Experimental Researches on Window Hoar Crystals, a General Survey*

By

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(*With Plates I–V*)

1. Introduction

The frost flowers which bloom on a cold morning on the window panes of any house or shop are objects of love and admiration to the people who pass the long winter in northern countries. This sort of ice crystal is obtained everywhere that moisture is present and the outdoor temperature is considerably below freezing point. Many photographs of a large variety of these crystals are reproduced in Bentley's book[1], who called them window pane frosts. Seligman also paid attention to this subject and his observation on the growth of these beautiful designs is described in his interesting book[2]. He proposes to classify the windowpane frosts of Bentley into two kinds; the window hoar and the window rime. The former is a product of sublimation and the latter is that of freezing. The present authors consider that his classification is adequate and follow his nomenclature in this and following papers on this kind of ice crystal.

In spite of the familiarity of this phenomenon, the subject seems so far not to have been taken up by physicists as an object of physical investigation. The present authors started the experimental researches on this subject by making window hoar crystals artificially in the cold chamber of the low temperature laboratory belonging to

* Investigations on Snow, No. 12.

1) Bentley and Humphreys, Snow Crystals, New York, 1931.

2) G. Seligman, Snow Structure and Ski Fields, London, 1936, pp. 57–60.

Journ. Fac. Sci., Hokkaidô Imp. Univ., Ser. II, Vol. III, No. 1, 1939.

our University. A description of the laboratory is given in the preceding paper, report No. 11.

2. Window Hoar and Window Rime

The general appearance of the ordinary window hoar is shown in Photos. 1 and 2, Pl. I, and that of the window rime is shown in Photo 3. The former is obtained when the supply of moisture is moderate and the temperature is far below freezing point, and the latter is likely formed on the window of a kitchen or a bathroom where the moisture is abundant and the temperature, or at least the indoor temperature, is just below the freezing point. In the former case water vapour condenses on the solid surface by sublimation, while in the latter the latent heat liberated by the condensation of excessive moisture on the surface overcomes the loss of heat by cooling and the vapour momentarily liquefies into a thin film of water. The characteristic design of window rime as shown in Photo. 3 was found to be due to the freezing of this thin water film. The mode of freezing of water film on a glass plate was examined under a microscope by cooling it from the back side of the plate with cold air evaporated from a liquid air reservoir. Solidification starts from a certain portion of the film and the crystals of ice grow in the form of strips arranged nearly parallel with each other. The rate of growth is fairly rapid under a microscope. An instantaneous photograph of the front of the growing crystal is shown in Photo. 4. The arrow marked in the Photograph shows the direction in which the crystals grow up. When the process of crystallisation is completed, the thin sheet of ice exhibits the characteristic pattern of window rime as shown in Photo. 3. The problems concerning window rime will be studied as a separate paper. In this communication the descriptions are confined to the window hoar, the sublimation products, only.

The hoar crystals represented in Photos. 1 and 2 are obtained under the same conditions, Photo. 1 being obtained on an ordinary window pane and Photo. 2 on the adjacent one which was previously rubbed off with a moist cloth. As pointed out by Humphreys a scratch on the pane is apt to serve as the starting point of the crystal. Photo. 2 shows that, besides scratches, streaks of moisture left on the glass surface act as the starting point as well.

3. Apparatus Used for the Artificial Production of Hoar Crystals

The principle is the same as that in the case of the artificial production of snow crystals described in the foregoing two papers. A shematical sketch of the apparatus is shown in Fig. 1. Water vapour evaporated from the reservoir R is brought up by natural convection and is condensed by sublimation on the glass surface G_1 or G_2. Usually the vertical plate G_1 was used, and the horizontal plate G_2 was introduced only occasionally for the purpose of comparison. The room temperature T_r varied between −20°C and −37°C, the water temperature being between 0°C and +9°C. The general appearance of the successive stages of crystal growth was photographed with the camera C, and after the crystal developed to a desired form the glass plate G_1 was taken out and was subjected to microscopic investigation. The microphotographs of the successive stages of a crystal were taken through a microscope M by observing the crystal from the back side of the glass plate.

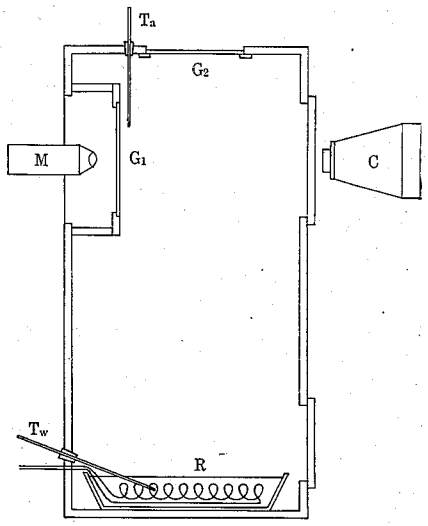

Fig. 1.

4. Hoar Crystals Produced on an Ordinary Glass Surface

As a first attempt hoar crystals were made to grow on a glass plate under ordinary conditions. The glass was washed roughly and exposed to the atmosphere for a few days. With this plate the germs* of hoar crystals appear about twenty or thirty minutes after exposing the plate to the supersaturated air in the apparatus. The general

* The very early stage of the crystal.

appearance of crystal is strongly influenced by the initial temperature of the glass plate. The process of experiment was established follows: the apparatus was set in the cold chamber and the water temperature raised to a desired value, then the glass plate kept in the holder was set in position. When a warm plate is introduced, that is, a plate kept in a desiccator at ordinary temperature and just before the beginning of the experiment the desiccator is brought into the cold chamber and the glass plate is quickly set in the apparatus, many isolated germs appear on the glass surface as the plate cools down. One example is shown in Photo. 5, Pl. I, which represents the initial stage of hoar crystals at thirty minutes after the introduction of the plate into the apparatus. These germs serve as the starting points and after two hours and a half the crystals develop into the familiar form of window hoar as shown in Photo. 6. In this case T_r was $-32°$C and T_w $+9°$C.

