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On the Structure of Gold-Leaf, and the Absorption Spectrum of Gold

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II. *On the Structure of Gold-Leaf, and the Absorption Spectrum of Gold.*

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[PLATE 1.]

GOLD-leaf, as seen under the microscope by transmitted light, presents a remarkable appearance which seems to have been hitherto either not at all or only slightly noticed. The colour of the transmitted light is bluish-green, unless silver in considerable proportion be alloyed with the gold; in this latter case the colour is purplish-blue. The amount of light transmitted is, as might be expected, not uniform, the thickness of the gold film varying within very small areas of the surface. All this is well known to anyone who has ever looked through a bit of the leaf.

But, in addition, numerous black lines are visible under very moderate amplification, ramifying irregularly over the surface, here and there showing some tendency to parallelism, but for the most part running into each other in the most irregular way. Fig. 1* illustrates this; it is a microscopic photograph of ordinary commercial gold-leaf, taken with an amplification of 75 diameters, and a distance from the eye-piece to the camera plate of 378 millims.

In FARADAY'S Bakerian lecture, read before the Royal Society on February 5, 1857, on the "Experimental Relations of Gold (and other metals) to Light,"† there occur two or three sentences which prove that this peculiar appearance did not escape his keen observation. For example, he says "when the thicker parts of the leaf were examined they seemed to be accumulated plications of the gold, the leaf appearing as a most irregular and crumpled object, with dark veins running across both the thicker and thinner parts, and from one to the other." Again, referring to specimens of gold-leaf which had been heated in oil, he says "it will be seen that it is the thicker folds and parts of the mottled mass that retain the original state longest." And again he remarks, "there is a little difficulty in admitting that such an irregular corrugated film as gold-leaf appears to be, can possess any general compression in one direction

* All of the microscopic photographs referred to in this paper have been presented to the Royal Society, but only Nos. 4, 6, and 8 have been reproduced for publication.

† 'Phil. Trans.,' 1857, pp. 145–181.

only." But FARADAY does not seem to have specially investigated the peculiarity in question, or its cause, and, in view of the process by which gold is extended into these thin films, the terms "plications" and "folds" which he uses must be understood as referring to the appearance only of the leaf and not to its actual structure.

The idea first suggested by the ramification and reticulation of black lines was that they might depend in some way on the crystalline structure of the alloyed gold used for making commercial gold-leaf, modified and distorted during the process of beating. Hence specimens of gold-leaf variously alloyed were compared with each other. The following samples were furnished me by the manufacturers, the W. H. Kemp Company, of 165, Spring Street, New York, with a statement of their composition :—

A. Dark or red gold-leaf, made with an addition of 18 grains of copper to each Troy ounce (480 grains) of pure gold, or, more strictly, gold assaying about 998–999 fine.

B. Gold-leaf of medium colour, made with an addition of 12 grains of copper and 12 grains of silver to each Troy ounce of fine gold.

C. Pale or light-coloured gold-leaf, made with an addition of 6 pennyweights (144 grains) of silver to the Troy ounce of fine gold.

Figs. 1, 2, and 3 show the appearance of these three samples respectively under the amplification already mentioned for No. 1, which represents the gold alloyed with copper only, No. 2 that containing both copper and silver, and No. 3 that containing silver only. The three exhibit some differences, but not much greater than are presented by different samples of leaf of the same composition, and the general character is evidently the same. In consequence of the small amount of light transmitted by the leaf, exposures of the photographic plates for two or three minutes were necessary, and changes in the state of the sky and character of the light during this time prevent the photographs giving quite a correct idea of the different degrees of translucency of the specimens. Owing probably to slight shaking of the floor affecting the position of the camera, the ramified lines do not appear quite as sharp and well defined as when viewed directly through the eye-piece of the microscope.

It was desirable to see whether the same appearance, if referable in any way to the original molecular structure of the metal, would present itself in leaf beaten from pure gold free from all alloy. On applying to two firms of gold-beaters—one in New York and the other in Philadelphia—to make for me a small quantity of leaf from fine gold, I was assured by both that it was impossible to beat pure gold thin enough to be seen through. Dentists' gold foil could be had, but it is quite opaque. The reasons assigned for the difficulty were the excessive tendency of the pure gold to cohere, so that it could not be manipulated without different parts touching each other and sticking together, and also the tendency of the pure metal to stick to the "gold-beaters' skin" or animal membrane used to separate the leaves in beating.

