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Author(s)	Yosida, Zyungo
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Window Hoar Crystals on Clean Glass Surfaces*

By

Zyungo YOSIDA

(*With Plates I–IV*)

§ 1. Introduction

Prof. Nakaya and Messrs. Hanazima and Dezuno investigated the production of artificial window hoar crystals and presented a general survey on this subject in the preceding number of this journal.[1] They examined many varieties of hoar crystals produced on the surfaces of various solids such as glass, quartz and mica. They studied also the relation between the cleanliness of the glass surface and the form of hoars as well as the effect of a change in the rate of supply of water vapour or the temperature of the place where the crystal is made. The present author followed their experimental procedure and investigated in more detail the mode of development of window hoar crystals which grow on an absolutely clean glass surface. The degree of drying of the glass surface after it had been washed was found to have remarkable influence upon the form of the crystals. The main purpose of this investigation was to reveal the manner in which the hoar crystals grow up. The mode of growth was observed under a microscope of great magnification, and several interesting phenomena were noted in the process of their formation.

§ 2. Experimental Procedure

The glass plate on which the hoar is to be developed was always washed "thoroughly clean" as described in the paper above cited.

* Investigations on Snow, No. 13.

1) Investigations on Snow, No. 12; Jour. Fac. Sci. Hokkaido Imp. Univ. **3**, 1. (1939).

Journ. Fac. Sci., Hokkaidô Imp. Univ., Ser. II, Vol. III, No. 2, 1939.

It was immersed in a strong solution of caustic potash and then in a sulphuric acid solution of potassium permanganate. Then it was washed with running tap water and finally rinsed well with distilled water. The glass thus cleaned was put into a desiccator containing phosphorus pentoxide and was dried at ordinary room temperature. When the glass plate was to be used, the desiccator was carried into the cold chamber and the glass plate was taken out of it just before using. The "time of drying" of the glass plate means the time interval during which it has been kept in the desiccator.

The apparatus used for the production of hoar crystals is the same as that used in the former experiment. Fig. 1 is a schematical sketch of the apparatus. It is a wooden box 30 cm. square and 60 cm. high. R is a water reservoir. The water vapour evaporated from R is condensed as hoar crystals on the glass plate G. A T-shaped brass rod E_1 which is held in position by an ebonite plate E is connected to a high tension electric source and serves as a pointed electrode. The other electrode E_2 consists of brass plate; it is pressed from behind against the glass plate G. These electrodes were used only in the experiments for examining the effect of surface charge upon the form of hoar crystals. In the other experiments they were removed.

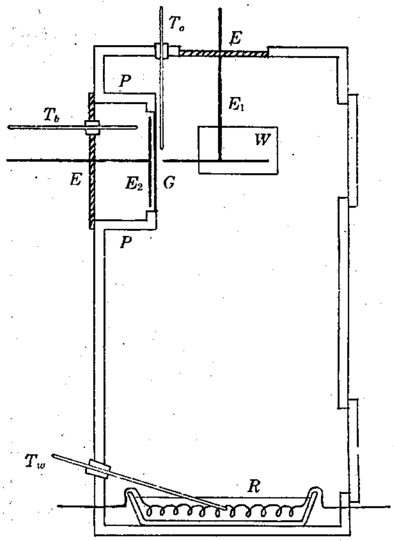

Fig. 1.

The glass plate used is an ordinary window pane. In the first course of the experiments the growth of the hoar crystals is observed with naked eye, and after the hoar has developed the plate is taken out for microscopic examination. During the course of the experiments it was found that observation of the initial stage of the development of hoar crystals has an important significance. The entire process of crystal growth must be observed continually under a microscope of great magnification. For this purpose window pane glass is not suitable, so it is replaced with a thin cover glass such as is generally used in microscopic work. A window W is made on the side wall of the box and movable frame is attached to the window. A cover glass, 55 mm. × 90 mm. in dimension and 0.2 mm. in thickness, is fixed to this frame. The hoar develops upon the inner side of the cover glass and the observation was made from the backside of the glass with a horizontal microscope. The cover glass above mentioned is thin enough for observing the crystals at a magnification of about five hundred times.

For the microphotography of such a large magnification an intense light must be used for illumination. An ordinary incandescent lamp cannot be used, as the heat ray melts the hoar in a short time. A tungsten arc lamp was found to be suitable for this purpose.

§ 3. Initial Stage of Hoar Formation

In this series of experiments the room temperature t_r was varied within the narrow range between −23°C and −27°C, and the temperature of water t_w between +2°C and +10°C. The temperature of the air in the apparatus t_a was measured by thermometer T_a; it varied between −18°C and −22°C. The temperature of the air t_b behind the glass plate was measured by thermometer T_b; it was about two or three degrees lower than t_a. When a beam of intense light was projected into the box, numerous fog particles were seen circulating violently in the box. The presence of these fog particles shows that the degree of supersaturation of water vapour is much less than that supposed before[2]; at that time these minute fog particles were overlooked owing to the insufficient intensity of the light.