When the initial temperature of the glass plate is low; that is, the desiccator containing the plate is left in the cold chamber for a few hours and the cooled plate is exposed to the supersaturated air in the apparatus, the vapour condenses on the surface instantaneously and in this case the greater portion of the surface is liable to be covered with a "uniform frost", as shown in Photo. 7, Pl. II. This uniform frost is composed of minute frozen droplets. There is always some clear space on the pane, and an isolated hoar is usually seen near the centre of the clear space. A microphotograph of the ordinary hoar crystal is reproduced in Photo. 8, Pl. II. As pointed out by Bentley and Humphreys, lines of crystals usually diverge at 90° and in less frequent occasions at 60°. This angle is found to vary within a wide range when the nature of the glass surface is altered. The minute structure of the ordinary hoar will be seen clearly in Photo. 8. It is composed of many short columns and the general appearance under a microscope is like that of a spinal column.

5. Cleanliness of Glass Surface and form of Hoar Crystals

When the glass surface is chemically clean the mode of deposition of hoar is quite different. A glass plate which has been immersed in a sulphuric acid solution of potassium permanganate, is rinsed in running tap water and then immersed in a strong solution

of caustic potash and the surface is rubbed with a cotton swab. The glass plate thus cleansed is washed thoroughly with running tap water, until the entire surface becomes wet with water film. The condition of the glass surface thus obtained will be called "thoroughly cleaned" in this paper. The mode of drying the plate also affected the matter and the following three cases were chiefly examined: i) the glass plate is left in a wide case to be dried in a natural course, ii) dried up thoroughly in a desiccator containing P_2O_5, iii) the plate dried in a natural course was rubbed gently with an ordinary clean cotten before using.

i) *The glass plate thoroughly cleaned is dried in a natural course.*

It is difficult to produce hoar crystals on this surface. Half an hour after setting the plate in the apparatus no trace of crystals is observed on the surface, the inner surface of the uncleaned glass plate used as the window of the apparatus being meanwhile covered with numerous hoar crystals in the early stage. Waiting two hours, thin uniform frost and a few detached crystals of diffuse character begin to appear on the pane. The general appearance in this stage is shown in Photo. 9, Pl. II. In this example T_r was $-20°C$, T_a $-13°C$ and T_w $+4°C$. Photo. 9 shows that the uniform frost obtained in this case is so thin that it can only be photographed by illuminating the surface with an intense light. The structure of this thin frost will be seen in the lower half of Photo. 10. It is composed of minute frozen droplets, the mean diameter varying between 0.05 mm and 0.02 mm. They are in the same order of magnitude as the frozen cloud particles attached to natural snow crystals[1]. The deviation of form from a spherical shape is more marked in the present case. The peculiar form of the hoar crystals that developed from the margin of the thin uniform frost is seen also in Photo. 10. The minute structure in the form of an accumulation of short columns, which was observed in the case of Photo. 8, is lost in this case and the branching streamers assume a wavy character. The detached hoar in this case is also composed of streamers of this wavy character.

Sometimes a peculiar form of hoar is observed, which is never seen among the natural hoar crystals produced on the ordinary

1) This Journal, Vol. I, Investigations on snow, No. 4.

window pane. It is composed of many curved strips and the general appearance under a microscope is like an arabesque design, the more marked example of which is observed among the hoar crystals to be described in the following section iii). A remarkable example is shown in Photo. 15, Pl. III. The arabesque design in the present case is much thinner in thickness and more diffuse in structure than that reproduced in Photo. 15.

ii) *The glass plate thoroughly cleaned is dried in a desiccator containing* P_2O_5.

When the glass plate is thoroughly dried in this way, the form of the hoar crystals becomes quite different from the case described above. Nine series of experiments were repeated, varying T_w between 0°C and +9°C and T_r between −37°C and −20°C. The grade of desiccation of the pane surface was controlled by the time interval during which the plate is kept in the desiccator. It was varied between 4 hours and about 20 hours. In these cases the hoar crystals are more likely to be obtained than in the preceding case i). Half an hour after the introduction of the plate in the apparatus, the crystals in the early stage are observed and the succeeding mode of growth is found to be similar to that on the ordinary pane under natural conditions. One example of the general appearance is shown in Photo. 11, Pl. II, and a microphotograph of the same is represented in Photo. 12. The plate had been kept in the desiccator for 20 hours in this case, T_r was kept at −20°C and T_w varied between 0°C and +1°C. Photo. 12 shows that the minute structure of the crystal obtained in this case looks like an intermediate stage between Photos. 8 and 10; that is, one can see the structure like a spinal column as well as the wavy character of the branches. It is of interest that the structure of the crystals obtained in this case is similar to that of hoars produced on a quartz surface as shown in Photo. 30, Pl. V. The difference observed in these two cases of i) and ii) must be due to the effect of a very thin water film adsorbed on the glass surface upon the form of hoar crystals. This point will be studied in detail in the future.

iii) *The plate dried in a natural course was rubbed gently with an ordinary clean cotton cloth before using.*

The surface of an ordinary pane is usually covered with some organic films. They can be cleaned off, perhaps not completely, by

washing the surface in the manner described at the beginning of this article. The hoar crystals obtained in the above two cases of i) and ii) are considered to be those developed on the glass surface which is almost perfectly clean while the ordinary hoar as shown in Photo. 8 grew on the surface covered with films of some organic compounds. In order to get a hint on the effect of traces of those organic compounds, the present experiment was made. Usually ordinary clean cotton contains some organic fatty acids[1], and a gentle rubbing of the cleaned surface with this sort of cloth is considered to leave a very small quantity of such organic substances on the surface. The peculiar window hoars in a spiral form which are sometimes observed in nature were frequently, though not always, observed in the present case. These remarkable crystals were often observed by Bentley and more than fifteen photographs of this sort of crystals are reproduced in his book. One example of our artificial window hoar of this type is shown in Photo. 13, Pl. III. In this case T_r was kept at $-31°C$, T_w at $0°C$, T_a varying between $-19°C$ and $-23°C$. Two sorts of crystals are seen in Photo. 13; the one is composed of well defined branches in a spiral form and the other is an assemblage of thin curved streamers of a diffuse character. The microphotograph of the former is shown in Photo. 14, Pl. III, and that of the latter in Photo. 15. Crystals of this kind observed in nature are the type of Photo. 14. For brevity's sake this type will be called "spiral hoar" in future in these papers. It has the spinal column structure like the ordinary hoar and Photo. 14 shows that the branches always extend out, with rare exceptions, on the outer side of the spiral.