After a good deal of persuasion I succeeded in inducing the manager of the W. H. Kemp Company—Mr. W. R. HANNA—to try the experiment of beating into leaf, as thin as could be had, a sample of fine gold which I sent him. This was "proof gold" from the assay department of the United States Mint at Philadelphia, and therefore of the highest attainable purity. The result was quite satisfactory for the intended purpose, though it would not have been so in a commercial sense, there being a good deal of waste, and many torn leaves and large holes. The microscopic appearance of this pure gold-leaf is shown in fig. 4 (Plate 1). It is in general like the commercial specimens, but the lines are bolder and more strongly defined—a consequence, as I think will be shown, of the greater softness of the pure metal.

Study of these microscopic appearances, and comparison of them with each other and with the micro-photographs of OSMOND, ROBERTS-AUSTEN, ARNOLD, ANDREWS and others, did not seem to support the idea that the lines in question are due to more or less distorted crystalline structure. In order to learn whether the lines are to be referred to, and originate in, the process of gold-beating by which the leaves have been produced, the attempt was made to obtain galvanically-deposited films of something like the same thickness, so that these latter might be microscopically examined by transmitted light.

Pieces of thin rolled silver foil, much larger than would be needed for microscopical examination only, were varnished on one side and then electrolytically coated with fine gold on the other, using a specially prepared pure cyanide solution and an anode of fine gold. As there was no guide by which to determine in advance the thickness of the gold film which would admit of being satisfactorily seen through, the current was passed for various periods of time, producing films of several different thicknesses, and, after the subsequent treatment, one or two were selected which gave the best results. About a square centimetre cut from each piece of foil was well washed with ether to free it from varnish, and was then cemented—the gilded face downwards—upon a slide of thin microscope cover glass by means of Canada balsam somewhat diluted with ether. After time had been afforded for the balsam to harden, the silver was dissolved off slowly by very dilute nitric acid, and the gold film was ready for microscopic examination. Fig. 5 shows the appearance presented, the amplification and distance from eye-piece to camera plate being the same as for fig. 1 and for all the other microscopic illustrations of this paper. It is evident that the mottled structure of this film, showing varying thickness, is unaccompanied by the ramifications of well defined black lines to be seen in beaten gold-leaf. No attention should be given to the two large bars of shadow crossing each other at right angles in this photograph; they are due to the shadow of a part of the window sash having been inadvertently allowed to fall on the illuminating mirror of the microscope.

To test whether the black lines are really due to minute threads or wires of gold with diameters considerably greater than the thickness of those parts of the leaf which can be seen through, it was proposed to protect a piece of gold-leaf by placing it between two sheets of silver foil, roll the whole down to a fraction of the original thickness, remove the silver by means of nitric acid, and see whether the lines in the gold had been broadened out by flattening of the wire-like threads if present. A rectangular piece of fine silver foil, ·019 millim. thick, was folded in two across the middle of its length, a piece of the "fine" gold-leaf which had been specially beaten for me by the W. H. Kemp Company was spread out flat between the two folds of silver, and then by the same firm the whole rolled down until the double thickness, ·038 millim., had been reduced to ·006 millim. Care was taken to introduce the folded edge first between the rolls, so as to prevent as far as possible slipping of one surface of foil upon the other. Examination with nitric acid of different parts of the rolled-down foil showed that, although there had been no small tearing of the gold and many holes had been produced in it, there were quite sufficient areas of it left in a practically continuous state. Assuming that the gold had been rolled out *pari passu* with the silver, each had been reduced to something like one-sixth or one-seventh of the original thickness.

A small piece of the foil in this condition was varnished on one side, and the other side stripped of silver by very dilute nitric acid. A number of specimens were spoiled at this stage, since the acid getting through any holes would attack the silver on the other side and eat its way between the varnish and the gold film, which was so exceedingly thin as not to bear any manipulation when unsupported. A few good specimens, however, were secured. These were cleared of varnish by soaking in ether, cemented by the gold face with diluted Canada balsam to slips of thin microscope cover glass, and, after hardening of the balsam, the second film of silver was gradually removed by very dilute nitric acid. Fig. 6 (Plate 1), representing, under the same amplification as in the other figures, the microscopic appearance of one of these specimens of rolled-down pure gold-leaf, exhibits very distinctly the flattening out of the minute metallic threads, favoured by the greater softness of the gold than of the silver which enclosed it.

