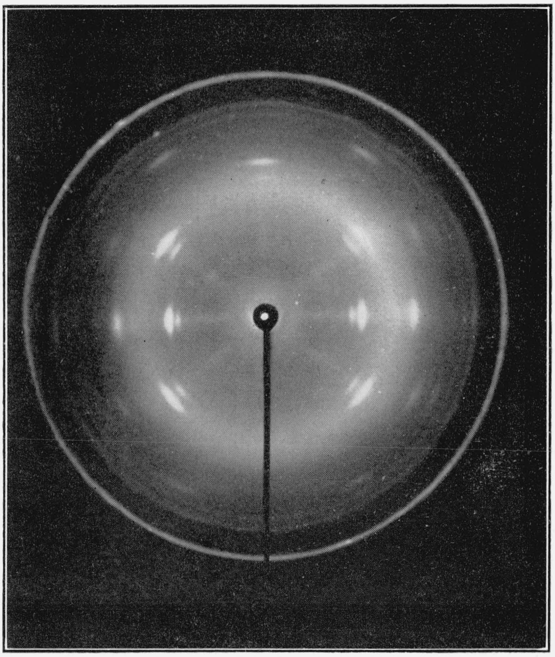

FIGURE 6.—*Pattern R64.*

Gel and sodium chloride. Stretched about 500 percent. Fiber axis 80° to beam. Room temperature. Exposure 16½ hours.

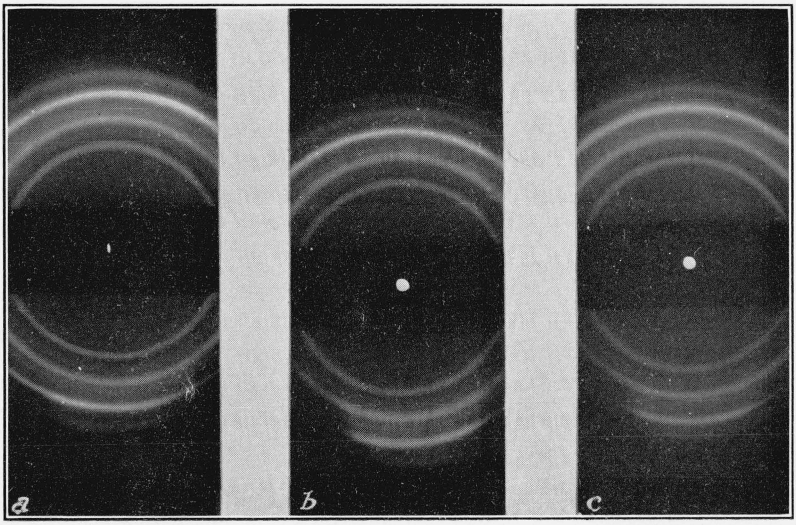

Figure 7.—*Frozen specimens.*

a, sol *R29*; b, *R28*; c, total *R34*. Cylindrical camera. Exposure 5 hours.

TABLE 5.—*Summary of interplanar spacings (d, in angstroms) for stretched and frozen rubber*

