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Studies on Small Ice Crystals. II.
On the Ice Crystals Formed on Hydrophobic Substances;
A General Survey.*

by

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(Manuscript Received November 1954)

Abstract

Since the hydrophobic surface which covers the glass plate may serve to protect the growth of crystals from the disturbing action of the glass surface, it is to be anticipated that the hoar crystals that grow on the surface will assume the forms similar to the snow crystals in the free atmosphere. Using several hydrophobic substances, e.g. Daiflon-2, polyvinyl formal, etc., we succeeded in producing the snow-like crystals on these surfaces.

In this paper, observations on the mode of such crystal formation will be described in detail by aid of many photomicrographs, and the problems relating to the mechanism of frost development in its early stage will also be discussed.

I. Introduction

There is no essential difference between snow and frost crystals, except that the former grow while freely suspended in air and the latter on the surface of various solids. As to the forms of frost crystals, therefore, they are much influenced by the character of the surface on which the frost is deposited and are also subject to distortion due to the non-uniform supply of water vapour.

The window hoar crystals, which are quite familiar to those living in northern countries, seldom assume the snow-like crystal forms such as hexagonal plate, column, needle, etc.

U. Nakaya and his cooperators carried out investigation on the artificial production of window hoar crystals, and observed a number of varieties of crystals formed on the variously treated surfaces of glass, quartz and mica. They also inquired into the relation between the cleanliness of glass surfaces and the form of hoar, besides the effect of the rate of supply of water vapour and of the temperature of the place where the crystal develops(1). Following the same experimental procedure, Z. Yosida investigated in more detail the mode of development of window hoar crystals which grew on a thoroughly cleaned glass surfaces(2).

Among the photomicrographs of artificial hoar crystals obtained by these investigators, only a few examples of snow-like crystals are given, which grew on

* Contribution No. 267 from the Institute of Low Temperature Science.
the glass rubbed with a cloth containing some reagent for fog prevention or on the cloven mica.

Now, since the hydrophobic thin film spread over the glass surface may serve to protect the growth of crystals from the disturbing action of glass surface, it is to be anticipated that the ice crystals that grow on the film will assume the forms similar to the snow crystals in the free atmosphere. It was the main object of the present experiment to see whether this anticipation comes out true or not, and further to seek for the conditions of the formation of ice crystals with rectangular plane form, the existence of which was previously reported by the present author\(^{(1)}\).

Another reason for attempting the experiment was that, since the crystals of rectangular form were observed by means of a replica method, it was apprehended that these crystals might possibly have been formed through condensation or sublimation directly upon the polyvinyl formal, which had polymerized and dried at some thinner portion of the layer of the replica solution, and then afterwards covered by the solution (probably while the slide glass was being transferred to the desiccator). Thus it seemed desirable first to put such a possibility to the test and see if the rectangular crystals can be found in the hoar frost produced on the polyvinyl formal. If there appeared solely rectangular crystals, it might be inferred that the above-mentioned apprehensions came out true, while on the contrary, if the snow-like structures manifested themselves, which may or may not include rectangular forms, it would indicate that the conclusion as to the formation of rectangular crystals stated in the previous paper was not so much probable as unambiguous, since in that case the polyvinyl formal would prove to be hydrophobic.

Previous to the present experiment, we tried an experiment using an apparatus as shown in Fig. 1, which was originally intended for getting some information as to the conditions under which rectangular crystals are formed. Some of the replica figures obtained are shown in Photos. 1, 2 and 3. Photos. 1 and 2 both represent a thin square crystal containing a semi-spherical ice droplet, and Photo. 3 a hexagonal crystal likewise with a droplet. In consideration of the con-
struction of this apparatus which was inadequate to the original purpose, we considered it very probable that these crystals were formed by the direct condensation (or sublimation) of the water vapor on the surface of polyvinyl formal. But we could get no definite evidence for this supposition, nor could we identify the observed square crystals with the rectangular crystals reported previously (cf. Photos. 4 and 5). The reason why ice droplets were so frequently observed in combination with the crystals (actually it is too frequent to be explained by "chance") remained also obscure.