As a further test of the black lines being due to minute wires or threads of gold, specimens of the fine gold-leaf were thinned down by partial solution, in order to see whether the lines would remain visible longer than the general surface of the leaf, and the thicker lines longer than the more delicate. The solvent used was a $\frac{1}{2}$ per cent. aqueous solution of potassium cyanide, to which had been added a little hydrogen dioxide. The result is shown in fig. 7, and in fig. 8 (Plate 1), the former of these representing a less, and the latter a more, advanced stage of the solvent attack upon the leaf. The more gradual obliteration of the black lines than of the rest of the surface is quite apparent.

As it seemed to be established that the black lines under examination represent microscopic threads or wires, and that these are developed in the gold during the process of beating, it was natural to look for their possible origin in some corresponding peculiarity of structure in the "gold-beaters' skin" or animal membrane between sheets of which the leaves of gold are extended. But this idea is not borne out by microscopic study of that material. The thin gold foil with which the process is begun is first beaten for about twenty minutes only between surfaces of "cutch" paper, which has simply the structure of a felted mass of vegetable fibres. The principal extension of the gold is brought about by beating for about four hours in a "shoder" or packet of leaves of old or previously often used gold-beaters' skin, the packet, containing a thousand leaves, being from time to time bent between the fingers to loosen the gold films and prevent their sticking to the membrane, and finally by beating for another four hours in a "mould" or similarly made up packet of leaves of new or much less used gold-beaters' skin, repeating the bending of the packet to maintain the looseness of the gold films. The cutch is beaten with hammers of about sixteen pounds in weight, striking about sixty blows a minute, the shoder with hammers of about ten pounds and at the rate of about seventy-five blows per minute, and the mould with six-pound hammers and at the rate of about ninety blows per minute. Figs. 9, 10, and 11 represent respectively the cutch paper, the already much used gold-beaters' skin of the shoder, and the new, or nearly new, skin of the mould. There is nothing in any of these to account for the black lines seen in the gold-leaf. As far as any distant resemblance to these is suggested by some of the vegetable fibres in fig. 9, it is to be remembered that fibres in relief would produce in the gold corresponding furrows, appearing as lines of greater, not less, translucency than that of the rest of the surface. The animal membrane or gold-beaters' skin in which by far the greater part of the beating is done, including all the later part of the work, exhibits in figs. 10 and 11 the simple and nearly uniform structure of the serous coat of the intestine—said to be the cæcum—of the ox which is used for the purpose.

A careful personal inspection of the process of gold-beating at the establishment of the W. H. Kemp Company in New York, has led me to the belief that the production of the ramified lines of microscopic wires or threads in the gold-leaf is due to the following cause. The face of the hammer used is slightly convex, and hence a blow struck with it tends to stretch each sheet of gold, and the animal membrane enclosing it, outwards in all directions from the centre of impact. The membrane is elastic and not absolutely uniform in thickness or tensile strength. Hence it tends to form, along lines of weakness, wrinkles running irregularly outwards, such as may be produced in any stretched piece of cloth by a push of the finger in any given direction. These wrinkles constitute microscopic troughs or furrows into which the soft gold is driven, forming corresponding rods or wires of extremely minute size. The elasticity of the membrane leads to the momentarily developed wrinkles being almost instantly obliterated, while the plasticity of the gold admits of no corresponding disappearance of the wire-like threads produced. The complicated ramification of the lines is no doubt due in part to the irregular distribution of lines of weakness, and therefore of easy stretching, in the membrane, partly to the blows of the hammer falling in rapid succession upon different adjacent parts of the surface, and partly to the lack of uniformity of support given by the other leaves above and below in the packet. The view now stated receives confirmation from a point strongly insisted upon by Mr. HANNA—the very intelligent superintendent of the W. H. Kemp Company's workshops—namely, that for success in the gold-beating process much depends on the condition of the animal membrane as to moisture or dryness. If it be very dry the gold-leaf cracks or breaks, while if the membrane be too moist the leaf sticks to it. The membrane requires to be dried or dampened to correct the opposite effects of change in the atmosphere. This accords with the idea that a certain amount of elastic stretching of the membrane, from which this recovers, is necessary for the permanent or inelastic extension of the gold. In fact, as the area of the gold-leaf is permanently extended by the beating, while that of the membrane is not, the one film manifestly must slide over the other. It is scarcely conceivable that this sliding shall occur at the moment at which a blow falls, when friction between the surfaces is at a maximum If not, it must occur just afterwards, as a result of the elastic resilience of the membrane, which leaves behind it the plastic gold.