The remarkable feature of the latter type, Photo. 15, is the structure of arabesque design composed of wavy streamers. This extraordinary form of hoar crystals seems not to have been observed in nature, and the authors cannot find reference to any in the literature at hand. This arabesque design is also observed among the hoars on a thoroughly cleaned glass surface, as described in section i) of this article. The glass surface has a strong affinity* with water

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1) Shaw and Jex (Proc. Roy. Soc., A, 111 (1926) 341) write: Lecomber and Propert say that in natural cotton the wax content is about 0.5 per cent, and Eyre says that natural linen has 2 per cent. wax and many other impurities.

* The word affinity is used here in the usual meaning, not in the meaning defined in physical chemistry.

when the organic film is removed. At present exact knowledge is lacking about the affinity of cleaned glass with ice, but it can be supposed that there exists some strong affinity also in this case. The arabesque design seems to be due to the deformation of crystal growth influenced by this affinity. In the present stage the writers proceed with this idea as a working hypothesis.

The origin of the spiral hoar is also a subject that has not been clarified yet. A suggestion will be obtained from the fact that an organic film of molecular thickness deposited on a solid surface is likely to be associated with spiral cracks, which was studied in detail by S. Tanaka.[1] Another possible explanation may be found in the influence of the residual electrical charge by friction. These points will be studied in future experiments.

6. Effect of Organic Film on the Glass Surface Upon the form of Hoar Crystals

a) *Paraffin wax.*

In order to learn the effect of an organic substance which can not be wet with water, paraffin wax was chosen. It was expected that little deformation will be observed in the crystal form of ice developed on the surface covered with an organic film of this kind. The film of paraffin wax was deposited on a glass surface in the following manner. The glass was cleaned by washing and kept in a desiccator for several hours. It was then exposed to the vapour of paraffin by keeping it in a horizontal position 5 cm above the surface of molten, not boiling, paraffin wax. The thickness of the deposited film was controlled qualitatively by the time of exposure, which was varied in three steps, 5 min, 15 min and 30 min respectively. With the exposure shorter than 15 min no trace of paraffin film on the glass surface was visible to the naked eye. Increasing the time of exposure to 30 min, the plate took the appearance of a slightly frosted glass after being cooled down.

When the time of exposure was shortest; that is, 5 min, a tendency was observed for small hoars to grow rather quickly on the surface. Half an hour after the introduction of the plate in the

1) S. Tanaka, Journ. Aeron. Res. Inst., Tokyo, 11 (1936) 367.

apparatus, it was covered with such small crystals as shown in Photo. 16, Pl. III. In this case T_r was $-32°C$, T_a $-25°C$ and T_w $+4°C$. The plate was left in the apparatus for one hour and a half under the same conditions and then the crystals were examined under a microscope. Most of them developed in the form shown in Photo. 17, which is an example. Both the wavy nature of the branches and the spinal column structure are observed and no essential difference is noticed from the case of Photo. 12, except the peculiar feature in the form of the aggregation of branches.

The expected result was obtained when the time of exposure was set at 15 min. In this case some portion of the surface was covered with uniform frost and many detached crystals were observed. Most of those detached hoars were accompanied with branches projecting upwards into the air. These crystals showed a quite different structure from those above described. The branches were usually of a plate type. One example is shown in Photo. 18, Pl. III. In this case T_r was $-22°C \pm 1°C$, T_a $-16°C$ and T_w $+6°C$. One will see that this crystal is quite similar in structure to the type of natural snow that is classified as the sector form. This phenomenon will be explained by the assumption that the thin film of paraffin wax intervening between glass and ice serves to protect the free growth of ice crystal from the action of glass surface, which otherwise is a cause of the deformation of ice formation.

A similar experiment was repeated with a glass covered with a thicker film of paraffin; that is, the exposure to molten paraffin had been 30 min. In this case hoar crystals were difficult to produce on the surface. Half an hour after the introduction of the plate in the apparatus crystals in the form of small dots began to appear and they grow very slowly. The microphotograph of one of these crystals is reproduced in Photo. 19, Pl. IV, which shows the stage one hour and a half after the beginning of the experiment. As seen in Photo. 19 the crystal is composed of an assemblage of irregular granules associated with small plates of crystalline structure. T_r was $-32°C$ in this case at which low temperature crystals can not easily grow in a beautiful plate or dendritic form, the similar phenomenon being observed also in the case of artificial formation of snow crystals, Investigations on snow No. 11.

b) *Effect of rubbing with a special kind of cloth which contains the reagent for fog prevention.*

There is found on the market a cloth which is used for the purpose of preventing fog formation on the glass of spectacles. When one rubs the glass surface gently with this cloth, water vapour condenses on the surface as a thin film of water without much damaging the transparency of the glass, the surface being otherwise covered with numerous minute droplets and transparency being lost, when the glass is brought into contact with warm water vapour. This sort of cloth usually contains some such reagent as ethylene glycol.

The effect of rubbing the glass surface with this cloth was examined at the present low temperature. The action of preventing "fog formation" is utterly lost in this case. Almost the whole portion of the glass surface is rather quickly covered with uniform frost and the general appearance is like that of a frosted glass. One example is given in Photo. 20, Pl. IV. In this case T_r was kept at $-23°C$, mean T_a at $-18°C$ and T_w at $+6°C$. This sort of cloth, therefore, is quite inefficacious for the original purpose, when the temperature is decidedly below freezing point.