With the aforementioned arguments and facts in mind, we proceeded to the following experiments, in which we used as hydrophobic substances polyvinyl formal, Methalack, G. E. Dri-film, and Daiflon-2, and succeeded in obtaining hoar crystals that grew in snow-like forms.

II. Methods

Cleaning of the glass plate

The glass plates which have been immersed in a sulphuric-acid solution of potassium bichromate are rinsed in running tap-water and in a vast volume of distilled water, and then dried in an electric oven.

Preparation of the hydrophobic coating

(i) Polyvinyl formal, whose 1% solution in ethylene dichloride is dripped on the glass plate and quickly spread into a thin layer by the use of a clean glass rod. After the solvent has completely evaporated (in a few minutes), the glass plate is kept in a desiccator containing CaCl₂ until just before the beginning of the experiment.

(ii) Methalack, methacrylic acid ester resin to be obtained from Fuji-Kasei Co., is diluted with an appropriate thinner. The coating procedure is the same as the preceding.

(iii) Dri-film, which is silicon grease dissolved in conc. HCl offered by General Electric Co, and is said to have a contact angle against water amounting to 90° is spread over the glass surface by means of a glass rod dipped in the solution. As we have regrettably no information about the proper technique of desiccation, we used it under the state as it was still more or less soft after it has been left in a desiccator for several hours.

(iv) Daiflon-2 (trifluorochloroethylene polymers produced in Osaka Kinzoku Kogyō Co. with the same characteristics as KEL-F made in N. W. Kellogg Co., U. S. A.) in the colloidal form dispersed in an organic solvent is painted or sprayed over the glass surface. The surface turns out snow-white after the solvent has evaporated at ordinary temperature. It is then put in an electric oven and heated up to about 250°C. After being kept at this temperature for a short time (meanwhile the white colour disappears), it is cooled down. The same treatment is
repeated twice or thrice lest there should be any pin holes left on the Daiflon film. Finally the temperature in the oven is gradually raised up to 300°C, whereby we get a uniform layer of semi-transparent Daiflon.

The hydrophobic character of these surfaces was estimated by observing the respective contact angles against water droplets: The coated slide was sprayed for a few seconds with minute water droplets blown off from an atomizer. The lateral view of the captured droplets was quickly photographed through a microscope, and the contact angles were observed as a measure for the water-repelling power of the surfaces. Examples are illustrated in Photos. 6–12.

- Photo. 6: Side view of the droplets on a clean glass.
- Photo. 7: Droplets on the glass plate coated with Dri-film.
- Photo. 8: Droplets on the Daiflon-2 plate.
- Photo. 9: Droplets on the glass plate coated with Daiflon-2.
- Photo. 10: The same with Methalack coating.
- Photo. 11: The same with polyvinyl formal coating.
- Photo. 12: Polyvinyl formal coating that was once put to the test and has been kept in the desiccator for about 48 hrs.

It is to be noticed from Photos. 11 and 12 that the water-repelling effect of polyvinyl formal remarkably decreases if it has once been wetted. Therefore we always used a fresh dry surface in each succeeding experiment.

The glass plates coated with hydrophobic substances were usually kept in a low temperature room prior to the experiment.

**Apparatus**

The apparatus designed for the present research is a very simple one as shown in Fig. 2.

The source of water vapour is the mixture of ice and water put in a large vacuum-flask and is maintained nearly at 0°C. As the liquid surface of the mixture is liable to be covered with thin ice film, it is necessary to stir the mixture at frequent intervals during the experiment.

**Experimental**

After the apparatus was set in the cold chamber, the glass plate was taken out of the desiccator and placed in position with the coated surface downwards.