It is evident that the statements to be found in the books as to the actual thickness of gold-leaf—based as they are upon weighing of measured areas—represent only *average* thickness, and that, in view of the decidedly greater thickness of these microscopic threads of gold running through the mass than of the intervening parts, the thickness of these latter parts must be notably less than the average. The following determinations were carefully made with several square decimetres of leaf in each case, accurately measured as to area, and weighed on a delicate assay balance. The results are stated in "microns" (thousandths of a millimetre).

		Average thickness.
Commercial gold-leaf, alloyed with copper only, represented by Fig.	1	·0797μ
,, ,, ,, copper and silver ,, ,,	2	·0822μ
,, ,, ,, silver only ,, ,,	3	·0937μ
Gold-leaf specially beaten from "fine" gold ,, ,,	4	·1082μ
A galvanically deposited film of "fine" gold ,, ,,	5	·1263μ
Maximum thickness of "fine" gold film which can be seen through—about		·2000μ
Dentists' "fine" gold foil		·9228μ

In connection with the microscopic examination of gold films by transmitted light, it seemed to be interesting to make some observations on the absorption spectrum of the metal, especially as there have been recently published the results of spectroscopic study of the light which the metal reflects.

It was proposed to examine for this purpose metallic gold in the following forms :—

1. Pure or "fine" gold-leaf.

2. Gold chemically reduced in a dilute aqueous solution of its chloride—so-called colloidal gold—the metal being in sufficient quantity and state of aggregation to transmit greenish-blue light.
3. Ditto, a less amount of more finely distributed gold transmitting ruby-red light.
4. Glass coloured by gold so as to transmit greenish-blue light—the so-called saphirine glass.
5. Glass coloured ruby-red by very finely divided gold.

It was found to be impracticable to secure any result for the gold-leaf, on account of the very small amount of light transmitted. For the colloidal gold in water, and the gold-coloured glass, the following results were obtained.

Visible Spectrum.

The source of light was a strong electric arc between closely placed carbon poles, with a slit of about $\frac{1}{2}$ millim. in width. Dispersion was obtained by a Rowland concave grating of 21·5 feet focal length, ruled with about 15,000 lines to the inch, using the spectrum of the first order. The photographs were taken on M. A. Seed dry plates ("orthochromatic, L"), specially sensitized for the region from green to red inclusive. The original photographs were laid side by side, so that the positions of like wave-lengths were the same for all, and then re-photographed together on a reduced scale. The results are shown in fig. 12, with a few positions indicated in Ångström units.

Taking the strips in order from the top downwards, the first (uppermost) strip represents the light transmitted simply through a sheet, about 2 millims. thick, of colourless glass of the same kind as that on which the gold ruby-red is "flashed," and which also formed the end plates of cells containing the colloidal gold in aqueous suspension—time of exposure about 2 minutes—the darkness at the less refrangible end is due, not to absorption, but to the insensitiveness of the photographic film for rays in this region. The second strip shows the effect of transmission through a column of water, 2·25 centims. long, containing 75 milligs. of metallic gold to the litre, reduced from the chloride by potassium acid carbonate and formic aldehyde, and exhibiting dark greenish-blue colour—time of exposure 30 minutes. The third represents also colloidal gold in watery suspension, but in a column of 9·25 centims. long, with 50 milligs. of gold per litre, and showing a blue or slightly violet-blue colour—time of exposure 20 minutes. The fourth represents the same, in a column of same length as the last, but with only 20 milligs. of gold per litre, and showing a clear ruby-red colour—time of exposure 10 minutes. The fifth, shifted over to the right to secure correspondence of position for equal wave-lengths, is the same as the first, but with shorter exposure; the right-hand end is in the region of slight sensitiveness of the film. The sixth (lowermost) strip shows the result of transmission through the "flashed" ruby-red glass, with very long exposure—1 hour and 10 minutes.

In these photographs there is no indication of well defined absorption bands. The general absorption belongs mainly to the middle portion of the spectrum, and is, on the whole, more marked at the less refrangible end, with notable increase of absorption in this region as the amount of gold present is increased. The position of maximum absorption is nearer to the long-wave end for the glass than for the colloidal gold in water. It is interesting to note that, while no photographed results could be obtained from the saphirine glass, the absorption being too far in the red for the sensitiveness of the film, eye observation of this glass, using sunlight and a glass-prism spectroscope, showed a distinct belt of absorption extending from about 5700 to 6250, beside the general absorption of rays of shorter wave-length. Allowance has to be made in the photographs for insensitiveness of the film at the red end of the spectrum.

Ultra-violet Spectrum.