Sometimes a small circular area or a narrow space is left clean from ice deposition, and a beautiful crystal of ice is sometimes observed at the centre of the circular area. One good example is given in Photo. 21, Pl. IV. The crystal showing a perfect hexagonal symmetry as in this case is seen only on rare occasions, but those composed of a few branches of similar structure to that of Photo. 21 are not rarely observed in this case; that is, when T_a is nearly at $-18°C$. When the room temperature is reduced to $-34°C$ and consequently T_a to $-27°C$, this sort of crystal is not obtained, the crystal developing into an accumulation of short columns associated with small planes.

c) *Alcohol vapour.*

The glass surface covered with an invisible film of paraffin wax gave snow-like crystals under favourable conditions. It is interpretated that the paraffin film intervening between glass and ice serves to protect the free growth of ice crystal. Alcohol vapour was chosen in order to see the contrary effect, as it is supposed that alcohol molecules will combine strongly with water molecules and the growth of ice crystal will suffer a marked deformation.

The glass plate thoroughly cleaned and dried was exposed to the atmosphere saturated with alcohol vapour at the ordinary temperature. A desiccator vessel containing ethyl alcohol at the bottom was used for this purpose, and the glass plate previously cleaned was held in a horizontal position 10 cm above the alcohol surface. The time of exposure was set at 1 hour and a half and at 18 hours.

With 18 hours exposure to alcohol, the expected effect was observed in a remarkable manner. In this case almost the whole portion of the glass surface was covered with thin uniform frost except some narrow space. The general tendency is similar to the case of Photo. 9, Pl. II; that is, the case when the glass is thoroughly cleaned and dried in a natural course. The ice crystals are observed in the narrow space, the general appearance being shown in Photo. 22, Pl. IV. In this case T_r is kept between $-21°C$ and $-24°C$, T_a nearly at $-18°C$ and T_w at $+7°C$. The structure of crystals observable in the narrow clear space is shown in the microphotograph Photo. 23, Pl. IV. Two sorts of crystals are seen. The one shows a structure similar to that of Photo. 12; that is, the structure like a spinal column as well as the wavy nature of the branches. The other is an aggregate of thin crystals like an arabesque design, which is similar in appearance to that shown in Photo. 15, Pl. III. Another example is shown in Photo. 24, Pl. IV, which was made under the condition that the time of previous exposure to alcohol vapour was 1 hour and a half and T_r is $-23°C$, T_a $-26°C$ and T_w $+6°C$. The two sorts of crystals above described are very clearly seen also in this microphotograph.

From the results of these experiments it will be understood that the organic film adsorbed on a glass surface exerts a powerful influence on the deformation of hoar crystal growth, when the organic substance has a power of combination with water molecules.

7. Hoar Crystals Developed on the Surface of Other Substances than Glass

In order to see the direct influence of the atomic force of the solid surface upon the form of surface hoars when the organic film is removed, a series of experiments, was carried out by the use of mica and quartz in place of glass.

a) *Mica.*

A sheet of transparent mica (phlogopite) 7 cm × 11 cm in dimension was used. The hoar crystals developed on the old surface did not show any marked characteristics, but those which appeared on a new cleavage-face showed peculiar features in form and structure. The sheet of mica is brought in the apparatus in the cold chamber and the whole system is set in working order. Then a thin surface sheet is torn off and a new cleavage-face is made. The cleavage-face is, therefore, brought in contact with atmosphere supersaturated with water vapour as soon as it is exposed to air.

The hoar crystals produced on the cleaved mica thus prepared showed the appearance as represented in Photo. 25, Pl. V. In this case T_r is kept at $-23°C$, T_a at $-16°C$ and T_w $+7°C$. One will see in the photograph many star-like patches and irregular streaks. The structure of these two sorts of hoars is shown in the microphotograph Photo. 26, Pl. V. It will be noticed that the streaks are composed of a bundle of thin strips arranged almost in parallel with each other, and the star-like patch is a peculiar form that has not been observed before.

The streaks seem to be mostly due to minute scratches made on the cleavage-face when the surface sheet is torn off, but a sample of mica was found which gives the star-like patches only. A good and transparent sheet of mica is chosen and a new cleavage-face is made with care. In such a case sometimes the star-like hoars only were obtained, as shown in Photo. 27, Pl. V. In this case T_r is $-25°C$, T_a $-19°C$, T_w $+3°C$: the microphotograph shows the stage of crystal development at 10 minutes after the exposure of the newly made surface to the water vapour. The directions of the branches of all crystals are arranged in parallel and they must be defined by the axes of the base crystal of the mica. It is well known that the crystalline system of mica is monoclinic and the cleavage-face shows a pseudohexagonal symmetry. The parallel orientation of NH_4I crystals grown upon cleaved mica is described and illustrated in Bragg's book[1]. The similar phenomenon is observed also in the present surface hoar experiment. The small star-like crystal observable in Photo. 27 develops in one hour or so into a form as shown in Photo. 28, Pl. V, which is a result of another set of experiments.

1) W. L. Bragg, Atomic structure of minerals, London, (1937), p. 210.

From these experiments it will be quite clear that the form of surface hoar is strongly influenced by the action of the atomic force of base solid. Detailed experiments on the deposition of ice crystal on a crystalline surface will be treated in a separate communication.

b) *Quartz.*

A circular disc of quartz was chosen. It was washed clean and left in the atmosphere for a considerable time. The hoar crystals developed on the surface are shown in Photo. 29, Pl. V, T_r being kept at $-27°C$, T_a at $-19°C$ and T_w at $+5°C$. The structure of these crystals is shown in Photo. 30, Pl. V. No essential difference in form and structure is observed from the case when a clean dried glass is used.

