dioxane of crystallization. After two recrystallizations from 70% alcohol, the melting range was 225.2° (first softening), 226.6° (first meniscus), 228.1° (final melting). This value was unchanged by recrystallization from 30% acetic acid, diacetone alcohol, and 70% alcohol. On the Dennis block, the material melted at 230.5° when placed on the hot bar or at 229.0° when warmed from room temperature. When a sample was heated at 230° for five minutes, then remelted, the range was 190.0–227.5°, indicating thermal decomposition.

Anal. Calcd. for $C_{13}H_{13}O_3N_3S$: C, 53.59; H, 4.50; N, 14.43; S, 11.00. Found: C, 53.47; H, 4.56; N, 14.53; S, 10.95.

The condensation was also run in pyridine in which case equimolecular amounts of 2-aminopyridine and N-acetylsulfanilyl chloride were used. The crude product so obtained contained a yellow impurity which was difficult to remove.

2-Sulfanilamidopyridine.—The acetyl derivative was hydrolyzed by boiling 29.1 g. (0.1 mole) with 10 g. (0.25 mole) of sodium hydroxide and 150 cc. of water for two hours. The excess sodium hydroxide was neutralized to *p*H 11, activated charcoal was added, and the hot mixture clarified, giving a colorless solution. On acidifying to *p*H 6, 23.1 g. of colorless crystals was obtained equal to 92.5%.

After two recrystallizations from 70% alcohol, the compound had the properties noted above, which remained unchanged on further recrystallizations from alcohol and chlorobenzene.

Hydrolysis of 2-Sulfanilamidopyridine.—Seventy-five grams (0.3 mole) of 2-sulfanilamidopyridine was boiled with 300 cc. of concentrated hydrochloric acid for one hour. After twenty min. crystals started to separate. The mixture was cooled to 15°, the crystals filtered, and washed with a little cold water; weight of crystals: 46.7 g. Titration by nitrite gave 100.2% purity, calculated as sulfanilic acid. The material decomposed gradually above 300°.

The mother liquor was evaporated to 50 cc. and a little more sulfanilic acid removed. Sodium hydroxide was then added in great excess and the oil layer separated. The aqueous layer was extracted with toluene. The toluene extract combined with the oil was dried over solid sodium hydroxide and distilled. The cut from 205 to 212° amounted to 21.0 g., with 2.0 g. of forerun and 1.3 g. of still residue; the total was 24.3 g. or 86% calculated as 2-aminopyridine. The setting point of the main cut was 57.9°, unchanged by admixture with 2-aminopyridine. The material did not resemble ordinary 2-aminopyridine in odor when freshly distilled, but on standing in the air for twenty-four hours the normal odor returned.

The aqueous mother liquors were titrated with sodium nitrite and accounted for 2.7 g. calculated as sulfanilic acid. Total recovery was 49.4 g. or 95.4%.

Melting Range Behavior.—Capillary melting ranges were determined by immersing the tube in a bath preheated to 180°. The values given are corrected. No difference was noted in melting range through use of sealed tubes filled with nitrogen. Some decomposition occurred on melting, as shown by heating a sample at 193° for five minutes in air and in nitrogen. The resulting melting ranges then were: sample melted in air, 154.0–184.5–189.9°; sample melted in nitrogen, 165.0–186.0–190.5°. This would indicate that decomposition on melting was both thermal and oxidative.

Summary

1. The preparation of 2-sulfanilamidopyridine and its physical and chemical properties are described.

2. Evidence in favor of the accepted formula for this compound is given.

BOUND BROOK, N. J. RECEIVED NOVEMBER 16, 1939

[CONTRIBUTION FROM RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO]

X-Ray and Optical Properties of Built-up Films

BY SEYMOUR BERNSTEIN

The discrepancy of about 3.6% between X-ray and optical measurements of the thickness per layer of barium–copper stearate films has been reported by C. Holley and S. Bernstein[1] and by C. Holley.[2] Investigations of refraction corrections in the X-ray measurements and possible phase change corrections in the optical measurements show that these cannot account for the discrepancy. Further investigation indicates that the discrepancy must be explained in terms of the structure of the films.