The temperature of the water-ice mixture $T_w$ and the room temperature $T_r$
are measured each with an ordinary fine thermometer. A third thermometer \((T_a)\) is placed in such a position that its bulb comes in slight contact with the coated surface of the glass plate. Since the plate has been kept in a desiccator for a long time (2–3 hrs.) previous to each experiment, the initial temperature of the coated surface (i.e., the temperature at the moment when the plate is placed in position) must be equal to the room temperature \(T_r\). The surface temperature will then rise rapidly, whilst the reading of \((T_a)\) falls until it reaches a minimum, thereupon to increase gradually up to a stationary value. The final reading of \((T_a)\) may, therefore, be regarded as corresponding to the mean temperature in the immediate vicinity of the surface when the stationary state has been attained. It is to be understood that the symbol \(T_a\) hereafter used means the final temperature indicated by the thermometer \((T_a)\).

As soon as the glass plate was put on the top of the apparatus, the hoar frost began to form instantaneously in a manner characteristic of each kind of hydrophobic substance. After the lapse of 4 or 5 minutes, the development of the hoar crystals seemed to be arrested as judged from their appearance, the temperature then being \(T_a\). The glass plate was then removed from the apparatus and a shadow-photograph was taken on a dry-plate or a bromide paper by the use of the apparatus as shown in Fig. 3.

Further, for the subsequent microscopic observations, a replica of the hoar crystals was prepared with the aid of “Methalack”\(^{(2)}\), which proved preferable to Schaefer’s replica solution for the use at temperatures below ca. \(-10^\circ\text{C}\).

III. Observations

**Hoar crystals on the clean glass surface.**

The mode of development of window hoar which grows on a clean glass surface has hitherto been investigated in detail, and the mechanism of development of uniform frost or isolated hoar crystals was thoroughly discussed by U. Nakaya and Z. Yosida.

In so far as our observations pertaining to the clean glass are concerned, there is nothing to be supplemented to their works, and so we shall give here only some photographs, which illustrate the typical development of hoar frost on the clean glass, for the sake of comparison with the crystal growth on hydrophobic...
substances.

Photo. 13 shows the uniform frost composed of minute frozen dew drops and the peculiar form of the hoar crystals (branching streamers) that develop from the margin of the thin uniform frost.¹

These branching streamers and also the detached hoar (Photo. 14) have a wavy character as was pointed out by U. Nakaya et al. It will be observed from Photo. 15 that the development of margin crystals is largely promoted by the capture of larger supercooled droplets.

On rare occasions a part of stellar crystal develops at the margin (Photo. 16) and a hexagonal column in the middle of uniform frost (Photo. 17). The existence of blank spaces around these crystals gives evidence that they grew only by sublimation, merging the surrounding water droplets into themselves, provided that there were some germs suited to the crystal growth of ice.

_Hoar crystals on the Dri-film._

The Dri-film covering the glass, which, as was previously described, we were unable to bring to a completely dry state, has a repellent action not only on water but also on Methalack. Consequently, when the Methalack is let fall over the hoar, it does not spread over the Dri-film but forms a large drop, with the result that the clustering of hoar crystals takes place and the investigation of the crystal form by aid of replica method becomes impossible. The observations were, therefore, confined to the shadow-photographs, which showed, as may be seen from Photo. 18 (negative print), that something like a lump or hexagonal graupel is produced in this case.

_Hoar crystals on the Methalack._

It is a remarkable feature of the surface coated with Methalack that the frost particles to be formed on it assume nearly spherical form, as can be seen from Photos. 19 and 20.

_Hoar crystals on Daiflon-2._

On Daiflon-2 as well as on polyvinyl formal, the uniform frost composed of minute frozen dew drops can rarely be observed, except at relatively high temperatures. The mode of crystal formation in this case bears a striking resemblance to that of artificial snow production. Photo. 21 is the shadow-photograph of hoar crystals obtained at $T_w = -1.3^\circ C$, $T_a = -25.7^\circ C$ and $T_r = -37.8^\circ C$ (4.5 min after setting the coated glass in position).