Summary

The difference in the origin and structure of window hoar and window rime is discussed. An apparatus for making window hoar crystals in laboratory is designed and the crystals grown on the glass surface are examined under various conditions of the surface. The relation between the cleanliness of glass surface and the form of hoars is investigated for three cases: that is, i) the glass plate thoroughly cleaned is dried in a natural course, ii) dried in a desiccator containing P_2O_5, iii) rubbed gently with cotton. It was found that the tendency of the water molecule to combine with glass exerts strong influence on the form and structure of hoar crystals. This hypothesis was confirmed by the experiments of making the hoars on the glass surface coated with a very thin film of paraffin wax, alcohol or another organic compound. The hoars developed on a new cleavage-face of mica showed a star-like pattern and it was made clear that the form of surface hoar is strongly influenced also by the action of the atomic force of the base solid.

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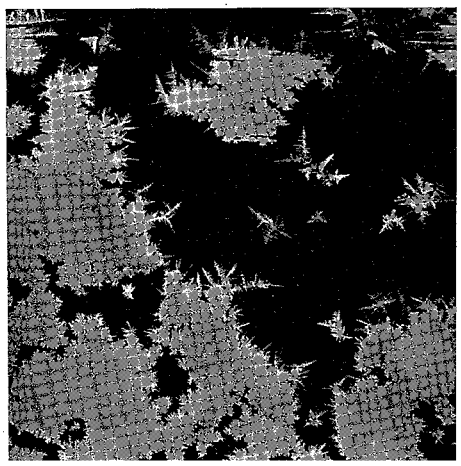

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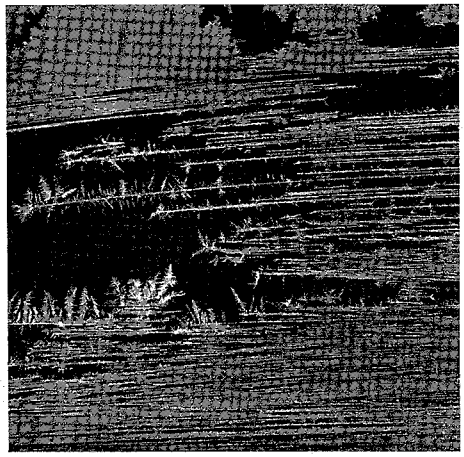

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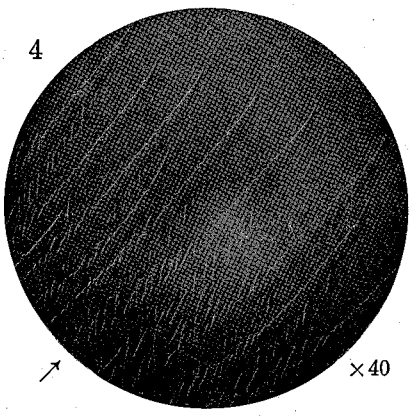

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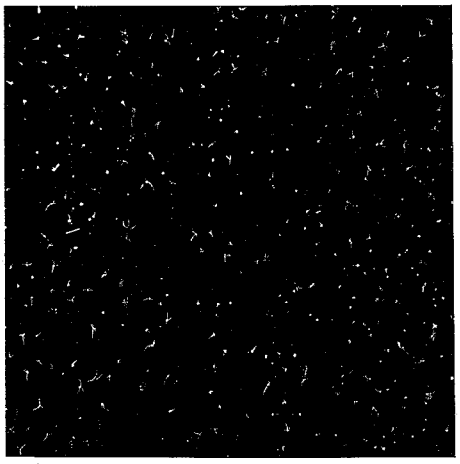

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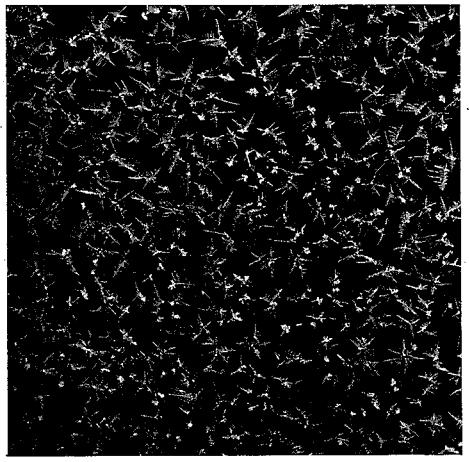

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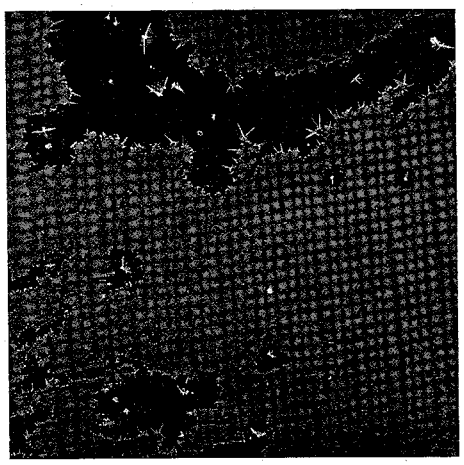

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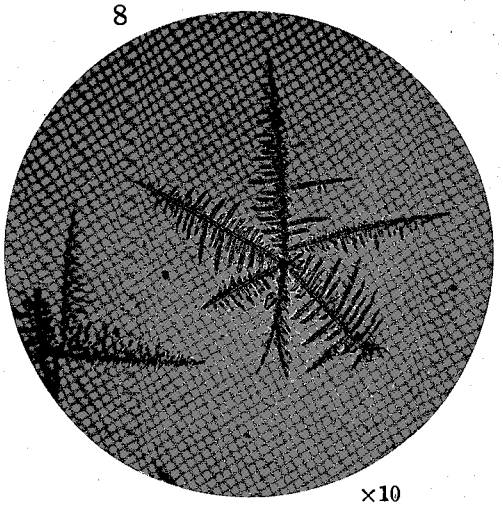

