350-397 SR
OR 2,104,949
Search Room

Jan. 11, 1938. A. M. MARKS 2,104,949

CRYSTALLINE FORMATION

Filed March 22, 1933

T2562

Fig. 1.

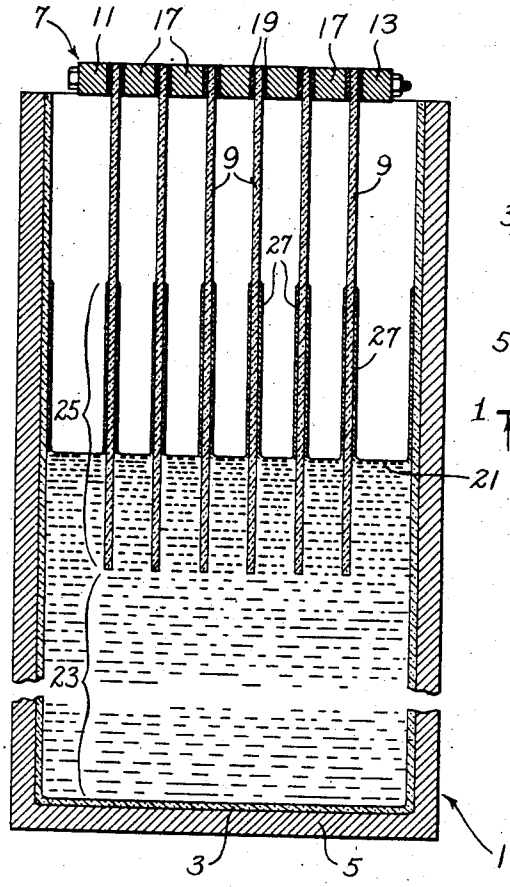


Fig. 2.

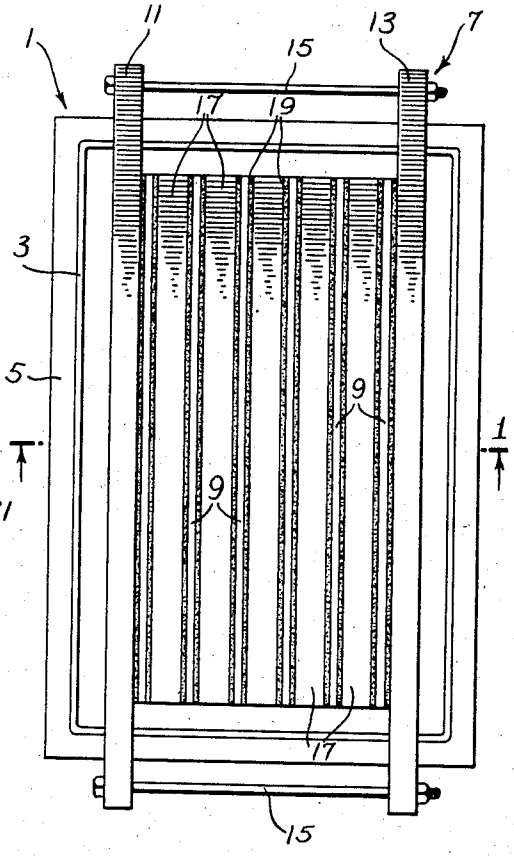
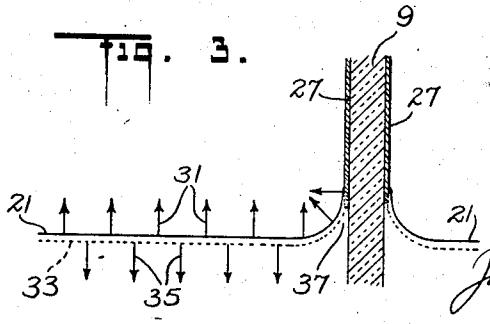


Fig. 3.



INVENTOR
Alvin M. Marks
BY
Janney Blair & Curtis
ATTORNEYS

Search Room

Patented Jan. 11, 1938

2,104,949

UNITED STATES PATENT OFFICE

2,104,949

CRYSTALLINE FORMATION

Alvin M. Marks, Whitestone, N. Y.

Application March 22, 1933, Serial No. 662,090

18 Claims. (Cl. 23—1)

This invention relates to crystalline formations and with regard to certain more specific features to a crystalline formation formed on a supporting medium, and to the process for producing the same.

One of the objects of the invention is to provide a method for forming on a supporting medium a layer of material of a substantially unitary crystalline structure.

Another object of the invention is to provide, as an article of manufacture, a supporting medium having thereon a layer of material of a substantially unitary crystalline structure.

Another object of the invention is to provide, as an article of manufacture, an optically active medium capable of polarizing light and which is relatively simple and inexpensive to manufacture and which is of durable construction.

Other objects will be in part obvious and in part pointed out hereinafter.

The invention accordingly consists in the features of construction, the combination of elements, the arrangements of parts as will be exemplified in the structure to be hereinafter described; the processes, and the sequence of steps for carrying out the processes as will be hereinafter described; and the scope of the application of which will be indicated in the following claims.

In the accompanying drawing, in which is shown one or more of the various possible embodiments of this invention:—

Figure 1 is a vertical section of an apparatus suitable for carrying out the process of the invention taken on line 1—1 of Fig. 2;

Fig. 2 is a top plan view of the apparatus of Fig. 1; and

Fig. 3 is a fragmentary detailed section of a supporting medium having a crystalline layer being formed thereon, showing the manner in which the solution, from which the crystalline layer is deposited, is drawn upon the surface of the supporting medium.

Corresponding reference characters refer to the corresponding parts throughout the several views of the drawing.