A few minutes after setting the plate in the apparatus, the surface is covered with a very thin layer of cloudy appearance. It will be missed if the observation is not carefully done. This cloudy layer vanishes quickly when the glass plate is taken out of the apparatus. It will be shown later in § 6, that this is an assemblage of tiny water droplets covering the glass surface. Soon after the appearance of the cloudy layer, many nuclei of hoar crystals begin to appear scattered over the surface. The portions of the cloudy

2) Investigations on Snow, No. 6. Jour. Fac. Sci. Hokkaido Imp. Univ. **1**, 206, (1935).

layer which surround the nuclei of hoars vanish by evaporation and clear spaces of nearly round form are seen about them. As the hoar crystals grow, the cloudy layer shrinks away and at last there remain only the hoar crystals on a clear background. In some parts where the nuclei of hoar crystals are sparsely scattered, the evaporation of the cloudy layer stops at a certain stage and it becomes thicker and thicker, changing suddenly into a film of glaring nature. This change of brightness means the freezing of water droplets. The assemblage of ice granules thus formed is the "uniform frost," according to the nomenclature proposed in the former report, No. 12. Photo. 1, Pl. I, shows the initial stage of a nucleus of hoar and the surrounding clear space in the cloudy layer. This plate shows the stage several minutes after the beginning of the experiment. This stage lasts another few minutes, attaining the appearance shown in Photo. 2. Then the cloudy layer transforms into the uniform frost. Photo. 3 which is taken a half minute later than Photo. 2, shows this uniform frost. These three photographs were taken by Mr. Dezuno in the supplementary experiment to that described in report No. 12. The author is heartily grateful to Mr. Dezuno for allowing these photographs to be reproduced in this paper.

From the margin of the uniform frost numerous branches of hoar crystals grow into the clear space. These will be called "margin hoar crystals" in this paper. The hoar which develops from the nucleus with a surrounding clear space, will be called "an isolated hoar."

§ 4. Effect of Time of Drying

Effect of time of drying is as follows. When a glass plate is used which has been kept in the desiccator for several hours, uniform frost covers the greater portion of the glass surface, while the isolated hoar crystals are rare. Photo. 6, Pl. I, shows the margin hoar crystals in this case. Isolated hoars are found here and there, among which one can see the crystals in the form of arabesque design* and the ordinary hoars as reproduced in Photo. 8, Pl. II, of the previous paper. As the time of drying is increased the domain of the uniform frost becomes smaller, and isolated hoar crystals

* The detailed description of this peculiar type of hoar is given in report No. 12.

increases in number. Among the isolated hoars, the one in a spiral form, an example of which is shown in Photo. 14, Pl. III, of the previous paper, is frequently observed. When the time of drying is longer than three or four days, the uniform frost disappears almost completely and the isolated hoar tends to take the form as shown in Photo. 7, Pl. I. The feature of this hoar is that it is composed of a hexagonal plate or a short thick column associated with an assemblage of branches in structure like a spinal column.

The change in appearance of the hoar crystals as the time of drying becomes longer, will be due to a very thin water film adsorbed on the glass surface, as pointed out by Prof. Nakaya in the previous paper.

§ 5. Effect of Electrical Discharge on the Surface

In relation to the point above described an interesting phenomenon was found by treating the glass surface electrically. Immediately after the glass plate had been set in position G of Fig. 1, a high tension electric surge was sent to the electrodes E_1 and E_2 by means of a condenser discharge, and then hoar crystals were made to develop on the surface. With a glass plate, which had been kept in the desiccator for less than three days, no noticeable change was observed. The effect of residual surface charge was observed only for a pane which had been desiccated to a larger extent. When the glass plate had been dried for more than four days, uniform frost was observed to condense along the path of the discharge over the surface, if the electrode E_1 was positive. An example is shown in Photo. 4, Pl. I. If the electrode E_1 was negative, no noticeable change was observed. Photo. 5 shows an example of frost formed in case of negative discharge. The author considers that such an abrupt change, with respect to the degree of drying, in the feature of surface hoars must be due to the sudden change in the nature of the glass surface, such as the removal of the adsorbed layer of water molecules from the surface.

The results obtained in the experiment above described must be due to the effect of the residual charge left on the glass surface. As the next step, similar experiments were carried out with high potential applied continually during the course of hoar formation. The point electrode was held about one centimetre distant from the surface of the pane, and a potential from ten to twenty kilovolts was applied between this electrode and that behind the glass. As the glass is slightly semi-conducting, some dark discharge or a weak brush discharge must be taking place in front of the point electrode. When the point electrode is positively charged, the hoar crystals that grow on the glass surface facing forward the electrode tend to develop in the form shown in Photo. 8, Pl. II. It will be seen that they are very different from the ordinary hoar crystals and that they resemble in form and structure the early stage of the artificial snow crystals. Many hexagonal plates and short hexagonal columns are observed in the photograph, the latter looking like the crystals that were made by Adams[3] by mixing warm and cold air. The crystals obtained in this case are much larger than those of Adams. Change in polarity of the electrode sometimes results in remarkable variation in the form and structure of the hoar crystals. Photo. 9, Pl. II shows an example when the negative electrode is used. In this case the hoars grow upwards into the air in form somewhat like a mycelium. This peculiar form of hoar is sometimes obtained in the case of positive electrode. The definite relation between the form of hoar and the polarity of electricity could not be worked out in this experiment.