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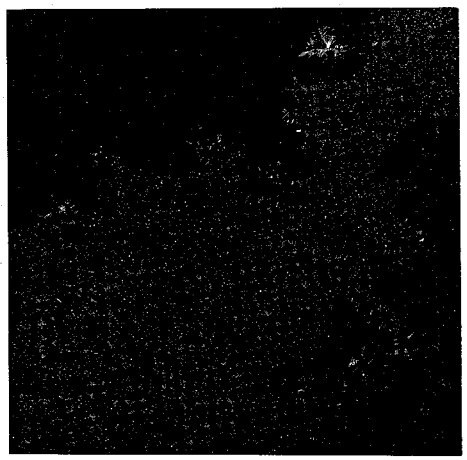

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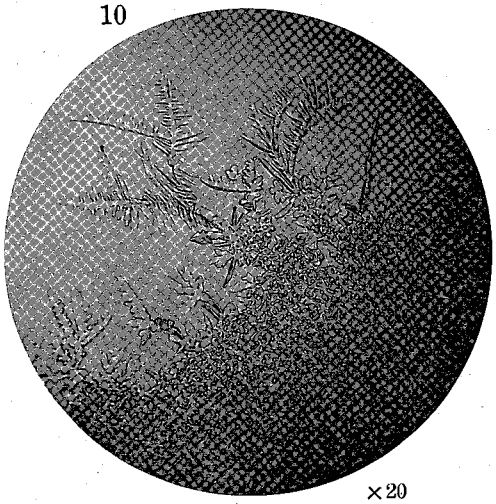

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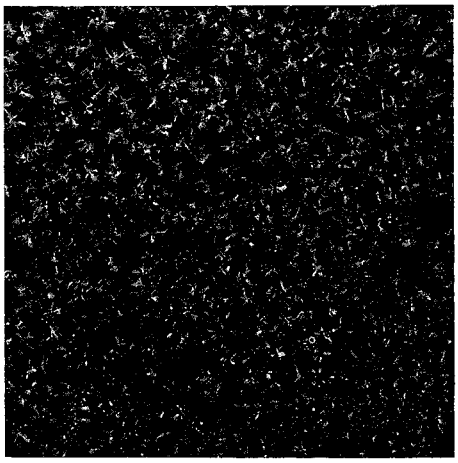

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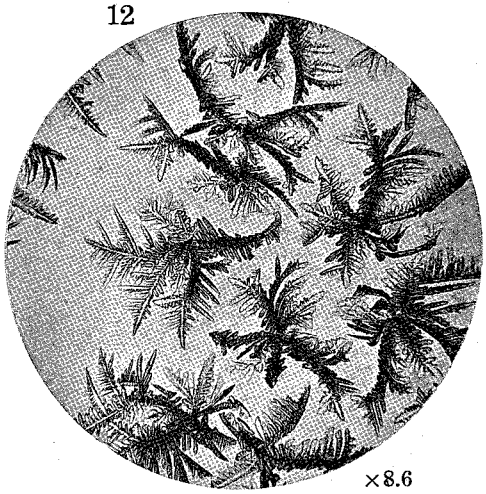

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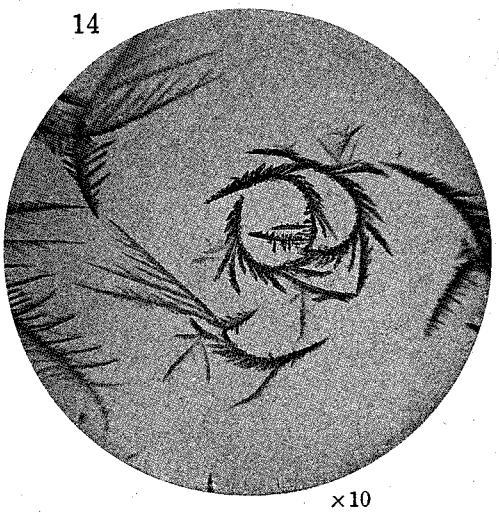
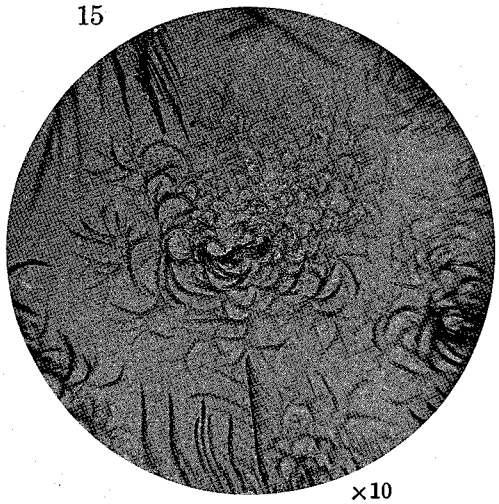
×1.7, $t = 2$ h