Hexagonal column, bullet type and their irregular assemblages are shown in Photos. 22, 23 and 24, among which the secondary development of a part of hexagonal plate can also be seen. Photo. 25 illustrates the crystal growth along the crack of the coated surface which just corresponds to the "irregular assemblage"

¹The simple expression "uniform frost" will be used in the following, just for convenience's sake, for the meaning "the uniform frost composed of frozen dew droplets".
of snow crystals in their early stage produced on a rabbit hair (cf. U. Nakaya: “Snow Crystals”(9), Photo. No. 1136). It is to be noticed that the small irregularities on the surface play an important role as nuclei.

We shall presumably be able to produce other crystal forms observed in snow crystals on the surface of Daiflon-2 by controlling \( T_a \) and the degree of supersaturation in the apparatus.

**Hoar crystals on the polyvinyl formal.**

Polyvinyl formal was most frequently used for the reason previously stated, and was found to be likewise suitable for producing ice crystals in snow-like form.

It is worth emphasizing the following two points concerning the mode of ice crystal formation on this surface:

(i) A number of ice crystals having snow-like forms are produced uniformly distributed over a wide area of the coated surface.

(ii) The ice crystals obtained on one and the same coated surface belong to the same crystal type determined by the specified conditions under which each experiment has been carried out.

These facts suggest that the mechanism of appearance of these ice crystals is essentially different, as will be described in Section IV, from that of the isolated snow-like crystals that happen to form within the uniform frost.

a) Columnar crystal (pyramid, bullet type, hexagonal column).

The mode of hoar development shown in Photo. 26 does not seem to differ, at first glance, from that on the clean glass. But photomicrographs 27–32 of a certain portion of Photo. 26 taken successively in larger magnifications reveal that the hoar is composed of fine crystals such as pyramid, bullet type, hexagonal column and the like* (cf. microphotographs 33, 34 and 35 which show the frozen droplets composing the uniform frost on the clean glass). We shall call hereafter such a mode of frost formation “uniform hoar”, for the sake of contrast with “uniform frost” (see the foot-note on p. 12).

These crystals were obtained under the conditions \( T_w = -0.5°C, T_a = -9.9°C \) and \( T_r = -20.6°C \). It must be remarked, however, that in this case the initial conditions were different, inasmuch as a warm plate kept in a desiccator at ordinary temperature was introduced into the cold chamber just before the beginning of the experiment and was quickly set in the apparatus.

The appearance of hoar crystals was then found very much delayed. For the first 4 minutes no trace of crystals was observed on the surface, and 18 minutes elapsed before we could take Photo. 26. Whether or not such circumstances will have any essential influence on the crystal form to be developed is for the moment

* There can be observed also comparatively larger, though few, amorphous frozen droplets, for which the casual existence of larger nuclei (something like dust) might presumably be responsible.
undetermined.

b) Plane crystal (branches in sector form, broad branches, stellar form, stellar crystal with plate at ends).

During our series of experiments we also tried the method of comparing the crystal formation on the clean glass with that on others under the same condition, that is, the method in which three slide glasses, one coated e.g. with polyvinyl formal in the middle and the other two clean ones on both sides, were used at the same time.

Thus, while we obtained the crystal form such as shown in Photo. 13 on the clean glass under the conditions $T_w = 0°C$, $T_a = -9.1°C$ and $T_r = -37.2°C$, we observed on the polyvinyl formal film the structure of hoar as shown in Photo. 36. The major part of this plate was covered with the uniform hoar (of which only a minor portion is reproduced in Photos. 36 and 37), while in an extended narrow region there appeared more or less sparsely distributed plane crystals. ($T_a$ is the temperature indicated by the thermometer $(T_a)$, of which the bulb was not in contact with the coated surface, but somewhat apart (6 mm) from it.)

It is quite interesting that the ice particles constituting the uniform hoar (Photo. 37) are the intermediate between the ice crystals (Photos. 29 and 30) and the frozen droplets (Photos. 33, 34 and 35) and also that almost all the observed plane crystals, such as stellar crystals, manifest eccentric development or irregular number of branches (cf. Photos. 38, 39, 40 and 41).