As conducive to a clearer understanding of the invention it is pointed out that there are many uses for relatively large crystalline surfaces or structures of a substantially unitary or united crystalline nature (in contradistinction to a structure made up of individual crystals arranged and joined in haphazard fashion). Although some natural crystals, such as tourmaline, have surfaces of relatively large areas, such crystals are limited in size and shape, cannot be obtained in a relatively thin unlimited curved or flat shape, and are so expensive as to preclude their use for many commercial purposes. Hence, it is another object of this invention to provide a unitary crystalline surface not subject to the disadvantages of such natural crystalline surfaces and structures as, for example, tourmaline, but which have all of the advantages of such a crystalline structure.

Apparatus

Referring now more particularly to Figs. 1 and 2, there is shown an apparatus suitable for carrying out the process of the invention. The apparatus includes a tank, generally indicated at 1, for holding a liquid solution used in the process. Inasmuch as it is desirable to prevent impurities from entering the solution it is preferable to provide the tank 1 with a seamless glass lining 3 surrounded by a protective box-like structure 5. The tank is formed relatively deep for the provision of a considerable excess of the solution used in the process. Supporting mediums 9, on which the crystalline film or layer is formed, are mounted in the tank 1 as shown in the drawing, by means of a clamping device, generally indicated at 7. The clamping device comprises parallel clamping members 11 and 13, and bolts 15 for drawing the members 11 and 13 together. Spacing blocks 17, provided with corked edges 19, actually contact with the supporting mediums 9 and hold them in parallel spaced relationship.

It has been found desirable, under certain conditions of operation, to space the plates 9 from one quarter to one half inch apart. It has also been found desirable to maintain the plates substantially perpendicular to the liquid level (indicated at 21) in the tank.

However, under certain other conditions of operation it has been found expedient to place individual plates back to back so that only one surface of each plate is exposed to the solution. In this way instead of obtaining a crystalline layer on two sides of the plate, it is obtained on only one side. With this operation it is preferable to arrange the plates back to back so that the solution in the tank cannot enter between them.

The supporting mediums 9 are preferably sufficiently rigid in their structure so that they will not flex to cause the crystalline film or deposit thereon to break or otherwise become separated from the supporting medium. When a transparent supporting medium is desired, I prefer to use glass plates which are free from faults or other

irregularities, inasmuch as my experiments indicate that such faults or defects on the surface cause irregularities in the crystalline structure deposited on the glass by the process to be hereinafter disclosed. For this reason it is also desirable to thoroughly clean the surface of the glass plates 9 before they are mounted in the tank. They may be cleaned with the usual solutions for removing substantially all the organic and inorganic impurities, both fluid and solid.

According to my present understanding of my invention, inasmuch as some evaporation of a solvent is essential, it is preferable to set up the apparatus where a draft may be provided to carry away the vaporized solvent which may later be condensed. As will be hereinafter described in detail, it is also desirable to have means for controlling the pressure, temperature and humidity above liquid in the tank. Under certain conditions of operation it is desirable to mount the tank on a foundation to which may be imparted vibrations of a controlled frequency and amplitude.

The process

The results of my experiment have led me to believe that my process is generally applicable to those crystalline substances which tend to form predominantly flat crystalline structures, i. e., crystals which tend to grow with an approximately constant surface area per unit of mass. For the purpose of describing the process, the following example is given for forming such a crystalline structure of iodoquininesulphate on a glass surface 9 as a supporting medium. (This example is of additional interest because iodoquininesulphate is optically active and the film of iodoquininesulphate thus formed on the glass, being a single crystal, is capable of plane polarizing light passing therethrough. Hence it is another object of my invention to provide as an article of manufacture a transparent medium having a layer of material thereon for polarizing unpolarized light).

Iodoquininesulphate is not a common substance and accordingly it is believed that the following description of a satisfactory procedure for obtaining the salt may be helpful in carrying out the process in the event that iodoquininesulphate is not commercially available.

Starting with:

Quininesulphate	gms.	16
99.5% acetic acid	cc.	50
Distilled water	cc.	100
Concentrated sulphuric acid	cc.	2

the 16 gms. of quininesulphate is dissolved by stirring it in a mixture of the liquids. To the resulting solution is added slowly a solution of 5 gms. of iodine in 240 cc. of methyl alcohol. The precipitate of iodoquininesulphate which forms is allowed to settle an hour or so and is then filtered with suction. The filtrate of iodoquininesulphate is washed with benzene until the benzene shows a materially reduced iodine coloration.

This filtrate after drying under suction for five minutes is further purified by being mixed into a paste with a small amount of ethyl alcohol and then heated to 50° C. in a total of 500 cc. of ethyl alcohol. The mixture is then allowed to cool to room temperature and is again filtered under suction. This purification or refining is repeated as often as necessary to obtain the desired purity. The resulting paste after the final treatment, is dried and allowed to stand in a circulating dry air draft maintained at a temperature of about 25° C. for ten days, which should be sufficient to dry the product and remove traces of benzene. The iodoquininesulphate thus obtained, when powdered, is predominantly black, and may be stored in a glass stoppered bottle.

The solution

The iodoquininesulphate obtained by the foregoing method is deposited on the surfaces of the glass plates 9 from a solution (preferably containing, as a component, a solvent having a relatively high vapor pressure and which will "wet" the supporting surface) of which a preferred one may be made up as follows:

Starting with a liter of ethyl alcohol containing 15% water by volume, a saturated solution (at 25° C.) of the iodoquininesulphate is made by adding more iodoquininesulphate to the alcohol and water than will dissolve upon agitation. This may be accomplished by adding about 2 gms. of the iodoquininesulphate per liter and agitating, filtering out any excess. The final solution will contain a little over one gm. of iodoquininesulphate per liter.

To this saturated solution is added 0.2 gm. of quininesulphate per liter and the whole is agitated. (Note that there are preferably five parts of iodoquininesulphate to one part of quininesulphate.) As will be hereinafter pointed out, my experiments have indicated that this is a preferred proportion or ratio.

The solution is now filtered and preferably stored in clean glass stoppered bottles.

This solution has been found to be satisfactory under most conditions of operation, but in varying it for other crystalline substances, and for other conditions of operation, it is desirable to consider certain general factors. For example, the crystalline substance should not be so soluble in the solvent as to interfere with the deposition of the crystalline substance from the solution; nor should it be so insoluble as to prevent the formation of any crystalline film or layer as will be hereinafter described.