This was examined with a quartz prism, and for the liquids a tube closed at the ends by plates of quartz. The source of light was electric sparks between cadmium poles placed pretty near each other. The results are shown in figs. 13, 14 and 15, a few of the positions being indicated by the wave-lengths of the cadmium lines, as before. No results could be obtained for the saphirine or the ruby glass, the glass alone absorbing all rays in the ultra violet. Fig. 13 represents the water with colloidal gold in suspension, 75 milligs. to the litre, in a column of 2·25 centims. long. Fig. 14 represents a like liquid, with 50 milligs. per litre, and in a column 9·25 centims. long. Fig. 15 is the same, with 20 milligs. per litre, and in a column also 9·25 centims. long.

In each of these three figures the three uppermost strips represent exposures for 3, 5 and 10 *minutes* respectively (counting from above downwards), the light passing through the colloidal gold liquid, while the four lower strips exhibit the results from sparks through air (no gold liquid interposed) for 1, 2, 5 and 10 *seconds* respectively. The general absorption, without indication of dark bands, begins to be well marked at about 3500, and increases toward the more refrangible portion of the spectrum, the effect increasing also with the amount of gold present.

Infra-red Spectrum.

This was examined, by the obliging permission of Professor S. P. LANGLEY, Secretary of the Smithsonian Institution, Washington, D.C., in the astrophysical laboratory of that institution, using sunlight, a rock-salt prism, and Professor

LANGLEY'S bolometer with photographic auto-registration of the results. These results were in general as follows :—

The specimen of ruby-red gold glass almost totally absorbs the light of the short-wave-length side of D, rapidly increases to the full transparency of the ordinary colourless (unflashed) glass at about A, and continues as transparent as this ordinary glass to about $2{\cdot}5\mu$. The saphirine or blue glass coloured by gold, cuts off the light to near C, then rises very rapidly to great transparency at and beyond A.

The red colloidal gold liquid No. 1, 20 milligs. metallic gold per litre, contained in a cell with end plates of thin microscope glass, 4·5 centims. apart, produces great general absorption in the visible spectrum, though not reaching to the point of completely, or almost completely, extinguishing any rays included within the region of spectrum studied, as was the case with the glass specimens. The absorption of this liquid becomes practically identical with that of distilled water at and beyond A.

The violet-blue colloidal gold liquid No. 2, 50 milligs. gold per litre, and the greenish-blue liquid No. 3, 75 milligs. gold per litre, behave on the whole like liquid No. 1, except that they diminish the radiations throughout the spectrum to a very great extent, as if by the interposition of opaque obstacles to the rays. Liquid No. 3 appears relatively less transparent in the visible spectrum, besides being generally less transparent throughout the spectrum.

I regret that the blue-print tracings of the bolometer curves are so faint as not to allow of photographic reproduction on a reduced scale.

For the microscopic and spectroscopic photographs I have to thank the kind assistance of Professor A. H. TUTTLE and Dr. W. J. HUMPHREYS of this University.

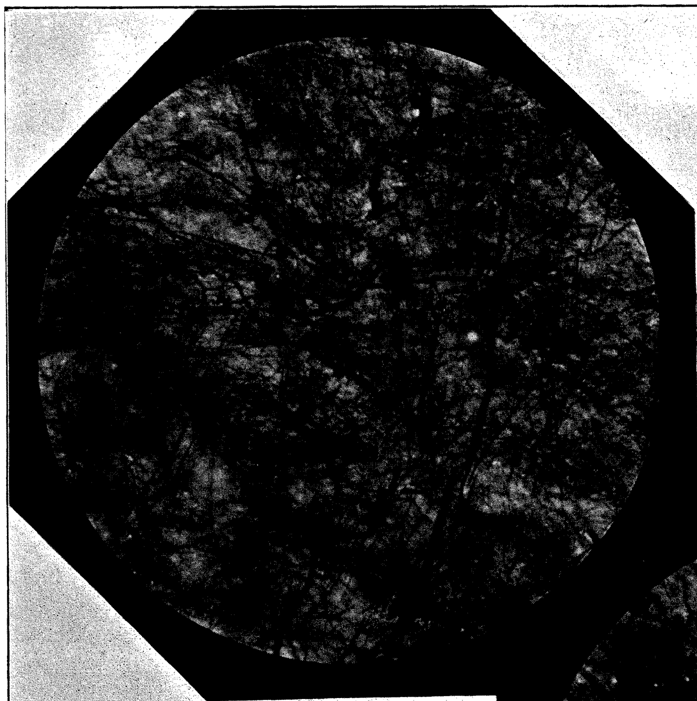

Fig. 4.

Fig. 6.