Phase Changes on Reflection

The film thicknesses were measured optically by measuring the fringe displacement between a step of 100 layers to 1000 or more layers of film deposited on an optical flat, as described by Mr. Holley.[2] In order to determine whether the phase change on reflection from the surface of the 100 layer portion was different from the phase change on reflection from the surface of the thicker portion of the films, a 1900-100 layer film was coated with aluminum by evaporation. Before having been covered with aluminum the

---

(1) C. Holley and S. Bernstein, *Phys. Rev.*, **52**, 525 (1937).

(2) C. Holley, *ibid.*, **53**, 534 (1938).

TABLE I

OPTICAL AND X-RAY MEASUREMENTS OF FILM THICKNESS

Film no.	Type	No. of layers	Average $\delta \times 10^6$	d_0, Å.	d_r, Å.	$d_0 - d_r$, Å.
1	Ba-Cu stearate	1100-100	5.1	48.57	50.45	−1.88
2	Ba-Cu stearate	1100-100	4.3	48.44	50.25	−1.81
3	Cu stearate	328	...	47.82	47.20	0.62
4	Cu stearate	1100-100	5.9	46.91	46.38	.53
5	Cu stearate	1100-100	4.7	47.67	46.91	.76
6	Cu stearate	404	...	48.08	47.15	.93
7	Ba stearate	319	6.1	48.52	49.92	−1.40
8	Ba stearate	316	...	48.19	50.30	−2.11
9	Pb arachidate	300	6.1	...	56.26	...

displacement between the 100 layer and the 1900 layer portion was an integral number of fringes, that is, the fringes were continuous across the boundary between the two portions. The fringes were continuous also after the film had been covered with aluminum. Since the total displacement was sixteen whole fringes, to account for the discrepancy of 3.6% the fringes from the thick and thin portions of the film should have shifted relative to each other by more than half a fringe. If the assumption is made that the thickness of aluminum on the thick and thin portions of the film was the same, then the fact that no shift of fringes was observed indicates that the discrepancy could not be due to phase changes on reflection.

Optical and X-Ray Measurements

The results of the film measurements are given in Table I. All of the films of Table I were kindly built for the writer by Dr. Katharine B. Blodgett of the General Electric Company. In Table I, d_0 denotes the thickness of a double layer as determined optically. All of the films of less than 1000 layers in thickness were measured[3] by Dr. Blodgett with an optical spectrometer. Films 1 and 2 were measured optically by C. Holley with the interferometer method described by him.[2] Films 4 and 5 were measured optically with the interferometer by the author. All of the X-ray measurements given in Table I were also made by the author. The symbol d_r used in Table I denotes the grating-space of the films, corrected for refraction and based upon the ruled grating wave length scale.

The X-ray apparatus used has been described by Mr. C. Holley.[2] The X-ray measurements were made by two methods. (1) The X-ray lines were reflected on both sides of the direct beam and the glancing angles determined from the distance between two corresponding orders and the distance from the axis of rotation to the photographic plate. (2) X-Ray reflections from the film were matched against those from a gypsum crystal. With the film used as the crystal, a photograph was taken of the fifth-order tungsten $L\alpha_1$ line, for example. The film was then replaced by a gypsum crystal and a photograph taken of the first order tungsten $L\gamma_1$ line. The photographic plate remained in the same position during the two exposures. The glancing angle of the $L\alpha_1$ line from the film was then determined from the known glancing angle of the reference line reflected from gypsum, by use of the distance between the lines, measured on the photographic plate and the distance from the plate to the axis of rotation of the crystal. The time of exposure for both methods was about three hours per order.