Further, the solution should be made up so that it tends to deposit out only one crystalline substance—in other words, it should contain constituents which tend to throw out the one crystalline substance, and should not contain substances which tend to withhold the throwing out of that one particular crystalline substance. To illustrate this, one of the reasons for adding the quininesulphate is to preclude the presence of free iodine in the above solution, as too much free iodine tends to interfere with the deposition of the iodoquininesulphate. In further illustration of this point it may be noted that the presence of the quininesulphate also acts according to the law of mass action to aid in the throwing out of the iodoquininesulphate.

In accordance with the above it is desirable to add to the solution, as may be determined by simple experimentation, substances which aid in the predetermined deposition of one crystal over all others present in the solution.

Furthermore, it is desirable to make up a solution containing all of the ingredients essential to the crystalline layer formed on the supporting surface, and in such a proportion that the one crystalline substance is far more readily thrown out of solution than other dissolved crystalline substances present. In this connection the presence of water in the above described preferred solution for iodoquininesulphate is desirable be-

Search Room

cause the iodoquininesulphate crystalline layer forms with water of crystallization. Accordingly, if there is no excess water present, over that required for the formation of the iodoquininesulphate, then this deposition is interfered with since ethyl alcohol itself has considerable attraction for the water. In other words, when no excess water is present, the ethyl alcohol itself interferes with the deposition of the iodoquininesulphate with water of crystallization.

To deposit the iodoquininesulphate on a glass surface from such a solution, the tank 1 is filled with the solution to a depth preferably ten times or more the vertical dimension of the deposit to be obtained on the glass plates 9. (Thus referring to Fig. 1, the distance 23 is preferably ten times the distance 25, assuming the plates are to be coated down to their lower edges). Such a depth assures that the composition of the solution will not be altered to any appreciable or injurious extent during the deposition.

The plates 9 after having been carefully cleaned and freed from impurities are lowered in position into the tank 1, where they remain stationary with respect to the tank as shown in the drawing.

It is desirable to keep the partial pressure of the solvent above the solution appreciably lower than the vapor pressure of the solvent in the solution and accordingly it is desirable to maintain a temperature, pressure and draft condition above the solution which accomplishes such a result. The difference in the pressures actually maintained may be varied within limits—the exact difference being determined in each instance by the result desired. In general, for a given rate of lowering of the liquid level, the greater the difference, the thicker the deposit. Further, it is desirable to maintain this difference constant during the deposition, other conditions being equal. It is preferable, in most instances, however, that the total pressure of the partial pressure above the solvent be above that of the vapor pressure of the solvent so as to prevent the solution from boiling which causes surface disturbances.

Working with the solution described, it has been found that a temperature of 18° C. to 27° C. at atmospheric pressure is satisfactory.

Likewise, to maintain the preferred water content of the solution as nearly constant as possible, it is desirable to maintain a humidity above the solution which will permit the water to evaporate at the same rate that the ethyl alcohol evaporates—in any event the humidity should not be high enough to permit the solution to absorb water to a harmful extent.

In general, it is desirable that the surface 21 of the liquid or solution, as well as the plates 9, be maintained substantially free from movement, except with respect to each other, and accordingly it is preferred to keep the apparatus free from vibrations such as come from the street or the like. However, for reasons to be discussed hereinafter, it is desirable, under certain conditions of operation, to subject the apparatus, during certain stages of the deposition, to controlled vibrations, and hence means for imparting the desired vibrations are preferably provided.

Ethyl alcohol, or other solvent used, which evaporates, may be recovered by condensation. Under certain conditions of operation in which the evaporation of the liquid is employed to move the liquid level 21 with respect to the plates 9, the amount of solvent which may be thus recovered may be of considerable value.

As hereinbefore pointed out, I have found it not only desirable to use a solvent having the desired vapor pressure at the desired temperature, but also employing one which wets the supporting surface on which the crystalline layer is to be formed. However, it is my present understanding that the degree to which the solution wets the supporting surface, or the surface tension existing between the solution, the supporting surface, and the atmosphere above, evidently has certain limits. If the surface tension is such that the angle at which the solution meets the supporting surface becomes substantially zero, or if the surface tension is such that the angle which the supporting surface makes with the liquid level of the solution is substantially 90°, the satisfactory operation of the process is hindered. Thus the desired degree of wetting is determined in each instance by the results obtained.

Operation

After the apparatus and solution have been thus set up, and the desired conditions determined and arranged as described, the liquid level 21 of the solution is slowly moved with respect to the surfaces of the glass plates 9 in such a way that the liquid level lowers with respect to the plates—or, in other words, the plates rise with respect to the liquid level. In the present example it has been found that the evaporation which naturally occurs when the partial pressures of the solvent above the solution having a high vapor pressure is maintained relatively low, produces a satisfactory "lowering of the liquid level", although under certain other conditions of operation other means for producing such a movement between the two mediums may be preferred.

Using the evaporation to "lower the liquid level" and working with the solution described without any substantial draft it was found that with a temperature between 18° C. and 27° C. and atmospheric pressure a lowering of 69 mm. was produced in forty-five days. However, it has been found preferable to maintain the surrounding temperature substantially constant, other things being constant. Of course, this illustration is by way of example only and is not intended as a limit.

It has been found that as the liquid level 21 is lowered a layer comprising a single crystal of iodoquininesulphate 27 (see Figs. 1 and 3) is deposited on the glass surfaces. However, the rate of the lowering must be within certain limits as determined by the conditions. If the lowering be too rapid the layer 27 may become too thin, or may not be satisfactory for some other reason. This factor is a matter of technique and is determined in each instance by the results desired.