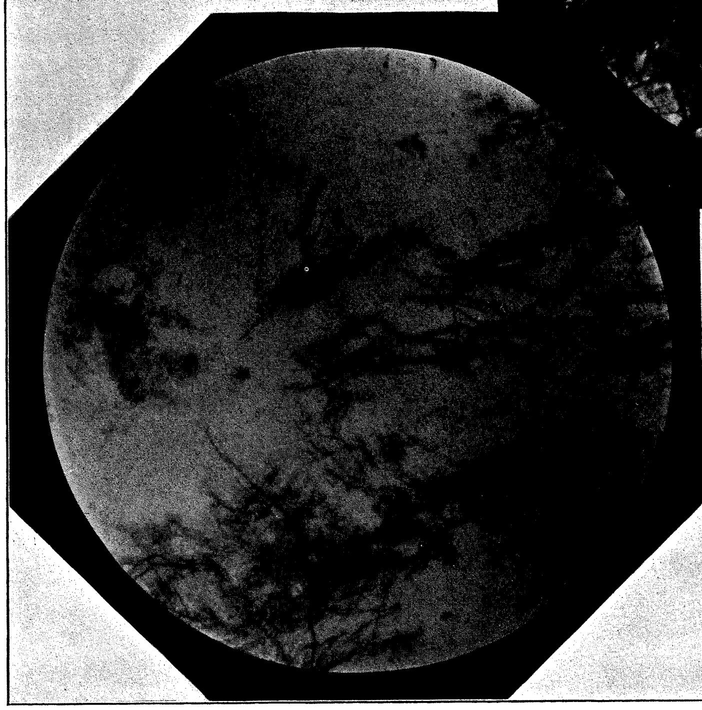

Fig. 8.