§ 6. Mechanism of Development of Uniform Frost

In order to ascertain the mechanism of development of isolated or uniform frost, the crystals produced on the inner surface of the cover glass fixed in window W of Fig. 1 were observed incessantly under a microscope. In this and the following sections are described the results obtained by this method.

At first the cloudy layer as described above in § 3 is observed just after the glass plate is fixed in the window W. This layer was found to be made up of numerous tiny water droplets. These droplets cover the whole surface of the glass and appear under a microscope as in Photo. 10, Pl. II. This photograph shows the stage about ten minutes after the setting of the glass plate, which has been previously dried for two days. The sizes of droplets do not vary uniformly. They may be roughly divided in three groups; the large, middle and small size. Nuclei of the large and middle droplets

3) Phys. Rev, **35**, 113, (1930); Proc. Roy. Soc. A, **128**, 588, (1930).

appear first on the surface and grow up quickly by collecting the surrounding small droplets, which are later produced between the large ones. The triangular figure in the centre of the photograph is liquid water. A piece of fibre accidentally left on the glass surface is covered with condensed water. It is a remarkable phenomenon that liquid water can coexist at such a low temperature with solid substance, which can easily act as nucleus of freezing.

In the region where the nuclei of isolated hoar crystals are scanty, the assemblage of these droplets begins to freeze and before long changes into a uniform frost. This change does not occur simultaneously all over the region. A small bright speck of reflecting character appears at some certain point and it enlarges itself, spreading wider and wider. At first its front line is distinct and then gradually becomes diffuse. Under the microscope the water droplets are seen to freeze suddenly, when the front of the bright region passes through the field of the microscope. It is noticed in this case that both the water droplets before freezing and the ice granules after freezing are separate and distinct from each other. The mechanism by which the freezing phenomenon is transmitted from one droplet to its separate neighbour will be explained in the next paragraphs.

In the earlier stage of the transmission of the freezing process, while the front line is distinct, the speed of its development is about 1~2 mm/sec. Details of the freezing process observed in the field of the microscope are as follows.

Freezing starts usually from the part where the assemblage of water droplets is composed of many large droplets and a small number of tiny ones that are scattered between the former. When the front of the reflecting region reaches a spot in the field of the microscope, all the large droplets are seen to change their shapes suddenly. The smooth boundary lines transform into somewhat angular ones, and irregular patterns appear in the interior of the droplet. This means, no doubt, the freezing of the droplet. At the same time a pattern in the form of something like a skirt, which is probably composed of ice film, appears around the boundary of the granule and it spreads out into the space between the large granules. The "skirts" of any two neighbouring droplets touch at some point. Meanwhile the small droplets which were scattered in the space between the larger granules vanish by evaporation. In a moment these skirts begin to shrink and there remains an assemblage of ice granules having no connection with each other. By these observations the mechanism of the spreading of the frozen region can be explained. When a droplet is frozen, the skirt spreads out from the boundary until it touches the neighbouring droplet. The latter droplet freezes at that moment and a skirt-like film again spreads out from the newly frozen droplet, which causes another neighbouring droplet to freeze and so on. Soon after freezing, the skirts shrink away and the connecting bridges between the frozen droplets are destroyed, leaving them separated from each other. Photos. 11, 12 and 13, Pl. II, show three stages in this freezing process. Photo. 11 represents the water droplets just before freezing occurs. Photo. 12 shows the state of frozen droplets just after freezing. In the photograph some of the connection bridges and traces of the skirts are still seen, although the greater part of the bridges have already disappeared. Photo. 13 shows the stage a few minutes later than Photo. 12. These photographs were taken successively in a cinematographical manner without touching the hoars.

As the area of the frozen region increases, its front line becomes diffuse. The speed of development decreases to about 0.1 mm/sec. In this stage the mode of transformation of the assemblage of water droplets into uniform frost is somewhat different from that above mentioned. In the parts, far from the starting point of the freezing, a large number of small droplets usually are seen. The process of freezing above explained occurs only between the large droplets, the small ones all vanishing by evaporation as in that case. The mean distance, however, between the large droplets is comparatively great in the present case. Connection between the large droplets can hardly take place by the extension of the skirt-like film. Without this action of transmission of freezing, the large droplets also can not freeze and evaporation takes place. Some clear space observable in the region of the uniform frost answers to the place where the evaporation of the droplets has occurred. The cause of the evaporation of these droplets will be the difference between the saturated vapour pressures over the super-cooled water and the ice granules. In Photo. 14, Pl. III is shown a part of the front line in the latter case. Photo. 15 is the aspect of the same place when the freezing is completed. A group of water droplets remains in the middle part at the right-hand side of Photo. 14. The droplets in the other part of the field are already frozen, except one extraordinarily large drop in the centre of the picture. This drop remains in a liquid state to the last stage and vanishes by evaporation. The last stage is seen in Photo. 15. The skirt-like ice films extending out from the tiny droplets are seen clearly in the frozen region of Photo. 14. The diffuse character of the front line in this case, when observed by the naked eye, is due to the formation of small clear spaces by the evaporation of droplets.

As the front line of the frozen region proceeds, it reaches a part where the occurrence of the large droplets is so rare that they cannot be connected with each other by the extention of skirt-like films around them. In this case the front line can no longer advance and the region of the uniform frost stops here. A clear space appears beyond the boundary of the uniform frost owing to the evaporation of the water droplets along the boundary of the latter. Afterwards margin hoar crystals begin to grow into this clear space.