As the liquid level drops and the iodoquininesulphate deposits in layers 27 on the surfaces of the plate 9, the amount of iodoquininesulphate present in solution of course tends to drop. This tendency may be counteracted by evaporation of the solvent, ethyl alcohol and water, when evaporation is employed as the sole means of lowering the liquid level. But, since it has been found preferable under most conditions of operation to maintain the solution always saturated with iodoquininesulphate, if the amount of iodoquininesulphate deposited exceeds the corresponding amount of solvent evaporated, then it is desirable to add additional iodoquininesulphate to keep the

solution saturated; without, however, disturbing the surface of the solution.

The product

The unitary crystalline structures or layers **27** thus deposited on the surfaces of the glass plates **9** are in effect single crystals. These crystals are firmly attached to the glass without the use of any intermediate binding medium, or atmospheric pressure. It is my present understanding that as the crystalline layer is deposited out there is a surface or molecular interpenetration, such as adsorption, by the crystalline molecules on the glass surface (or other supporting surface) in such a way that the resulting crystal is mechanically interlocked with the glass surface.

Inasmuch as each layer of the iodoquininesulphate **21** is a single crystal, and inasmuch as iodoquininesulphate crystals are capable of polarizing unpolarized light, the article produced by my process, as illustrated in Figs. 1 and 3 (if the glass plates **9** are transparent) may comprise a transparent isotropic plate, coated with a layer of substance capable of plane polarizing light in the same direction over the entire plate. The size of such a crystalline coated surface, apparently depends only on the size of the original plate or supporting surface, which within reasonable limits may be of any size.

My experiments have further indicated that the crystals **27** formed on the surfaces of the plates **9** when comprising iodoquininesulphate and deposited according to the foregoing example plane polarize the light at an angle which may be parallel to the solution surface **21**.

Further, the crystal layers **27** of iodoquininesulphate thus formed on the plates **9** are not easily detached therefrom, nor are they subject to any substantial deterioration from light, moisture or other atmospheric elements. However, I have found it desirable under certain conditions to provide the crystalline surfaces or layers **27** with a thin coating of protective substance such as a transparent colorless varnish. This protective coating of varnish has the further property of tending to offset any tendency for surface irregularities of the crystalline film to scatter light passing therethrough, and so improves the article for use in transmitting light.

It is thus seen that not only has a new article of manufacture been provided by the invention, namely, a supporting surface having a single crystalline layer deposited thereon without the use of any additional binding material, but also a new process has been provided, namely, a process of joining an unlimited unitary crystalline sheet to the surface of a support, or, in the case of iodoquininesulphate and glass, a process of attaching an unlimited crystalline anisotropic sheet to the surface of an isotropic substance.

I have observed from the experiments described above, that, wherever faults, cracks or particles of foreign substance occur on the glass surface, at these places the single crystalline layer stops, and that what I term haphazard crystalline areas, are deposited around such places. These areas usually comprise small individual crystals which may or may not be joined to each other, and which have no particular arrangement.

Further, my experiments indicate that whenever there is a tendency for two crystalline substances to deposit out simultaneously, what I term twinning areas occur. These areas usually comprise individual crystals, having some degree of uniform arrangement, and in all instances joined together.

Effect of vibrations

Under certain conditions of operation, I have found that as the above described layer **27** first starts to deposit on the surfaces of the glass plates **9**, it is not in the form of the single crystal, but is made up of a number of small crystals. One explanation for the formation of these small crystals arranged in a haphazard way is that when the plates **9** are lowered into the tank, the surface of the plates is wet by the solution in a haphazard way above the upper line of contact between the solution and the plates **9**. The solvent of these wet spots on the plates **9** evaporates, depositing the crystalline substances with no particular arrangement. As the liquid level moves with respect to the plates **9**, and as the crystalline substance is deposited out, there is a tendency for the crystals initially deposited to grow to produce a crystalline layer, not of a single crystal but of a number of crystals. This tendency, however, is offset and overcome by the tendency for the solution to deposit out a unitary crystalline structure on the surfaces of the glass plates. I have found that the deposition of the haphazard crystalline formation at the beginning may be checked at an earlier period during the process when it is carried out in the presence of vibrations of low amplitude. However, if the vibrations are of too high an amplitude, they may entirely prevent the formation of the single crystalline film by disturbing the surface of the liquid. Hence, it is preferable under certain conditions of operation to set up the apparatus for carrying out my processes in the presence of such low amplitude mechanical vibrations as will tend to choke out the twinning areas made up of small crystals in favor of the single crystalline layer.

Variations in solvent compositions

A. Water content.—As hereinbefore pointed out, when the crystalline substance being deposited crystallizes out with water of crystallization, it is desirable to have a certain amount of water present to aid in the deposition. However, this water content may be varied within limits. In general, with a lower water content, the tendency is for the crystalline substance to form with many minute holes and very small crystals, whereas with a higher water content, larger crystals form. Examples of the effect of water on the deposition are as follows:

1. Using 95% ethyl alcohol and 5% water, a saturated iodoquininesulfate solution deposited out a crystalline layer having many minute holes and minute oriented crystals with no aggregate polarizing effect.

2. A solution of 90–93% ethyl alcohol and 10–7% water, saturated with iodoquininesulfate deposited out a crystalline layer having some aggregate polarizing effect, but in which there were still present, arranged to form medium size, twinning areas.

3. A 77% ethyl alcohol and 23% water solution, saturated with iodoquininesulfate, gave large twinning areas of iodoquininesulfate, with few holes therein.

(In the above solutions no quininesulfate was present inasmuch as these experiments were carried out for the purpose of determining the effect of the variation of the water content on the deposition).

B. Other variations in the solvent composi-

88. OPTICS

Search Room

65

tion.—The results of the following experiments show the way in which the percentage composition may be varied, and various solvents which may be used: (ethyl alcohol used was 95% absolute by volume)

1. A solution of 60% ethyl alcohol and 40% methyl alcohol, saturated with iodoquininesulfate (containing sufficient water to provide the water of crystallization) deposited out a satisfactory unitary crystalline layer.