14



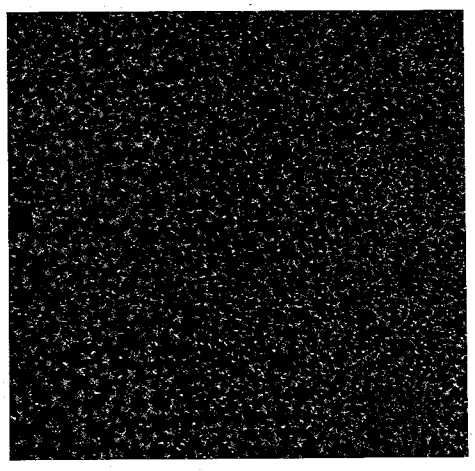
×10

15



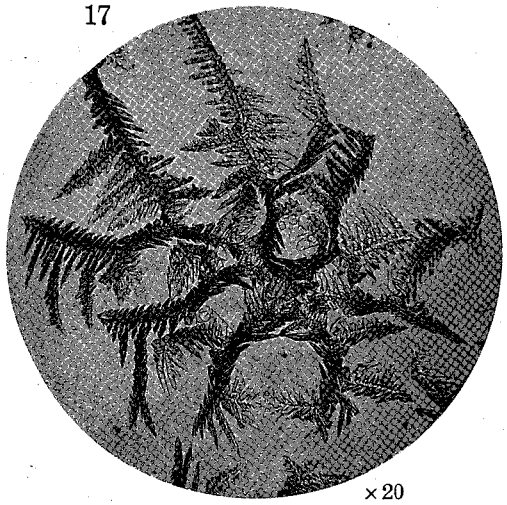
×10

16



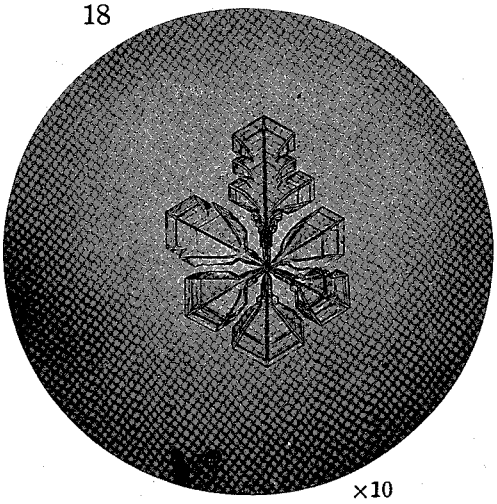
×1.7, $t = 0.5$ h

17



×20

18



×10

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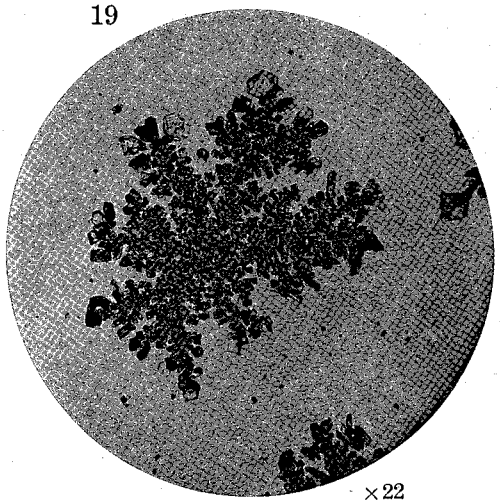
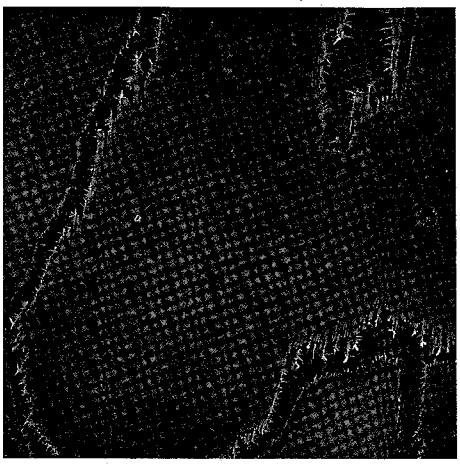