The index of refraction of the films for X-rays was determined from the absolute measurements of the first method by use of the apparent grating-spaces in the different orders according to the method of Stenstrom.[4]

The experimentally determined value of the unit decrement, δ, for all of the films was found to be more than 1.5 times as great as the value 3.4×10^{-6} calculated by Lorentz dispersion theory from the density measurements of barium–copper stearate films determined by R. W. Mattoon. This discrepancy between the observed and calculated index of refraction cannot account for the discrepancy between X-ray and optical measurements of the grating-space because the entire correction for refraction in the fifth order of the tungsten $L\alpha_1$ line amounts to only 0.3%.

The optical measurement given in Table I for Film 4 is the result of 200 measurements of the fractional part of a fringe, made before the film was exposed to X-rays. The measurement shown for Film 5 is the result of two sets of 200 measure-

---

(3) K. B. Blodgett, THIS JOURNAL, 57, 1007 (1935).

(4) Compton and Allison, "X-Rays in Theory and Experiment," p. 280.

ments of the fractional part of a fringe, one set of 200 measurements having been taken before, and one set after, exposing the film to X-rays. The average of one set of measurements was the same as the average of the other set to 0.01 fringe. The total number of fringes for Films 3 and 4 was eight.

From Table I, the following conclusions can be made. (1) The X-ray grating-space is greater than the optically measured thickness of a double-layer for barium–stearate and barium–copper stearate films; for copper stearate films the optical measurement is the greater. (2) For barium stearate and barium–copper stearate films the difference between the X-ray and optical measurements is about 3.5%; for copper stearate films this difference is about 0.7%.

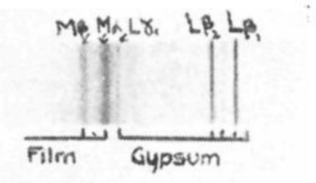

Fig. 1.—Barium stearate.

Fig. 2.—Barium stearate.

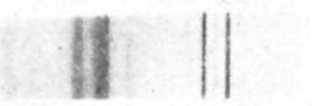

Fig. 3.—Barium–copper stearate.

Fig. 4.—Barium–copper stearate.

Fig. 5.—Copper stearate.

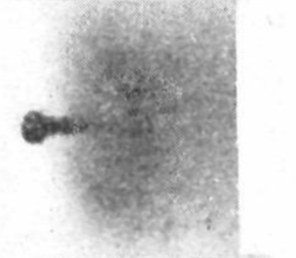

Fig. 6.—Rotation photograph of metal stearate film.

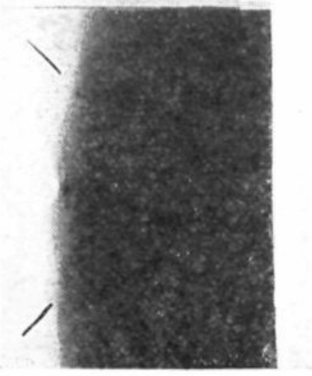

Fig. 7.—Rotation photograph of ethyl stearate film.

Variation of Measurements with Film Composition.—Measurements of a set of films of varying proportions of barium stearate and copper stearate show that although a change in film thickness measured optically is accompanied by a change in X-ray measured thickness of the same sign, there is no close correspondence between the magnitudes of changes in the optical and X-ray measurements of film thickness.

TABLE II

Fig.	Film no.	Barium acetate, M	$KHCO_3$, M	Copper acetate, M	KCN, M
1	7	10^{-4}	....	......	....
2	10	10^{-4}	2×10^{-4}	......	5×10^{-4}
3	11	10^{-4}	2×10^{-4}	3.5×10^{-6}	....
4	12	0.3×10^{-4}	2×10^{-4}	3.5×10^{-6}	....
5	3	......	....	10^{-4}	....