2. A solution of 93% ethyl alcohol and 7% of normal butyl alcohol, saturated with iodoquininesulfate (and containing sufficient water to provide the water of crystallization) deposited out a fairly satisfactory unitary crystalline layer with a few twinning areas—the deviations or angles between crystallographic axes of the crystals of said twinning areas being slight.

3. A solution of 100% methyl alcohol saturated with iodoquininesulfate (containing water sufficient to provide water of crystallization) gave a poor film made up of crossed individual crystals with substantially no aggregate polarizing effect.

4. Solutions of methyl alcohol and normal butyl alcohol, starting with 100% methyl alcohol and increasing the amounts of normal butyl alcohol and correspondingly reducing the amount of methyl alcohol, and saturated with iodoquininesulfate, deposited out crystalline layers containing twinning areas which became larger, and with smaller deviations, as the percent normal butyl alcohol was increased until with 93% methyl alcohol and 7% normal butyl alcohol a satisfactory film was obtained.

5. A solution of 93% methyl alcohol and 7% isobutyl alcohol, saturated with iodoquininesulfate, gave a crystalline layer which had no aggregate polarizing effect and which was made up of many crystals.

6. Solutions containing even traces of acetone, or benzene, yielded poor crystalline layers having twinning areas. With increasing amounts of these substances, the quality of deposit was further lowered.

In the experiments described above under numerals 1, 2, 3 and 4, it was found that no quinine sulfate was required to bring about a satisfactory unitary or united crystalline layer deposition. One of the explanations of this fact may be that with the smaller amounts of water which were used in the solution, there was less tendency for the iodoquininesulfate to break up into quininesulfate and iodine.

The results of the foregoing experiments have also led me to believe that more successful crystalline films are obtained from solutions in which at least one of the solvents has a symmetric molecular structure in the sense described below. Further, the experiments indicate that solvents having an OH group at the end of the structural formula of the molecule improve the result. Ring compounds, such as benzene, and such compounds as acetone and isobutyl alcohol, containing an O, or OH group respectively at the center of a chain structure appear to interfere with the deposition of the unitary crystalline film.

From the foregoing it is clear that many solvents may be employed for making up the saturated solution of the iodoquininesulfate for carrying out my process, and accordingly, the examples given are not intended to be limiting in any sense, but merely exemplary of some solutions which may be used.

Mechanics of the deposition

According to my present understanding, a theoretical explanation of the process described is as follows:

Referring to Figure 3, there is shown a section of the glass plate **9** partially submerged in the solution in the tank **1**. A crystalline layer **27** has been deposited on the glass plate **9** and extends down to the level of the liquid solution. At the point where the solution contacts with the plate **9**, it is drawn upwards to a considerable extent due to the surface tension between partly the glass and partly the crystalline layer, the liquid and the atmosphere above the solution. As hereinbefore described, the apparatus is set up in such a way that evaporation occurs approximately evenly over the entire liquid surface, as represented by the arrows **31**, i. e., it is assumed that an equal amount of solvent escapes per unit area of liquid surface. Hence, in the layer **33** (shown in dotted lines) located immediately under the liquid surface, the solution is more concentrated in iodoquininesulfate than in a layer deeper in the liquid, and as a consequence, there is a diffusion of the molecules of iodoquininesulfate downwardly to the less concentrated layers of the solution. (This diffusion downwardly is represented by the arrows **35**).

However, at the point where the surface layer bends upwardly to meet the glass, as generally indicated at **37**, the ratio of the evaporation area of the liquid surface to the downward diffusion area becomes greater than one, and the solvent is removed faster than the diffusion of the iodoquininesulfate downwardly can take place; as a result, the solution in the region of the glass plate **9**, and the surface of the liquid, tends to become oversaturated, this tendency being offset by the rejection of the excess solute (iodoquininesulfate) from the liquid into the solid phase (in this case into the crystalline solid phase).

This rejection of the excess solute into the solid phase being accomplished in close conjunction to the glass surface results in a crystal being formed on the surface of the glass, and it being my present understanding that this film is held to the glass by the intermolecular attraction existing between the crystal and glass interfaces.

Further, liquid, as at **37**, which is in the vicinity of the glass, and which is above the horizontal liquid surface **21**, is under tension in a vertical direction as a result of the surface tension between the liquid, the glass and crystalline layer and the atmosphere; and it is my present understanding that the tension acts to align the solution molecules in such a way that the iodoquininesulfate molecules, in crystallizing out of the solution, are definitely oriented so as to form effectively or actually a single crystal in contradistinction to a number of haphazard crystals. It is my present understanding that under other conditions of operation the molecules may be subjected to the influence of other types of stresses or tensions or lines of force to assist in the predetermined orientation of the molecules.

Furthermore, as was mentioned hereinbefore, the character of the structure of the molecules making up the solvent appears to have a marked effect upon the results obtained—the presence of an OH group at the end of a hydrocarbon chain improves the result. Also, the length of the chain of the molecules making up the solvent appears to affect the results. Thus, if the solvent is made up of short chain molecules only, in contradis-

tinction to medium or long chain molecules, the deposition may not be satisfactory. This unsatisfactory deposition may be corrected by adding to the solution a solvent comprising long chain molecules. However, for practical reasons a solution comprising only long chain molecules is unsatisfactory. Hence, a preferable solvent, or solution, contains either short chain molecules and a proportion of long chain molecules, or molecules of medium length chains. Thus, the short methyl alcohol chain apparently gives a film made up of many crystals, whereas the addition thereto of a long chain molecule, such as N-butyl alcohol, gives a film comprising a single crystal.

However, whatever may be the theoretical explanation of the mechanics of the process, it is my present understanding that the following factors enter into obtaining desirable results: the surface tension between the solution, the atmosphere above the solution and the supporting medium (the resultant should draw the liquid up); the size, geometry, groups and immobility of the solvent molecule; the solubility of the crystalline substance dissolved in the solvent; the vapor pressure of the solvent and the partial vapor pressure of the solvent above the solution; the temperature of the system; and, according to the above theoretical explanation, the ratio of the evaporating surface area to the area of diffusion at the place where the liquid surface is bent upwardly as at 31, and the rate of diffusion of the crystalline substance from the liquid surface downwardly into the less concentrated body of the liquid.