Ice granules of uniform frost produced in the manner above described grow thicker with the subsequent supply of water vapour. Some of the granules combine with each other in that case. The structure of the "uniform frost" which has developed to its full extent, shows the appearance represented in Photo. 16, Pl. III, which is a stage about twenty minutes after its formation.

With respect to the starting point of the uniform frost, the following facts are observed. Examining the assemblage of water droplets under a microscope, a droplet is found on rare occasions which contains a particle of solid substance. An example of this sort of droplet is shown in Photo. 23, Pl. IV. Such a droplet lasts a considerable time till it freezes suddenly. If one looks at the glass plate with the naked eye in this case, it is found that uniform frost starts from a point near the droplet above mentioned. So that it is probable that the droplet with some solid substance inside can freeze by itself and then act as the starting point of the uniform frost. Such a fragment of solid substance can not be the germ of an isolated hoar crystal. The germ is invisible even under a microscope of great magnification and is of unknown nature, as will be explained in the following section.

§ 7. Development of Isolated Hoar Crystals

As described above in § 3, when a glass pane is set in position G of Fig. 1, the temperature t_b of the air behind the pane is three or four degrees above the air temperature t_r of the cold chamber. This is because the air behind the pane is not in free connection with the air in the cold chamber, as is shown in Fig. 1. When a thin cover glass is fixed in window W as in the cases of the foregoing and the present sections, the back side of the glass plate is exposed directly to the air of the cold chamber. The cover glass is cooled more rapidly in this case than in the previous one. Consequently the manner of the formation of hoar crystals is somewhat different. Uniform frost is apt to develop easily and isolated hoar crystals are rarely formed. Using a cover glass which has been dried for several days, it is observed that the surface is covered all over with the uniform frost. A pane set in position G was usually covered with isolated hoars, when it had been dried for such a long while. After a few experiments it was found that the cover glass dried for one or two days was most suitable for obtaining those isolated crystals. The apposite water temperature—the ice temperature t_w—was between $-1°C$ and $-2°C$. With the cover glass which has been dried to a greater extent, the uniform frost again tends to develop, in contradiction to the previous case of the pane set in position G.

As the microscopic field is so limited and the position of the appearance of the isolated crystals cannot be predicted, it is, in this case, very difficult to follow the process of crystal development from its beginning. Many trials were made in vain, and at last the following procedure was adopted. A grown up hoar crystal was brought into the field of the microscope, and it was melted and dried off by blowing hot air on the glass surface from the back side with an ordinary hair drier. Viewed through the microscope, the glass surface became entirely clear. Stopping the hot air current, there began to appear shortly several tiny water droplets here and there. Then suddenly a speck of irregular form appeared at the point where the centre of the disappeared crystal had been located. Several streamers extended out very quickly from the speck, while the surrounding water droplet evaporated. The streamers increased in length and width, and soon after a familiar hoar crystal was obtained.

When the crystal is melted and dried off again, a new crystal appears at the same place by following the same process of growth. The results of a series of experiments carried out in this manner are shown in Photo. 17, 18 and 19, Pl. III. The crystal in Photo. 17 is the second isolated hoar, developed after the original hoar had been dried off. This crystal was melted off and then the third crystal appeared as shown in Photo. 18. This crystal was melted off, then waiting a little while the fourth crystal began to appear at the same position, the early stage of which is shown in Photo. 19. In these photographs one will see that the effect of the previous crystal upon the newly formed one presents itself not only in the location of the crystal but also in the general form. Photos. 20, 21 and 22, Pl. IV, belong to another series. The photograph of the second crystal is taken in its early stage, which is shown in Photo. 21. In this series a part of the hoar developed always into a plate form from a fixed point on the glass surface. Judging from the results of the repeated formation of hoar crystals, it is supposed with some certainty that the invisible germ of the crystal plays an important role in determining the form of the subsequent growth of the hoar crystal proper.

When a hoar crystal is melted by the hot air current, it contracts into a water drop. But usually this water drop does not cover the point where the centre of the melted hoar crystal was located. Allowing the water vapour to condense after this water drop has been dried off, an assemblage of many small water droplets appears covering the place where the dried off water drop was located and before long it combines itself into a larger drop similar to the pre-existing one. So that the newly developing crystal starts at a point outside this drop and freezes it when it is touched by one of the streamers growing out of the crystal centre. The large water drop shown in Photo. 19 in the neighbourhood of the hoar crystal is an example of such a water drop. In Photos. 17 and 18, the corresponding drop has already frozen. In rare cases, however, the position of the centre of the disappeared crystal is covered by the water drop. In these cases the newly appearing water drop remains unfrozen for some time and then suddenly freezes. Many ice streamers start from its boundary, but the shape of the htus produced hoar crystal is much different from the pre-existing one. These facts show that the germ of the hoar crystal is firmly stuck to the surface of the glass and cannot be moved or dissolved easily by the water which flows or resides over it. But it must be remarked that sometimes the position of the centre of the original crystal fails entirely to be a germ of the second crystal. In such a case there appears a comparatively large water droplet in place of the crystal and this droplet behaves just like the common large droplet. This fact seems to show that sometimes a germ of water droplet can temporarily attain a character to be a germ of hoar crystal.