The variation of X-ray grating-space with film composition can be observed in Figs. 1, 2, 3, 4, and 5. The solutions used by Dr. Blodgett in building the films with which these photographs were taken are given in Table II. Corresponding optical and X-ray measurements were made for Film 7 of Fig. 1 and Film 3 of Fig. 5. In going from the pure barium stearate film of Fig. 1 to the pure copper stearate film of Fig. 5, the X-ray grating-space decreases from 49.92 to 47.20 Å., a difference of 5.5%; while the optical measurement of the thickness of a double layer decreases from 48.52 to 47.82 Å., a decrease of approximately 1.5%. The X-ray and optically measured thicknesses both decrease with increasing copper content and with simultaneously decreasing barium content, but the X-ray grating-space decreases at a much greater rate.

Skeletonized Films.—Dr. Blodgett and Dr. Irving Langmuir have described the process of skeletonizing a film.[5] After a film is built it is dipped into benzene. That portion of the film which consists of pure stearic acid is dissolved by the benzene; the portion which consists of metal stearate remains on the slide. If the proportion of stearic acid in the film is too high the film collapses. If the proportion of stearic acid is not too high the optically measured film thickness changes by only 1 or 2%.

X-Ray measurements were made of a skeletonized and an unskeletonized film of lead arachidate. The two films were built by Dr. Blodgett at the same time from the same solution, after which one of them was dipped into benzene for one minute. According to Dr. Blodgett a test film made from the same solution showed that 40% of the material had been removed by soaking

(5) K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 980 (1937).

the film in benzene for one minute and that a change in thickness of 1 or 2% had taken place. The X-ray measurements for the two films are given in Table III. These measurements show that the grating-spaces of the skeletonized and unskeletonized films are the same within experimental error. The relative intensities of the first three orders for the two films were also the same.

TABLE III

COMPARISON OF GRATING-SPACES OF A SKELETONIZED AND AN UNSKELETONIZED FILM

	Distances in cm.		
	1R to 1L	2R to 2L	3R to 3L
Unskeletonized film	3.207	6.285	9.382
Skeletonized film	3.204	6.287	9.387
Difference, %	−0.1	+0.04	+0.05

In Table III, the values given are the distances measured on the plate from a given order of $WL\alpha_1$ line on one side of the direct beam to the same order on the opposite side of the direct beam. Thus 1R to 1L denotes the distance from the first order $L\alpha_1$ line on one side of the beam to the first order $L\alpha_1$ line on the opposite side of the direct beam.

This identity of the grating-spaces of the skeletonized and unskeletonized films seems to indicate that the X-ray photographs give a measure of the grating-space of crystals of metal stearate contained within the films, and that such a measurement should not be compared with an optical measurement of the film thickness.

Rotation Photographs of Metal Stearate Films.—The zero layer-line reflections from which the grating-space measurements of Table I were made have shown that the films have a regular arrangement of molecules in a direction perpendicular to the surface upon which they are built. The question arises as to whether or not the films have regular arrangements of molecules in planes parallel to the surface on which they are built.

Figure 6 is a rotation photograph taken with one of the barium–copper stearate films. Only the zero layer-line reflections appear. The background is badly fogged because of scattering from the glass plate upon which the films were built. However, it may be concluded that either reflections on layer-lines other than the zero layer-line are very much weaker than the zero layer-line reflections or that they do not appear at all. The fact that they do not appear would indicate that the films do not have a regular arrangement over an appreciable area in planes inclined at an angle to the surface of the slides upon which the films are built or in planes parallel to these surfaces. Every one of several other films of barium–copper stearate, copper stearate, and barium stearate also showed only zero layer-line reflections.

Suggested Structure of Metal Stearate Films.—The following film structure is suggested as one which is consistent with the results described above.

The film consists of many small crystals of metal stearate embedded in a matrix of amorphous stearic acid or stearic acid crystals. These crystals of metal stearate all have the same, or nearly the same, orientation in a direction perpendicular to the slide upon which the film is built but have a random arrangement in planes parallel to the foundation surface. The X-ray measurements are a measure of the grating-space of the metal stearate crystals. The optical measurements are a statistical average of the thickness per layer.

The similarity in the X-ray photographs taken with X and Y films[6,7] indicates that the film structure is independent of the type of deposition.