Lotmar and Meyer			Present investigation							
					Frozen rubber					
					Cylindrical camera			Flat-film camera		
Intensity	Indices hkl	Stretched rubber	Intensity	Pattern *R*64 (stretched)	Sol	Gel	Total	Sol	Gel	Total
		A		A	A	A	A	A	A	A
s	002	6.29	*s*	6.30	6.17	6.21	6.21	6.18	6.14	6.18
vw	111	5.50	*mw*	-----	5.52	5.54	5.54	5.49	5.47	5.50
s	012	5.00	*s*	4.98	4.96	4.99	4.99	4.96	4.94	4.96
vs	200	4.24	*vs*	4.23	4.15	4.18	4.18	4.33	4.30	4.32
m	020	4.10	-----	4.13	-----	-----	-----	4.14	4.11	4.13
ms	210 013 211	3.76	*ms*	3.77	3.70	3.74	3.71	3.70	3.68	3.70
w	120 121	3.70	-----	-----	-----	-----	-----	-----	-----	-----
w-m	$21\bar{1}$ $12\bar{1}$ 022 212	3.45	*m*	3.45 3.43	3.43	3.48	3.48	-----	-----	-----
w	004	3.14	*mw*	3.13	-----	-----	-----	-----	-----	-----
w	220 023 221	3.01	-----	-----	3.07	3.02	3.00	-----	-----	-----
vw	114	2.86	-----	-----	-----	2.82	-----	-----	-----	-----
w	$22\bar{1}$ 222	2.78	*w*	-----	2.77	-----	2.69	-----	-----	-----
w	312 311 214 130 131	2.58	*w*	-----	-----	-----	-----	-----	-----	-----
vw	$22\bar{2}$	2.56	-----	-----	2.56	2.56	2.53	-----	-----	-----
vw	124	2.39	*vw*	-----	2.38	-----	-----	-----	-----	-----
vw	230 231	2.29	-----	-----	-----	-----	-----	-----	-----	-----
vw	304	2.23	-----	-----	2.20	2.22	-----	-----	-----	-----
vw	224	2.20	*vw*	-----	-----	-----	-----	-----	-----	-----
w	$22\bar{4}$	2.08	*mw*	-----	-----	-----	-----	-----	-----	-----
vw	034	2.06	-----	-----	2.06	2.07	2.08	-----	-----	-----
vw	421 420	1.92	*w*	-----	1.95	-----	1.96	-----	-----	-----
	-----	-----	*w*	-----	-----	-----	1.83	-----	-----	-----

6. SOL AND GEL RUBBER CRYSTALLIZED FROM SOLUTIONS

In earlier papers [21] to which reference has been made, crystals of sol and gel rubber which were produced from solutions of these fractions were shown to be fine needles. They were birefringent between crossed nicols, an indication of crystallinity in some system other than cubic. Their melting behavior was reported, their analysis conformed to the composition C_5H_8, and their refractive index was the same as that of uncrystallized rubber at the same temperature. They have now been investigated by X-rays to confirm their crystalline character.

The rubber was deposited on a Cellophane disk, about 2 cm in diameter, the upper surface of which was roughened with sandpaper to hold the deposit in place. The disks had been extracted previously with hot water and with hot alcohol to remove plasticizing agents. Crystals formed slowly from dilute solutions during 2 or 3 weeks at temperatures between −38 and −48° C. In this range of temperature the velocity of crystallization is suitably repressed. The deposit was washed once with ether at −60° C, and transferred to cold 95-percent ethyl alcohol, in which it was shipped from the National Bureau of Standards to the University of Illinois, surrounded by solid carbon dioxide. At low temperatures the fluidity of ethyl alcohol is quite low, so that there was little splashing and the deposit usually adhered to the disk. At the University of Illinois, the specimen was kept cold by suspending over liquid air in a vacuum flask until the X-ray exposure could be made.

The flat-film camera maintained specimens at temperatures between −20 and −40° C during exposure. The camera, pinhole, specimen holders, and forceps were cooled by solid carbon dioxide and acetone. With the cooled forceps the specimen was transferred to a piece of porous plate placed upon solid carbon dioxide, and much of the alcohol was removed. Sometimes, especially in the early trials, the specimen was also covered by a celluloid disk. In the final experiments, no disk was used, and the specimen was simply spread over the pinhole. This had a diameter of 0.01 cm. The camera was properly aligned with the X-ray tube to give a beam of maximum intensity, before the film was inserted. The exposures required about 10 hours.

After considerable experimentation with crystalline sol a diffraction pattern was finally obtained which was reproduced several times and which definitely showed faint crystalline interferences, not suitable for accurate measurement and analysis, but confirming the crystalline nature of the specimen. The crystalline material is sometimes more compact than at other times. With the crystalline gel, powder patterns were obtained with specimens *R*38 and *R*39, which are reproduced in figure 10. Many trials were made before the proper conditions were established. It is hardly necessary to emphasize the extraordinary experimental difficulties involved in work of this kind.