As described in § 3, the evaporation of the pre-existing water droplets gives rise to a clear space around an isolated hoar crystal. Usually these water droplets do not disappear entirely. Sometimes large ones survive and remain as droplets of definite size, though they become much smaller than they were initially. These droplets may be seen in Photo. 24, Pl. IV, scattered in the field of microscope. A remarkable phenomenon is observed with respect to these droplets. They do not suffer any change even when the extending streamer of a hoar crystal approaches them very closely. For example, the droplet marked by an arrow in Photo. 24, still remains as a water droplet, although it is nearly touched by an ice streamer. When the streamer touches the droplet completely, the latter does not freeze in its original form, but spreads over the streamer. There remains no trace of the droplet and it appears under a microscope as if the droplet were suddenly swallowed up by the streamer. The liquid matter in the droplets seems to have spread over the surface of the streamer. It will be seen that the droplet marked by the arrow in Photo. 24 has disappeared in Photo. 25. Sometimes the streamer touches a droplet with its tip. In this case, though not always, the droplet freezes as it is, and branching of the streamer is seen to start from that point. These phenomena occur at a temperature twenty or more degree below 0°C. At such a low temperature the saturation vapour pressure over the surface of supercooled water exceeds by 20% that over the surface of ice. From this standpoint it will be difficult to explain how the water droplets can exist so near the hoar crystal as shown in Photos. 24 and 25. The author refrains here from any hasty discussion or conclusion, until more detailed observations can be made with respect to these complicated phenomena.

In conclusion the author expresses his cordial thanks to Prof. Nakaya for his direction and encouragement throughout this work.

Summary

Window hoar crystals are produced artificially on the surface of glass plate which was dried in a desiccator after it had been washed clean. As the time interval during which the glass plate is kept in the desiccator for drying is varied, the hoar crystals which develop on it change in their manner of formation. It is considered that this change is due to the change in the property of the film of water molecules adsorbed on the glass surface. Applying a high tension electric surge on the surface of the glass plate, a Lichtenberg's figure which is composed of many ice granules is obtained. Another electric treatment of the glass plate, viz., continuous application of high tension electricity to the glass plate, produces hoar crystals of simple form such as a hexagonal column or plate which is observed in the early stage of the artificial snow crystals.

With a powerful microscope the hoar crystals are observed incessantly as they develop. "Uniform frost," which is an assemblage of separated small ice granules, is found to be produced by the freezing of an assemblage of water droplets which have been developed previously by the condensation of water vapour on the surface of the glass plate. This freezing, however, does not occur at the same moment all over the assemblage of water droplets. The action of freezing starts at a definite point and extends over the surface, the frozen state being transmitted from one droplet to its neighbour in a peculiar manner. The isolated hoar crystal, i.e. hoar crystal composed of several branches extending out of a centre, has its birthplace in the part of the glass surface where no peculiarity is ever perceived. After an isolated hoar crystal has been melted and dried off by blowing the back side of the glass with hot air, however, a new crystal can be produced at the same place and almost in the same form as the former crystal. Thus the germ of an isolated hoar crystal is so small as to be invisible even under a powerful microscope but it seems to possess a power to determine in large extent the form of the hoar which develops from it.

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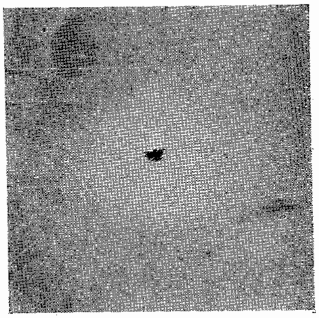

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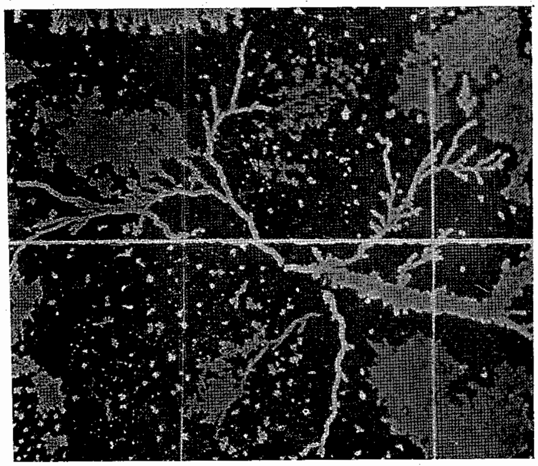

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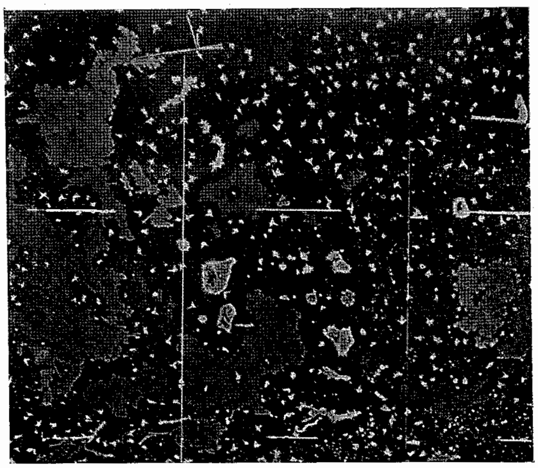