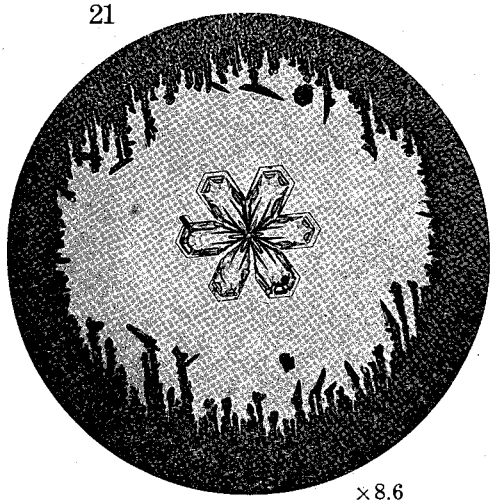
×22

20



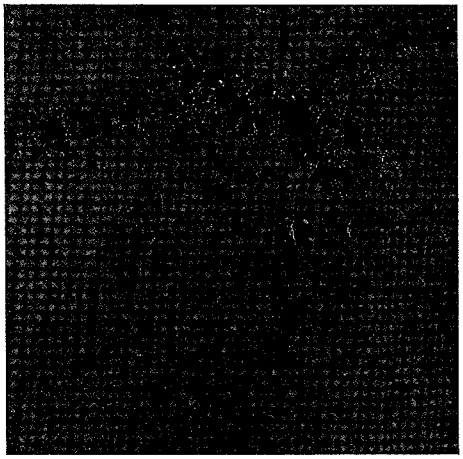
×1.7, $t = 2$h

21



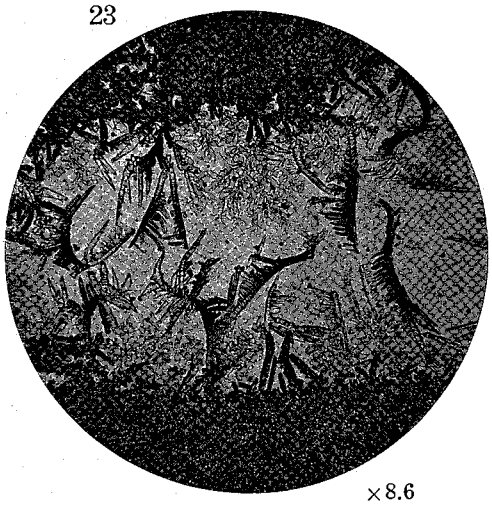
×8.6

22



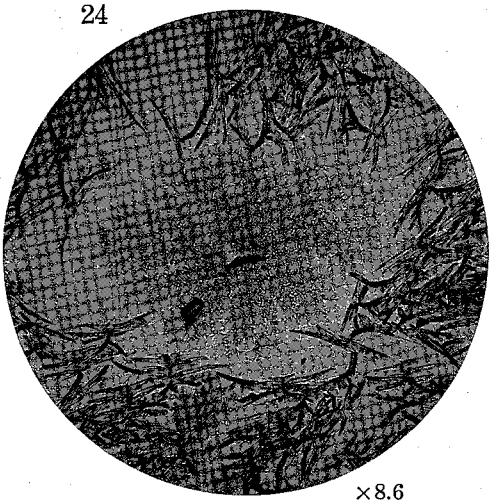
×1.7, $t = 1$h

23



×8.6

24



×8.6

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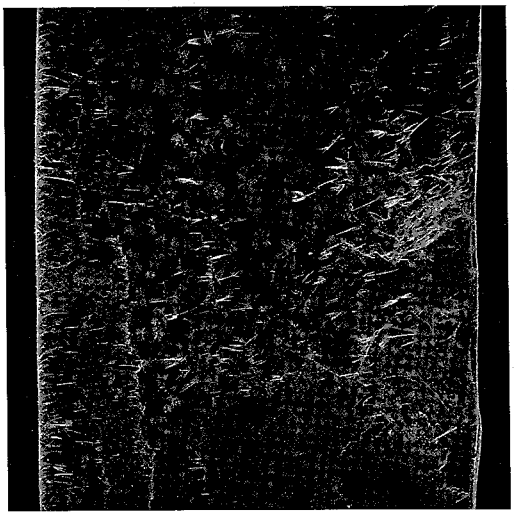
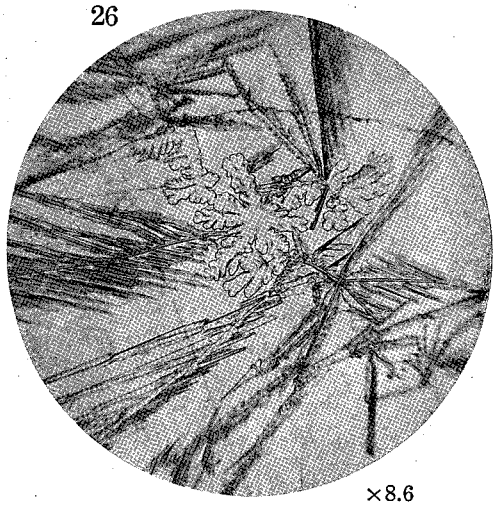


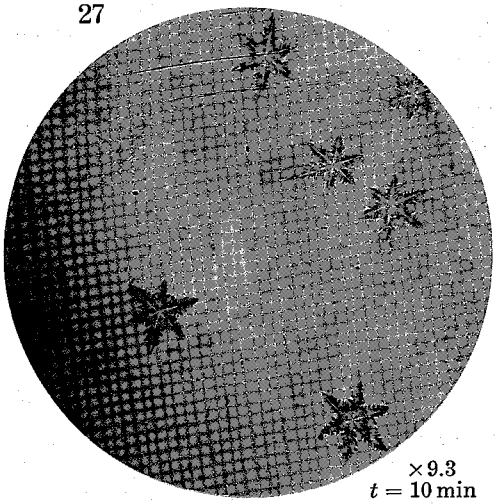
×0.77, $t = 1.5$ h

26



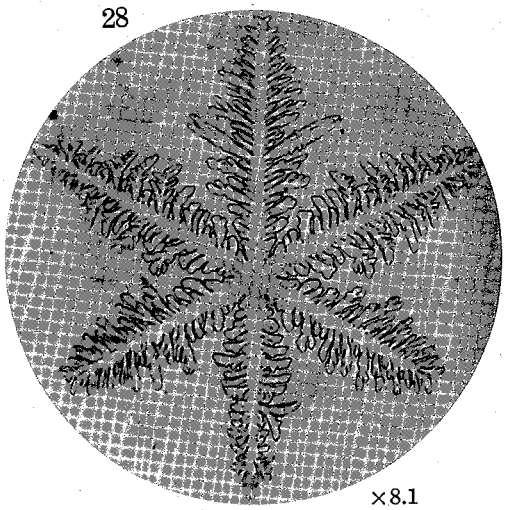
×8.6

27



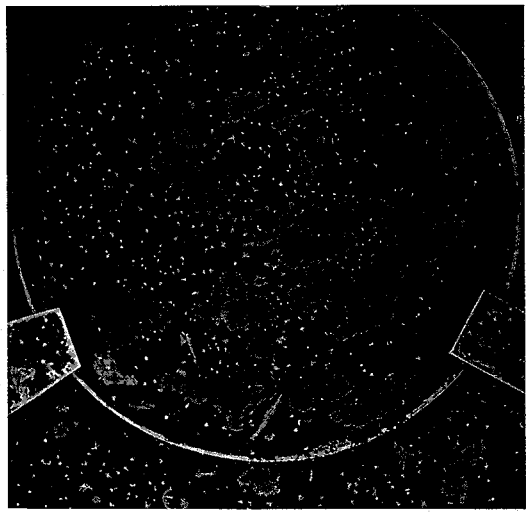
×9.3
$t = 10$ min

28



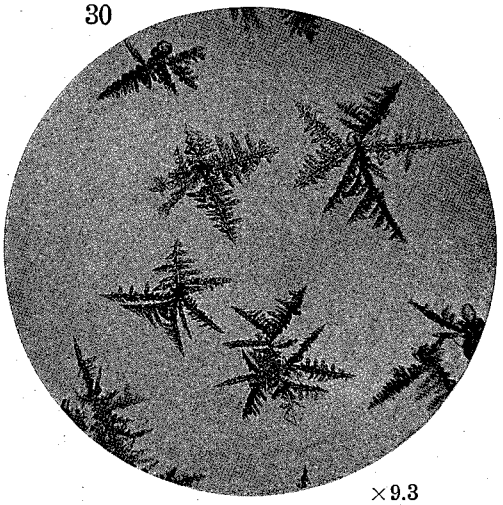
×8.1

29



×0.68, $t = 1.5$ h

30



×9.3

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