Such irregular developments may be ascribed to the fact that two or more ice particles are likely to link together (from some unknown cause) to form a group (see Photo. 37). Thus, provided these groups are sufficiently apart from one another, so that the vapour supply per group is sufficiently large, each particle within a group may act as an independent germ, yielding the irregular development as a whole.

c) Needle crystal.

The uniform hoar (Photo. 42) obtained under the conditions $T_w = -0.8°C$, $T_a = -22.6°C$ and $T_r = -36.9°C$ consisted of columnar crystals, their irregular assemblages, and the rounded needles that secondarily extended from the columnar crystals (Photos. 43−46).

The secondary extensions, what we have called needles, have an appearance resembling those observed by U. Nakaya, which extend perpendicularly from the hexagonal plane bases of snow crystals. (cf. "Snow Crystals" Photo. Nos. 708 and 715). But the conditions, under which we obtained needles, differ markedly from those expected from Nakaya's $T_aT_w$-diagram."

Here we do not intend to take a step farther and attempt to discuss about the relation between the crystal form and the temperature and degree of supersaturation. It will be left to future investigation, for which more cautious and
d) Uniform frost and isolated hoar crystals.

When the temperature of the surface where the ice crystals develop is relatively high, that is, at $T_a$ above ca. $-10^\circ$C, uniform frost is likely to develop on this surface, and when the supply of water vapour is abundant enough, say at $T_w = \text{ca.} +8^\circ$C, the dendritic type of development makes its appearance frequently at the margin of the uniform frost. In the middle of the uniform frost, there appear sporadically isolated hoars, amorphous or of the same type as was obtained in Nakaya and Yosida's investigation.

Photos. 47 and 48 illustrate the dendritic development observed at $T_w = +8^\circ$C, $T_a = -10.8^\circ$C and $T_r = -22.6^\circ$C, and Photo. 49 is the shadow-photograph of the uniform frost obtained at $T_w = -0.5^\circ$C, $T_a = -10.6^\circ$C and $T_r = -20.8^\circ$C. It will be observed that the frozen dew drops composing the uniform frost (see Photo. 50) are more spherical than those on the clean glass (cf. Photos. 33, 34 and 35) and are connected with one another by ice bridges. Photos. 51-54 show the isolated hoars observed among them.

IV. Discussion

Since in the foregoing sections there were given only some results so far obtained, the matters discussed in this section are not so much ultimate conclusions as tentative propositions to be verified by the experimental researches in future.

The mechanism of development of uniform frost composed of frozen dew droplets is, according to Z. Yosida, as in the following: At first the foggy layer composed of numerous tiny water droplets covers the whole surface of the glass, then if any one of the droplets gets frozen, the "skirt"-like thin ice film spread out from the boundary until it touches the neighbouring droplet. The latter droplet freezes at that instant and a skirt-like film again spreads out from the newly frozen droplet, which causes another neighbouring droplet to freeze, and so on.

It is highly probable that the same mechanism holds as regards the uniform frost formed on the hydrophobic surface, since, as has been confirmed by the preparatory experiment sketched in the following paragraph, there exist numerous condensation nuclei on the hydrophobic surface.

The apparatus made use of was originally designed by D. Kuroiwa for the study of fog nuclei (Fig. 4). At first, the air in the vessel which is lined with wetted filter paper is saturated with respect to water at the room temperature, and yet the condensation on the coated surface does not occur. When the water maintained at 0°C is poured into the vessel and the cover glass is thereby cooled down, considerable supersaturation is obtained near the surface. After several minutes, there appear, as seen through the microscope, numerous tiny water-
droplets simultaneously over the whole coated surface.