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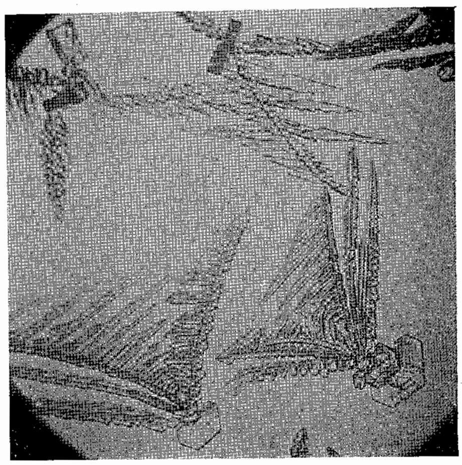

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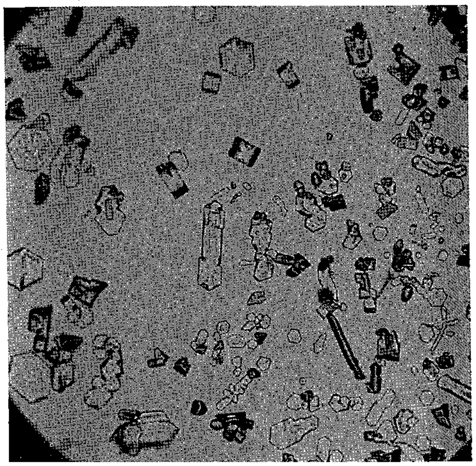

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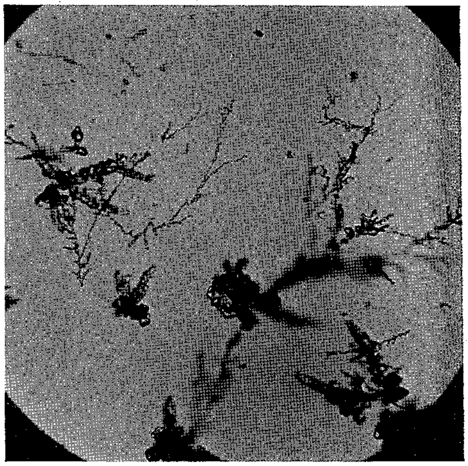

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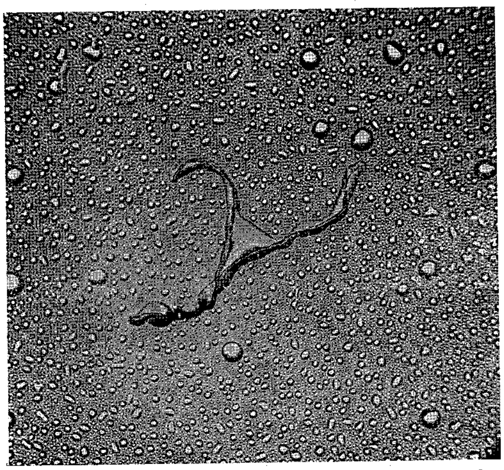

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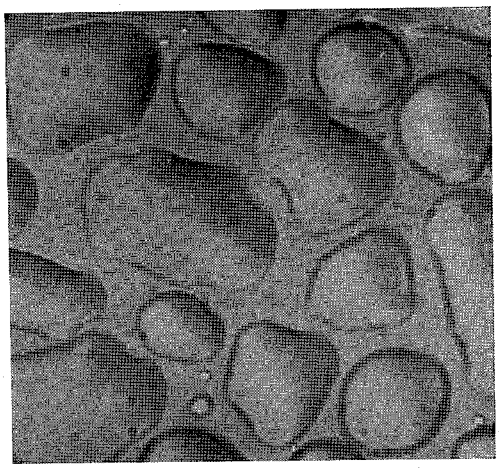

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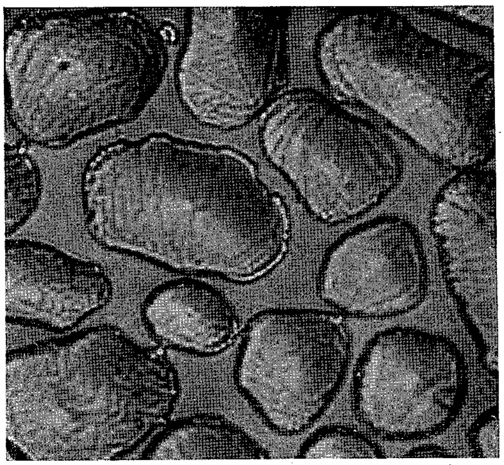

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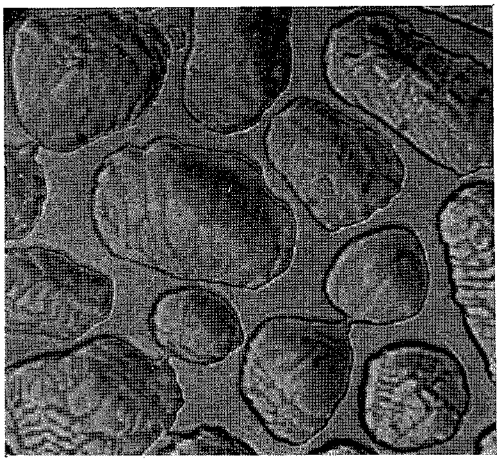