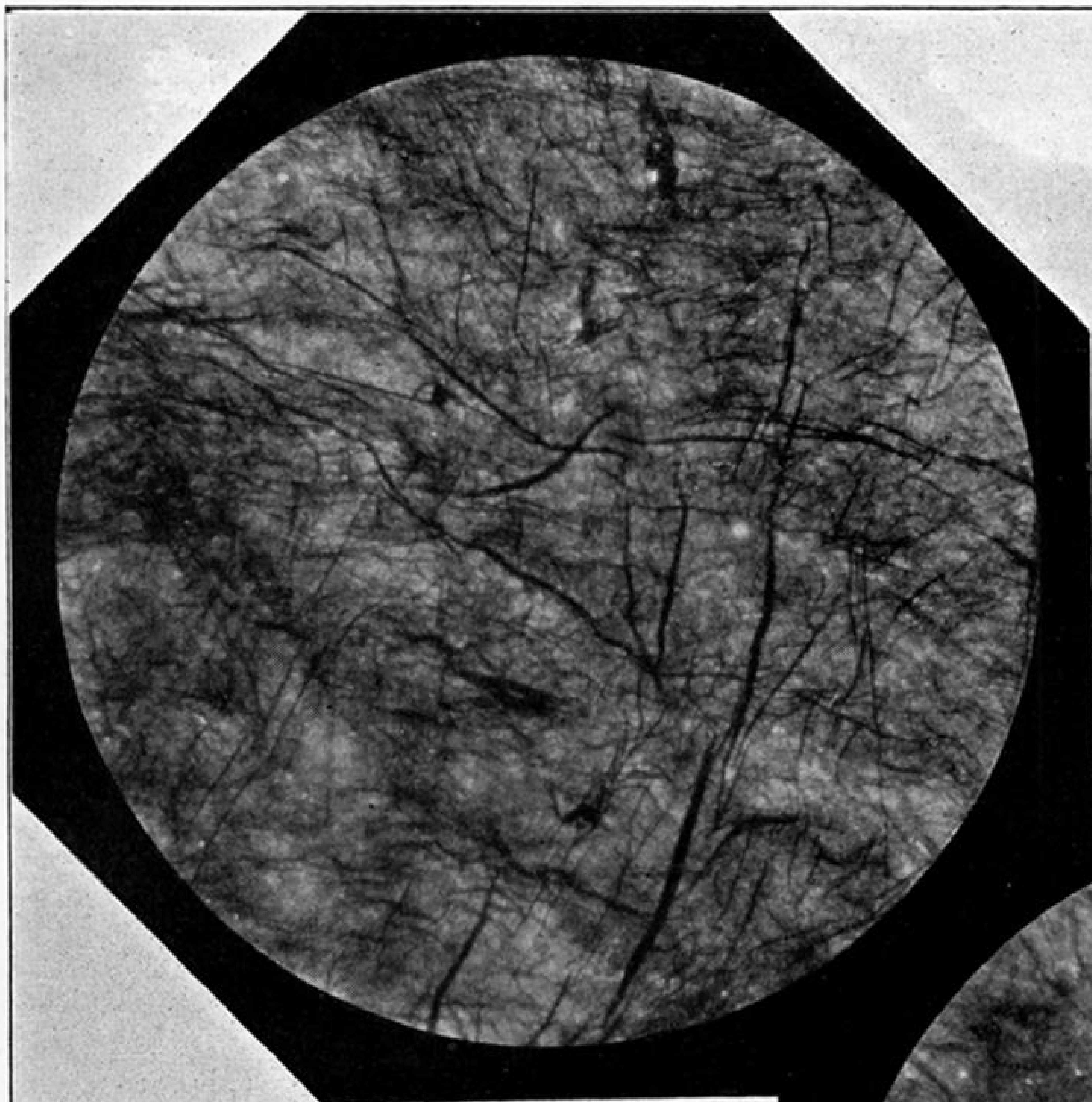

Fig. 4.

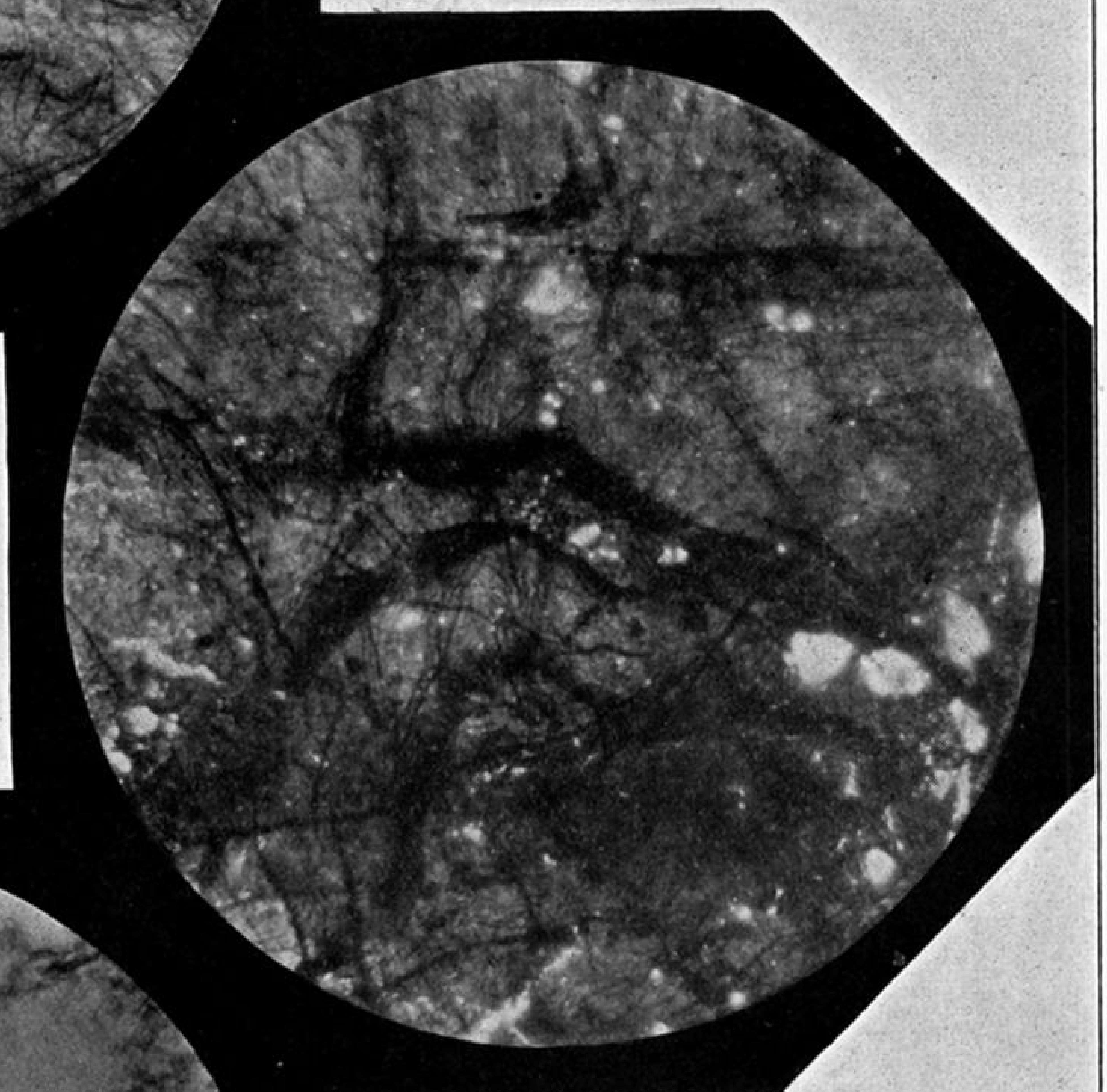

Fig. 6.