The suggested film structure is also consistent with Dr. Langmuir's interpretation[8] of the contact potential measurements of Porter and Wyman.[9]

Films of Ethyl Stearate.—Stenhagen reported[10] the use of ethyl stearate, along with a number of other substances, in building films. These films differ from stearate films in that there is no question of degree of saturation. In the case of stearate films, the stearic acid on the water surface is partly changed to metal stearate by the metal ions in solution. In the case of ethyl stearate, if the *p*H of the water is not too low or too high, the ethyl stearate placed on the water surface is transferred unchanged to the slide.

Stenhagen found the following X-ray and optical values for ethyl stearate films: X-ray grating-space, 25.7 Å.; optical measurement of the thickness per layer, 28.0 ± 0.5 Å. The writer built several films of Eastman Kodak Company ethyl stearate and found the apparent X-ray grating-space in the second order to be 25.2 Å. Stenhagen, in his optical measurement, assumed that the index of refraction for ethyl stearate films is

---

(6) C. Holley and S. Bernstein, *Phys. Rev.*, **49**, 403 (1936).

(7) S. Bernstein, THIS JOURNAL, **60**, 1511 (1938).

(8) I. Langmuir, *ibid.*, **60**, 1190 (1938).

(9) E. F. Porter and J. Wyman, *ibid.*, **60**, 1083 (1938).

(10) E. Stenhagen, *Trans. Faraday Soc.*, **34**, 1328 (1938).

the same as the index for barium–copper stearate films. The average of the two X-ray measurements is about 9% less than the optical measurement. This difference cannot be due to Stenhagen's assumption of the equality of index of refraction of barium–copper stearate and ethyl stearate films.

The available evidence, then, seems to indicate that the discrepancy found for metal stearate films persists in the case of ethyl stearate films.

A rotation photograph taken with an ethyl stearate film differed from those of the metal stearate films in that reflections other than those of the zero layer-line appeared for the ethyl stearate film. The rotation photograph is shown in Fig. 7. The presence of these reflections indicates that in the case of ethyl stearate films all of the small crystals have the same orientation.

The suggestion that many small crystals form of themselves within the films is indicated also by the fact that the average of the two X-ray grating-space values for ethyl stearate is the same as the value for one of the natural crystalline forms of ethyl stearate found by T. Malkin.[11] Also, as Stenhagen already has pointed out,[10] these tiny crystals can be seen in the ethyl stearate films under a microscope.

The writer is greatly indebted to the following people for their help: To Dr. Katharine B. Blodgett of the General Electric Company for her coöperation. In addition to building many of the films and making optical measurements of some of them, Dr. Blodgett gave freely of her time to the discussion of the many problems which arose in the course of the investigation. To Professor Arthur H. Compton and Dr. Elmer Dershem for their careful guidance. To the Charles A. Coffin Foundation of the General Electric Company for the grant of a fellowship which enabled him to continue with the work.

Summary

X-Ray refraction corrections and possible optical phase change corrections fail to account for the discrepancy between X-ray and optical measurements of the thickness of built-up stearate films. The results indicate that the discrepancy must be explained in terms of the film structure. X-Ray measured thicknesses of barium–copper stearate and barium stearate films are greater than the corresponding optical measurements; X-ray measured thicknesses of copper stearate films are less than the corresponding optically measured thicknesses. Measurements of a set of barium–copper stearate films of varying proportions of barium stearate and copper stearate show that the film thickness varies greatly with film composition and that a change in X-ray measured thickness is not accompanied by a change in optically measured thickness of the same magnitude. Skeletonized and unskeletonized films of the same original composition were found to have the same X-ray grating-space. Metal stearate films give only zero layer-line reflections. An ethyl stearate film showed other than zero layer line reflections in addition to those of the zero layer line. A film structure is suggested which is consistent with the X-ray and optical measurements and with reported contact potential measurements.

CHICAGO, ILL. RECEIVED NOVEMBER 20, 1939

---

[11] T. Malkin, *J. Chem. Soc.*, 2796 (1931).