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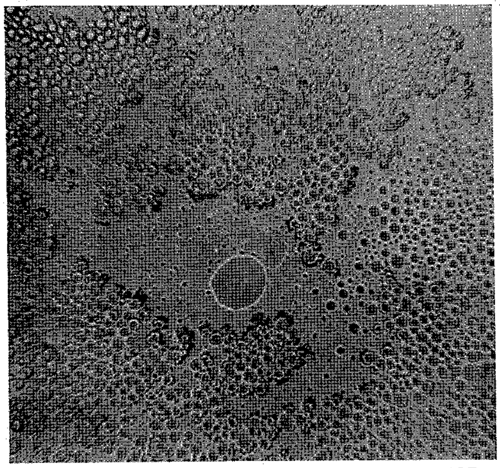

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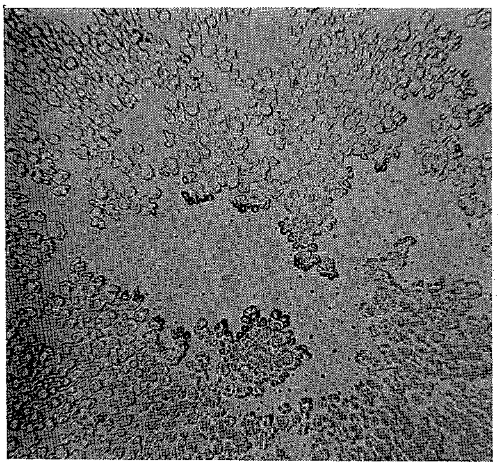

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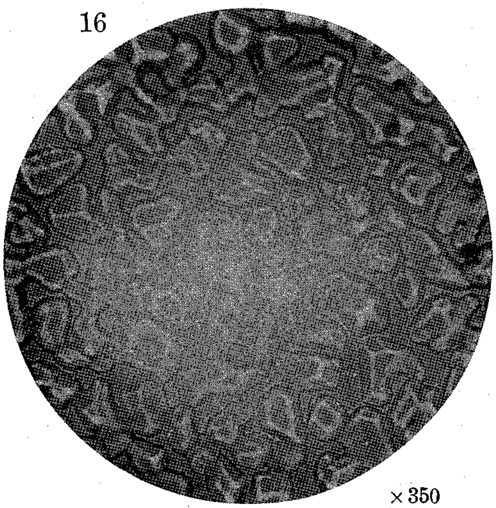

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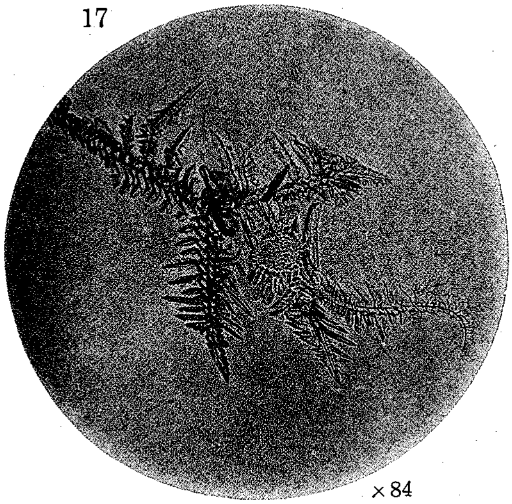

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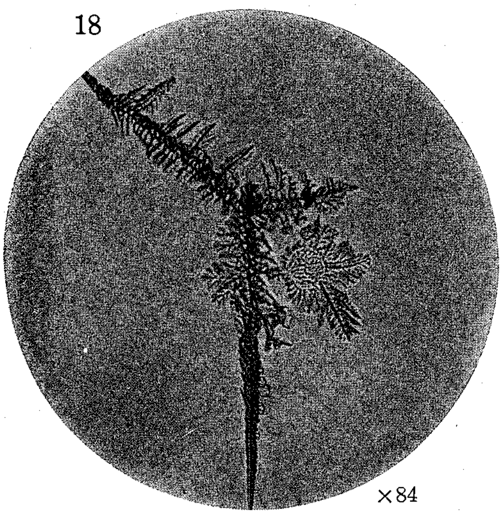

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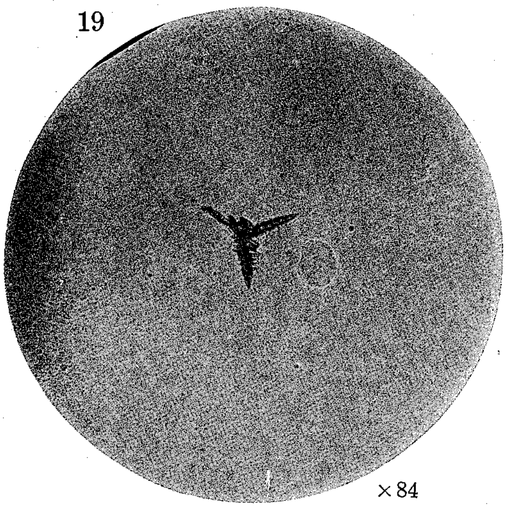
19