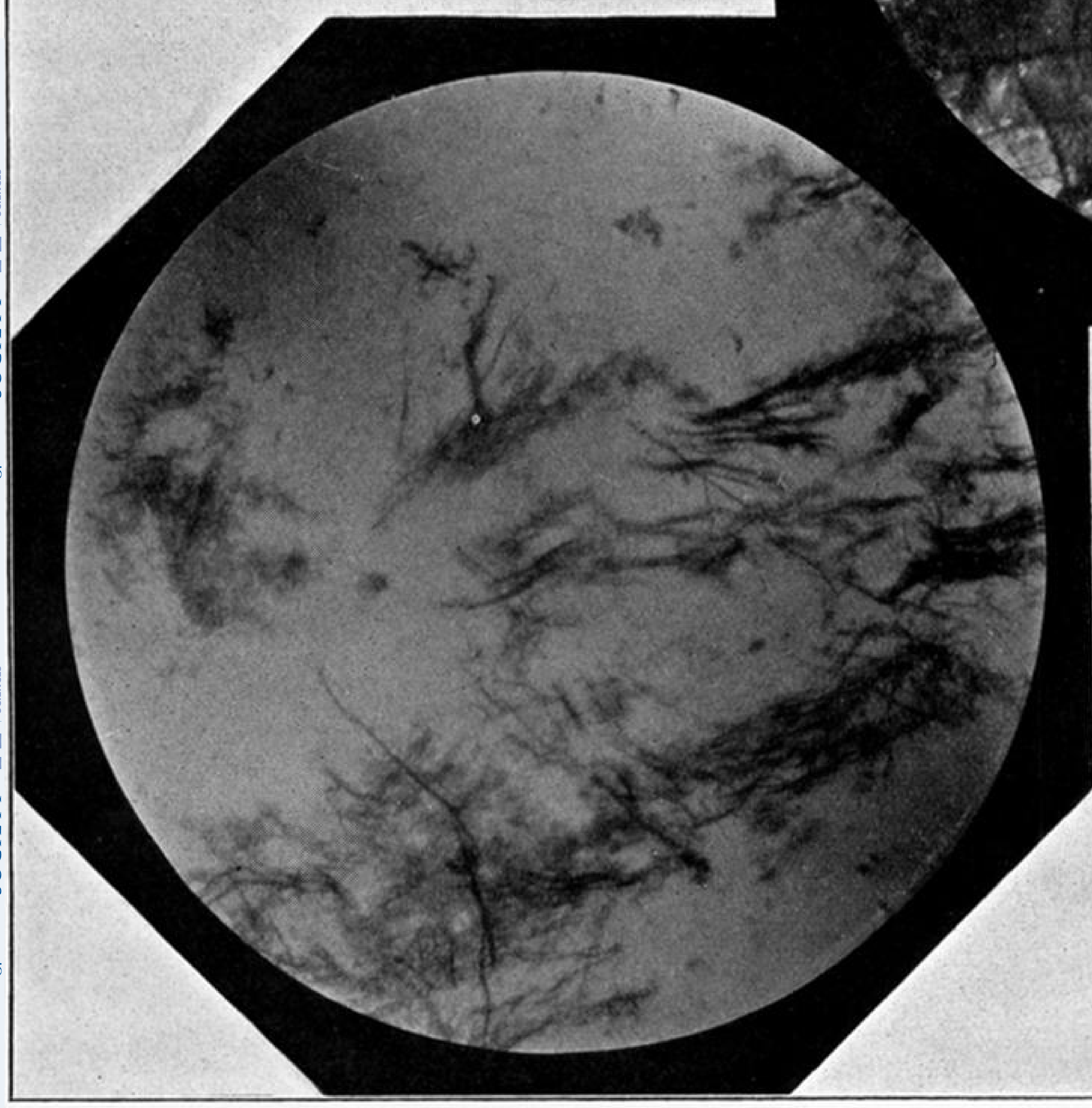

Fig. 8.