From the foregoing experiments which have been described, it is clear that the process which I have described is capable of coating a supporting surface with a single crystalline layer, or with a crystalline layer made up of definitely oriented crystals, without the use of any intermediate binding agent—and, if the crystalline substance deposited on the supporting surface is anisotropic, the process may give, as a result, an isotropic substance coated with an anisotropic substance.

It is also clear that the process described involves the throwing of a crystalline substance out of solution and depositing the same on a supporting surface in a layer or coating which is a single crystal, or which consists of a number of small crystals definitely oriented.

Other crystalline substances

For the purpose of further illustrating and describing my process, a few more examples of depositing other crystalline substances on supporting surfaces are given:

A. Iodo cinchonidine sulfate.—A preferred method of preparing what I term iodocinchonidinesulfate for use in my process is as follows:

A solution of

	cc.
H_2SO_4 Sp. gr. 1.84	1.75
H_2O (distilled)	22.00
Normal propyl alcohol	19.00

is first prepared and 2.50 gms. of cinchonidinesulfate is dissolved therein at room temperature. For purposes of description this solution will be designated as #(1).

Next, a solution of 3.75 gms. of iodine in 22.5 cc. of normal propyl alcohol is prepared by dissolving the iodine in the alcohol while heating it on a water bath, and agitating it until the iodine dissolves. This solution is now cooled and will be referred to as solution #(2).

Now, 0.85 cc. of the iodine solution #(2) is slowly added, while stirring, to the total solution of #(1). The resulting solution is at first a clear deep amber color, but as it stands (with agitation) minute straw-tan colored crystals form and thicken the solution to a sludge.

To this sludge about 48 cc. of distilled water are added and the sludge takes on a yellow-tan color. This mixture is now preferably heated on a water bath to 60° C., while stirring, to dissolve the crystals to obtain a clear deep amber solution.

This solution is now allowed to cool. At about 48° C. fine crystals begin to form, and at 36° C. to 32° C. a relatively large quantity of the crystals have crystallized out. (These are the crystals, which for purposes of description, I prefer to call iodocinchonidinesulfate.) If, during the cooling, the solution suddenly turns murky brown, it may be cleared up again by stirring.

The crystalline precipitate is now preferably filtered (under suction) in the range of 36° C.–32° C. A better yield may be obtained if the filtering is carried out between 28° C.–26° C., but I have found that there is a tendency for a fluffy, maroon-brown, needle-like, crystalline precipitate to form, when the precipitate is allowed to stand at these temperatures. Thus, when filtering between 28° C.–26° C. precaution should be taken to avoid the formation of this fluffy precipitate, which I term, for purposes of description, a secondary iodine compound.

The filtered iodocinchonidinesulfate is freed from as much of the filtrate as possible by mechanical means, and then dried at room temperature. It may be stored in stoppered bottles. A yield of about 0.25–0.26 gm. of iodocinchonidinesulfate is obtained with this procedure.

The cinchonidinesulfate in this yield is less than 10% of the cinchonidinesulfate originally added, and accordingly, the greater percentage of the cinchonidinesulfate still remains in the filtrate. Now, by again adding some of solution #(2) to this filtrate (which I will refer to as #(3)), a fine, green-black precipitate forms, which dissolves on heating to 60° C. But, in addition, there is another black, tarry, non-crystalline material present, which, when the solution is heated to about 72° C., and stirred, forms a globule at the bottom of the solution. The supernatant liquid may be decanted, and this liquid, on cooling, gives a new yield of iodocinchonidinesulfate which may be filtered as before.

These experiments have led me to adopt the following cyclic procedure, to obtain a maximum yield of iodocinchonidinesulfate with a minimum waste of ingredients.

To the filtrate solution #(3) obtained from the first crystalline yield, cinchonidinesulfate is added in an amount slightly in excess of the cinchonidinesulfate removed by the iodocinchonidinesulfate, and thus the cinchonidine of the cinchonidinesulfate is replenished. For example, I have found that the addition of 0.60 gm. of cinchonidinesulfate is satisfactory.

To this solution is added 0.85 cc. of the iodine solution #(2). A green-black, fine precipitate results, which dissolves completely at 73° C. forming a clear, deep amber solution. The tarry, dark material, which also forms, collects as a globule (upon stirring) and remains at the bottom. The supernatant liquid is now decanted into another container and allowed to cool, on standing.

The iodocinchonidinesulfate this time begins to crystallize out at a temperature above 48° C., and I have found that stirring is even desirable

Search Room

at 55° C. to keep the solution clear and to cause larger crystals to form. The solution is filtered while between 36° C.–32° C., and the crystals of iodocinchonidinesulfate treated as before. The yield this time is approximately 0.328 gm. The weight of the tarry substance is about 0.055 gm.

The filtrate thus obtained may again be treated with cinchonidinesulfate and the #(2) iodine solution as described to obtain a new yield of iodocinchonidinesulfate, and so on. However, my experiments have led me to believe that, if the yield of tarry substance decreases too much, this indicates that the cinchonidinesulfate concentration has become too high, and hence in the next cycle little or no cinchonidinesulfate is added; likewise, if the yield of tarry substance increases too much, this indicates that the amount of cinchonidinesulfate present is insufficient, and accordingly, in the next cycle more is added. Thus, the yield of tarry substance may serve as an indicator for desired concentration of the cinchonidinesulfate.

It is also my present understanding that in carrying out the above described cyclic process the proportion of iodine and cinchonodinesulfate should be maintained substantially constant. Further, with subsequent repetitions of the cyclic process, the preferred range for filtering may rise so that after, for example, ten cycles, the preferred filtering range may have risen to 45° C. This is probably due to the increase in the normal propyl alcohol concentration.