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[21] See footnote 12.

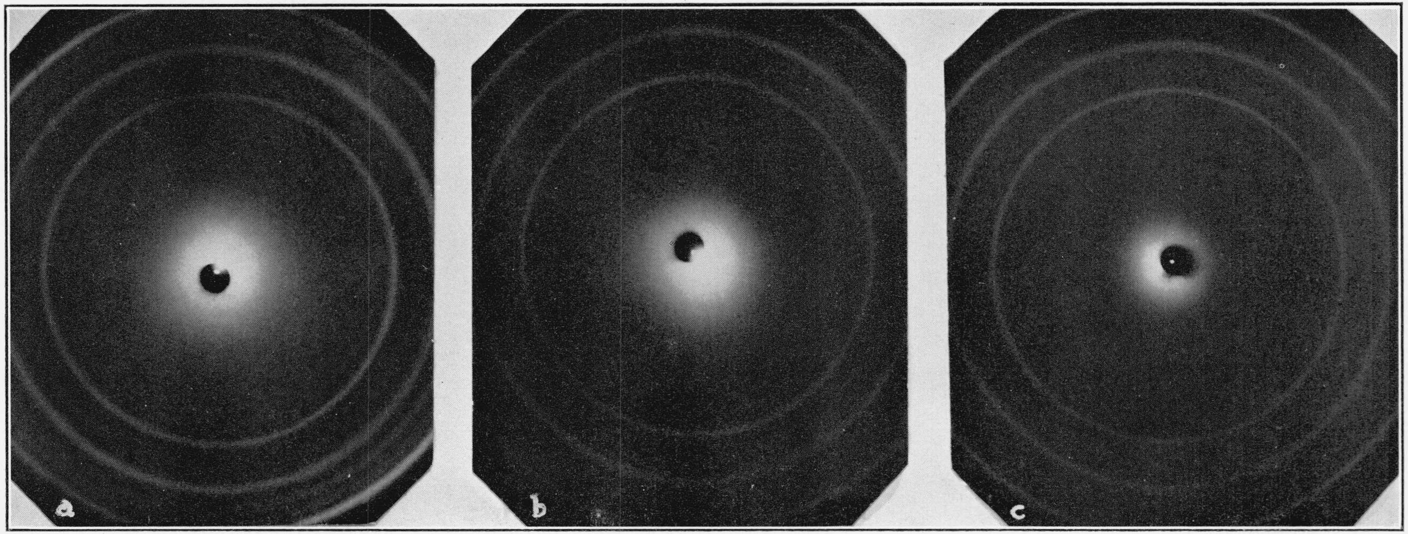

Figure 8.—*Frozen specimens.*

a, sol *R20*; b, gel *R22*; c, total, *R24*. Flat-film camera. Exposures 8 to 11 hours.

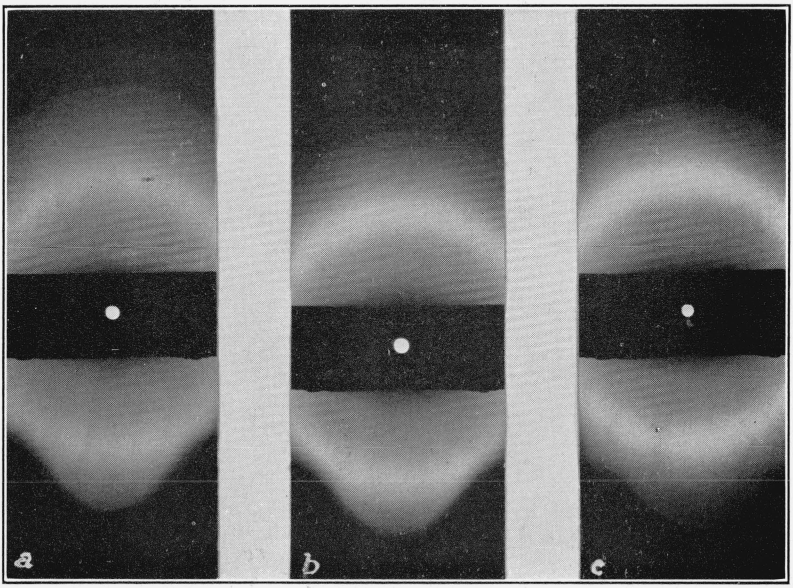

FIGURE 9.—*Specimens at room temperature.*

a, sol *R33*; b, gel *R32*; c, total *R36*. Cylindrical camera. Exposure 5 hours.