×84

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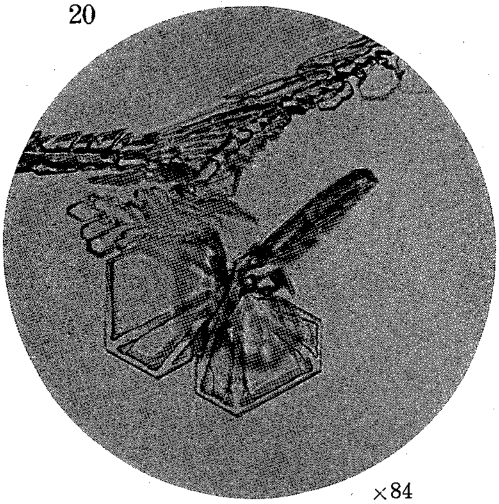
20



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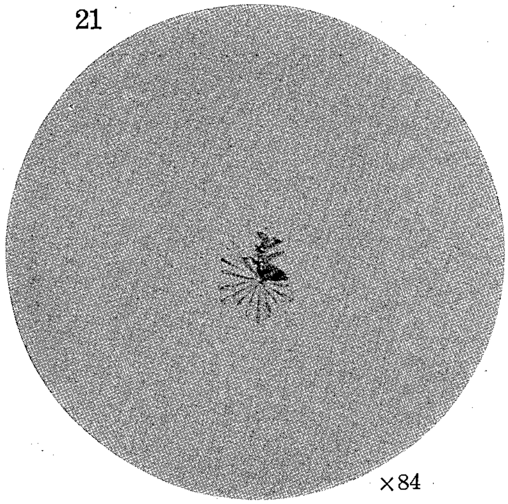
21



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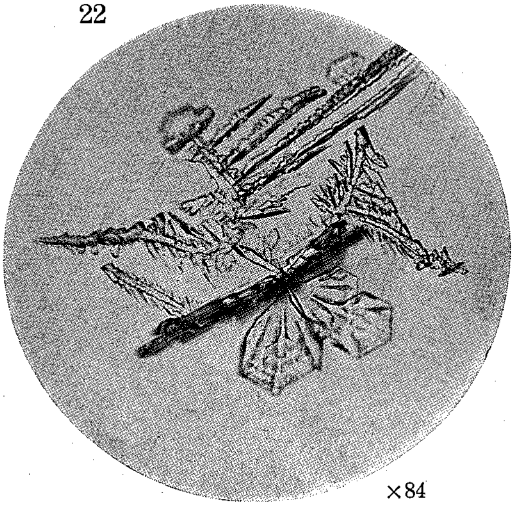
22



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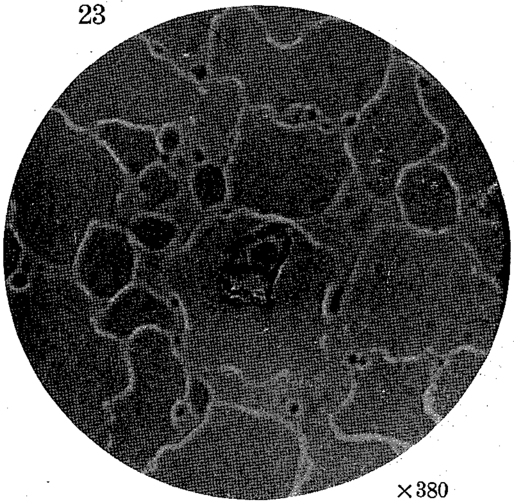
23



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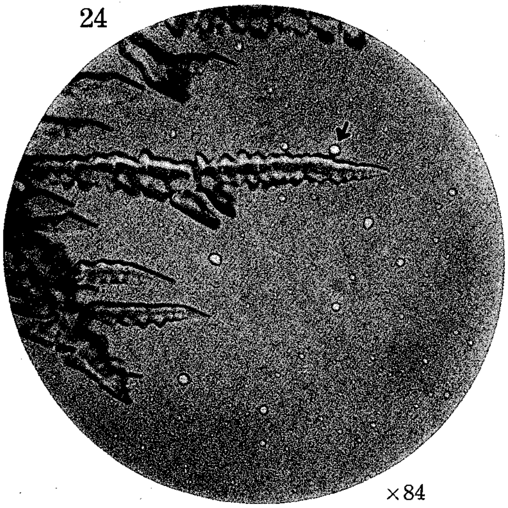
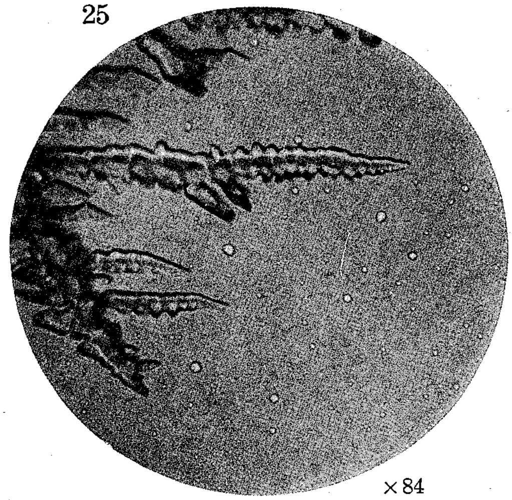


×84

25



×84

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