A preferred solution of the crystalline substance prepared by the foregoing procedures, and which I term iodocinchonidine sulfate, is made up by dissolving the iodocinchonidine sulfate to saturation in a solution comprising 93% ethyl alcohol absolute and 7% distilled water by volume. This may be accomplished without the use of heat by crushing the iodocinchonidine sulfate in the bottom of the glass container with a glass rod until the resulting solution is a dark amber color and is saturated. A small excess of iodocinchonidine sulfate is preferably allowed to remain in the bottom of the container to insure the saturation of the solution with iodocinchonidine sulfate at all times.

I have found that the presence of a small amount of the "secondary iodine compound" aids in the deposition of the unitary crystalline film.

The solution, thus prepared, is then placed in tank 1 and the plates 9 are lowered, as described in connection with the first example. When evaporation is relied upon to lower the liquid level, I have found that, if the temperature is maintained at about 25° C. the liquid level lowers at about the rate of 3.2 mm. per day without forced draft. As the liquid level thus lowers, a single crystalline film of iodocinchonidine sulfate is eventually deposited on the surface of the glass plates 9.

The film has a metallic green-golden hue by reflection in ordinary light, and is effective to plane polarize light without markedly favoring the transmission of any one color component of white light, even when the incident light is polarized white light.

My experiments with this crystalline film have indicated that, while the percent of water present in the solution may be varied to some degree, it is desirable to have present always some water—that if no water is present the single crystal of iodocinchonidine sulfate does not form—probably for reasons already set forth in connection with the description of the deposition of iodoquinine sulfate.

I have also found that, if the percent water present exceeds 40% or more by volume, the film is likely to end abruptly and to refuse to deposit further.

Other solvent mixtures for iodocinchonidine sulfate have also given satisfactory results. For example, a solvent comprising 90% methyl alcohol and 10% water (by volume) has produced satisfactory films.

B. Potassium nitrate.—Potassium nitrate dissolved in excess in 8 volumes of water and 2 volumes of normal propyl alcohol, when placed in the tank 1 with plates 9 and allowed to evaporate to lower the liquid level, produced a transparent unitary crystalline film of potassium nitrate. However, when using this potassium nitrate, it is desirable to remove the water vapor above the solution to prevent the disintegration of the film formed into parallel needles of single crystals.

C. Potassium bichromate.—Potassium bichromate dissolved and present in excess in 8 volumes of water and 2 volumes of normal propyl alcohol produces a satisfactory unitary crystalline film on the surface of the glass plates 9.

D. Iodine.—Iodine dissolved to saturation in methyl alcohol and allowed to evaporate in the tank to lower the liquid level deposits a single crystalline layer of iodine on the surface of the glass plates.

The inventions pertaining to the manufacture of iodoalkaloids, of iodocinchonidine sulphate, and of light polarizing plates manufactured using iodocinchonidine sulphate are being covered in divisional applications copending herewith.

As various embodiments might be made of this invention and as various changes might be made in the construction herein described, in the process described, and in the steps for carrying out the process, all without departing from the scope of the invention, it is to be understood that all the matter herein set forth and shown in the accompanying drawing is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. Method of forming a crystalline substance having a natural tendency to grow more rapidly along the x and y axes than along the z axis into a unitary crystalline structure which comprises dissolving the crystalline substance in a solvent, so partially immersing a supporting medium in said solution that surfaces of said medium are at approximately right angles to the plane of the liquid level, causing evaporation of the solvent to cause rejection of the solute on the supporting medium and so slowly moving said liquid level and supporting medium with respect to one another to reduce the immersion that the continuity of the crystalline structure being deposited at the air, solution, supporting medium interface is not broken.

2. Method of forming a crystalline substance having a natural tendency to grow more rapidly along the x and y axes than along the z axis into a unitary crystalline structure which comprises dissolving the crystalline substance in a solvent, so partially immersing a supporting medium in said solution that surfaces of said medium are at approximately right angles to the plane of the liquid level, causing evaporation of the solvent to cause rejection of the solute on the supporting medium, so slowly moving said liquid level and supporting medium with respect to one

another to reduce the immersion that the nature of the crystalline structure deposited is not disrupted, and producing a vibration of low amplitude between the supporting medium and the solution to aid in controlling the nature of the crystalline structure deposited.

3. Method of depositing a crystalline substance on a clean surface capable of taking a high polish which comprises dissolving the substance in a solvent capable of wetting said surface to form a concave meniscus therewith, of partially immersing said supporting surface in the solution thus formed so that said surface is approximately at right angles to the surface of the solution, of so continuously evaporating said solvent as to cause a super-saturated condition in the vicinity of the solution surface to cause rejection of the material on said supporting surface in the vicinity of the air, surface and solution interfaces and of so moving the solution and surface with respect to each other as to continuously remove from solution the crystalline structure deposited without breaking its continuity.

4. Method of depositing a crystalline substance on a clean surface capable of taking a high polish which comprises dissolving the substance in a solvent capable of wetting said surface to form a concave meniscus therewith, partially immersing said surface in the solution thus formed so that said surface is at an angle to the liquid level of the solution, so continuously evaporating said solvent as to cause a super-saturated condition in the vicinity of the liquid surface to cause rejection of the material on said surface in the vicinity of the air, surface and solution interfaces, so relatively moving the solution and surface as to continuously remove from the solution the crystalline structure deposited without breaking its continuity, and controlling the rate of said movement to control characteristics of the crystalline structure deposited.

5. The method of depositing a crystalline structure on a supporting surface which comprises dissolving the crystalline substance in a liquid medium, at least partially immersing said supporting surface in said liquid medium, causing said substance to be crystallized from said medium and to be deposited on said surface with a regulated orientation, and simultaneously relatively so moving said liquid medium and supporting surface in such manner as not to break the character of the crystalline structure deposited.