Now, the latent heat released in the process of condensation or freezing will be for the most part lost by conduction through the glass plate. The more hydrophobic the surface, the smaller becomes the contact area between the water droplet and the surface and so the rate of heat-loss through conduction, since the heat loss is proportional to the contact area, while the released heat is proportional to the mass of water condensed. Thus, as the condensation proceeds, it should become more and more difficult for a water droplet on the surface to freeze, unless it is inoculated with an ice particle or the like; in other words, the above-mentioned mechanism of uniform frost formation is to be expected also in this case. It would have been interesting, if we could trace the actual frost development through visual observation. But since the present experiment was confined to the microscopic observation by the use of replica method, that is, to the observation of the temporal cross section of frost development, we cannot assert the truth of the above argument with confidence. We have found however that, as will be seen from Photo. 50, there appear a number of ice bridges connecting tiny frozen droplets having the diameters 6 to 20 μ, which fact seems to furnish good evidence in support of our tentative reasoning.

In the case of uniform hoar composed of tiny ice crystals as shown in Photos. 31 and 32, no trace of bridges can be observed. The same mechanism as assumed in the case of uniform frost must therefore be rejected.

Here it is worth while to make reference to the fact observed by K. Kozima that, when small droplets are sprayed on the surface of an ice crystal of hexagonal plate form, they get frozen on contact with the surface while they assume semi-spherical form, and that further supply of water vapour causes the frozen droplets to develop into the crystals of hexagonal form, of which both a- and c-axes are parallel to those of the base crystal. The frozen droplet must, therefore, be considered to have internal crystalline structure.

The structure of the uniform hoar may well be accounted as arising from the same process of crystal formation as observed by K. Kozima. Under the condition of high degree of supersaturation, as is actually the case, there are produced in the air tiny water droplets of a few microns in dia., any one of which upon coming into collision with the cold surface will solidify keeping its spherical shape but with internal crystalline structure so that it may act as a germ for
further growth into an ice crystal of regular form.

Whether the droplet on contact with the surface will remain liquid or will be frozen might be governed by various factors, such as the temperature and the cooling rate which depends upon the liberation of latent heat and the conduction across the contact surface, but any detailed theoretical consideration has not yet been given.

The contribution of tiny water droplets to the growth of snow crystals has been emphasized by U. Nakaya et al., who observed the phenomena of sudden disappearance of a minute droplet coming close to an ice surface. If an ice germ is once produced, the water droplet that happens to be in close proximity to it evaporates suddenly and condenses over it by sublimation, which is caused by the vapour-pressure difference of ice and water.

U. Nakaya also suggested another possibility that the droplet comes in contact with the ice whereupon the surface diffusion of water molecules takes place. This, he supposes, is supported by the existence of liquid water film on the ice surface.

What is more interesting is the fact that larger droplets 10μ or more in dia. play an important part in the dendritic development of the margin hoar: As can be inferred from Photos. 47 and 48, the water droplets directly captured on the tip and such like of the dendritic branches get frozen successively by the help of ice bridge and constitute a new branch. The development of such dendritic branch is illustrated in Photo. 55. It looks as if it were composed of water droplets carried along by the diffusion of water vapour.

As for the ice crystal of rectangular plane form, we could not after all find any such sharp figures as previously reported, in spite of our particular efforts throughout the period of microscopic observation. The figure shaped something like a rectangle is shown in Photo. 56, which was obtained among the plane crystals on the glass plate coated with polyvinyl formal. Attention should be directed also to the fact that many of the minute water droplets in the neighbourhood of the dendritic branches extending from the margin of uniform frost over the polyvinyl formal surface have more or less angulate—square or rectangular—shape (cf. Photos. 48, 57 and 58).

Acknowledgments

In conclusion, I wish to express my cordial thanks to Prof. T. Hori and Dr. D. Kuroiwa for their kind advices and criticisms. Many thanks are also due to Dr. Y. Ozawa of the Institute of Applied Electricity, who offered me Daiflon-2, and to Mr. K. Higuchi of Department of Physics, who lent me his own shadow-camera.
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(6) Nakaya, U. Ditto p. 244.