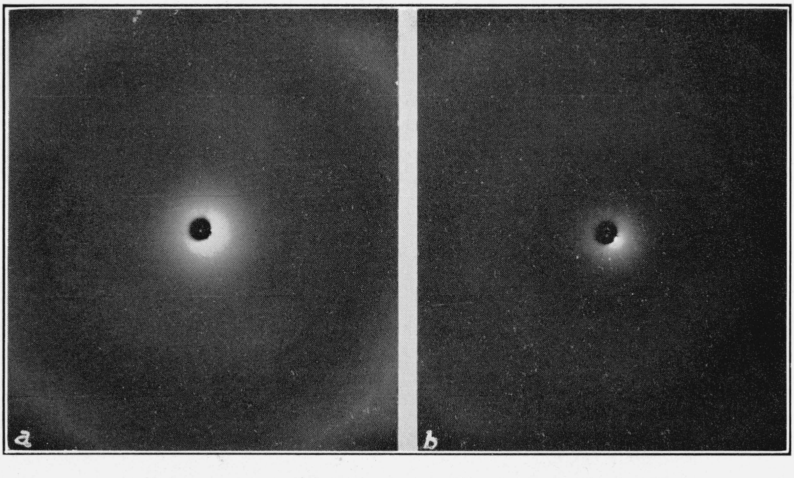

FIGURE 10.—*Gel rubber crystallized from solution.*

a, *R38*, exposure 11 hours; b, *R39*, exposure 14½ hours.

When the data in table 6 are compared with those obtained with frozen rubber, an excellent agreement is found for the three strongest interferences. There is no doubt therefore that the material is truly crystalline, and that the structures of the crystals are identical with those of crystals which form in massive, frozen rubber.

TABLE 6.—*X-ray diffraction data on crystallized gel rubber; see figure 10*

[Distance from specimen to film 10.32 cm.]

*R*38			*R*39		
R (cm)	*θ*	*d*	*R* (cm)	*θ*	*d*
		A			A
2.65	7° 12′	6.14	2.62	7° 7.5′	6.19
3.33	8°56.5′	4.95	3.31	8°53.5′	4.97
4.06	10° 44′	4.13	4.04	10°41.5′	4.14

IV. SUMMARY

Sol, gel, and total rubber were prepared by a method which avoided the effects of light and oxygen. The total rubber when stretched and exposed to an X-ray beam behaved like other specimens and produced the characteristic crystal fiber pattern. Stretched sol rubber produced no evidence whatever of this pattern, even at 1,000 percent elongation. With stretched gel rubber, the pattern was formed above 100 percent elongation, and at 200 percent was sharp and intense. The measurements of interplanar spacings agree excellently with the results reported recently by Lotmar and Meyer.

A large, interplanar spacing of 54 A was found in the unstretched gel. It was absent in the sol.

Specimens of frozen sol, gel, and total rubber were examined with a cylindrical, and with a flat-film camera, to compare the spacings and intensities with those of stretched gel. Within experimental error, sol, gel, and total rubber produce similar patterns. The spacings are similar to those in stretched rubber, with the exception of the (002) spacing in frozen rubber, which is 6.18 A instead of 6.30 A, the value in stretched rubber.

The pattern of gel, crystallized from solution, is similar to those of stretched and frozen rubber.

We appreciate the cooperation of L. G. Polhamus, Bureau of Plant Industry, U. S. Department of Agriculture, who supplied latex of authentic origin.

WASHINGTON, July 15, 1937.