6. Method of depositing an iodoalkaloid compound on a supporting medium in the form of a crystalline structure comprising preparing an alcohol solution of the iodoalkaloid compound, of partially immersing a supporting medium in the solution, of continuously evaporating the alcohol to cause deposition of the compound on said supporting medium in the vicinity of the air, solution supporting medium interfaces, of so relatively moving the supporting medium and the solution level to reduce the immersion that the crystalline structure is removed without breaking its continuity and regulating the water content of the solution to govern the nature of the crystalline structure deposited.

7. Method of depositing an iodoalkaloid compound on a supporting medium in the form of a united crystalline structure comprising preparing a solution of the iodoalkaloid compound in a mixture of low and high molecular weight alcohols, of partially immersing a supporting medium in the solution, of continuously evaporating the alcohol to cause deposition of the compound on said supporting medium in the vicinity of the air, solution, and supporting medium interfaces, of so relatively moving the supporting medium and the solution level that the crystalline structure is continuously removed without breaking off its continuity, and of regulating the ratio of the amount of the lower to the higher alcohols used in the solvent to govern the nature of the crystalline structure deposited.

8. The method of depositing a crystalline substance from solution onto a supporting surface to form a thin crystalline structure thereon, which comprises at least partially immersing said supporting surface in a solution of said substance so that the supporting surface is at an angle to the surface of the solution, causing said substance to be rejected from said solution and simultaneously crystallized on said supporting surface in the vicinity of the interfaces of the supporting surface, the solution, and the medium above said solution, and so relatively moving said solution and supporting surfaces as to remove the crystalline structure deposited from the solution without breaking the continuity of the crystalline structure.

9. The method of depositing a crystalline substance on a supporting surface which comprises dissolving the substance in a solvent capable of wetting said surface to form a concave meniscus therewith, partially immersing said supporting surface in said solution so that the supporting surface is at an angle with respect to the solution surface, evaporating said solvent to cause rejection of the material from the solution and crystallization on said supporting surface in the vicinity of the interfaces of the supporting surface, the solution surface and the air, and relatively moving the solution and supporting surface to remove the crystalline structure deposited in such manner as not to break its continuity.

10. The method of depositing a crystalline substance on a surface from solution to form a thin united crystalline structure thereon which comprises dissolving the substance in a solvent capable of wetting said surface to form a concave meniscus therewith, partially immersing said supporting surface in the solution so that the supporting surface is at an angle to the solution surface, causing rejection of the substance from the solution and simultaneous crystallization on said supporting surface in the vicinity of the interfaces of the solution surface, the supporting surface, and the medium above said solution, relatively moving the solution surface and supporting surface to remove continuously the crystalline structure deposited from the solution and maintaining the rate of said movement substantially uniform to cause the crystalline substance to deposit on the supporting surface with uniform orientation.

11. Method of depositing a crystalline substance on a supporting surface from solution to form a crystalline structure of regulated orientation which comprises partially immersing said supporting surface in a solution of said substance, causing rejection of the crystalline substance from said solution and crystallization on the supporting surface in the vicinity of the interfaces of the supporting surface, the solution surface and the medium above the solution, relatively moving the supporting surface and solution surface to remove the crystalline structure deposited without breaking the continuity of the crystalline structure, and producing a vibration between the supporting medium and the solution surface to aid in con-

[redacted]

Search Room

trolling the nature of the crystalline structure deposited.

12. The method of crystallizing an iodoalkaloid compound on a supporting surface which comprises preparing an alcohol solution of the iodoalkaloid compound, supplying the supporting surface with the solution by immersion therein, causing crystallization of the iodoalkaloid compound from the solution directly on the supporting surface while subject to surface tension force influencing the orientation of the crystalline structure deposited, relatively moving the solution surface and supporting surface so as to form a continuous crystalline layer of uniform orientation, and regulating the water content of the solution to govern the nature of the crystal deposited.

13. The method of depositing a crystalline substance on a supporting surface which comprises partially immersing the supporting surface in a solution of the substance, continuously evaporating the solvent of said solution in the vicinity of the supporting surface to cause crystallization of the substance onto said supporting surface and relatively moving the solution and supporting surface to remove from solution the crystalline structure deposited without breaking its continuity.

14. The method of depositing an iodoalkaloid compound on a glass plate in the form of a crystalline structure having substantially uniform optical orientation comprising preparing an alcohol solution of the iodoalkaloid compound, partially immersing the plate in the solution, continuously evaporating the alcohol to cause deposition of the compound on the plate in the vicinity of the interfaces of the solution, the plate and the atmosphere above the solution, and continuously relatively moving the solution surface and plate to remove from the influence of the solution the crystalline structure deposited to obtain a continuing crystalline layer of uniform orientation.

15. An article of manufacture, comprising a supporting medium having a substantially rigid surface coated with an optically active substantially continuous crystalline layer directly crystallized thereon from solution, and forming effectively a single crystal of substantially uniform optical orientation.

16. A light polarizing device comprising a transparent supporting medium having a surface coated with a crystalline substance having the inherent characteristic of polarizing ordinary incident light, said coating comprising a substantially continuous crystalline layer directly crystallized on the surface from solution and forming effectively a single crystal of substantially uniform optical orientation.

17. A light polarizing device comprising a supporting medium having a surface coated with a crystalline substance having the inherent characteristic of polarizing ordinary incident light, said coating comprising a substantially continuous crystalline layer directly crystallized on the surface from solution and forming effectively a single crystal of substantially uniform optical orientation, the crystalline substance thus being so arranged that for each unit surface area a maximum amount of ordinary incident light is transmitted and a maximum amount of the transmitted light is polarized per unit of thickness of the crystalline substance.

18. A light polarizing plate comprising a glass plate having a surface coated with iodoquininesulphate, said coating comprising a substantially continuous crystalline layer directly crystallized on the surface from solution and forming effectively a single crystal of substantially uniform optical orientation whereby the iodoquininesulphate is so arranged that for each unit surface area a maximum amount of ordinary incident light is transmitted and a maximum amount of the transmitted light is polarized per unit of thickness for the iodoquininesulphate.

ALVIN M. MARKS.