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METHOD OF PROTECTING THE SURFACES OF SOLUBLE SALT CRYSTALS

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This invention relates to a method of preserving crystal surfaces. It is of particular utility in the growing of crystals from normally liquid solutions and provides a method of preserving mirror-like crystal surfaces free from cracking, checking or deposits of very fine crystals thereon. It is also useful in the protecting and preserving of the detail of crystal surfaces which have been etched by a selective solvent for the crystal material.

According to conventional procedure, crystals of various salts, for instance, are formed by slowly cooling a saturated liquid solution of the salt. The solvent most commonly used is water but alcohol and other solvents are sometimes used, depending upon the solubility characteristics of the particular salt. The crystals thus formed are removed from the saturated solution or mother liquor in which they are grown and dried. By carefully controlling the rate of cooling of the salt solution, as well understood in the art, single crystals of almost any desired size, many have mirror-like surfaces, can be formed. However, serious difficulties have been encountered in preserving these mirror-like surfaces.

Crystals of various materials are widely used in diffraction studies. Also, they have more recently been used with advantage in microscopy, as more fully described and claimed in my copending application Ser. No. 514,397, filed concurrently herewith.

It is highly desirable, if not essential, that the crystals used for such purposes have at least one mirror-like surface of adequate size free from cracks or other imperfections.

It has been found that where crystals are grown to suitable size and dried in the conventional manner, cracks and other imperfections develop on their mirror-like surfaces. The cause of this cracking is not definitely known but it is my present belief that it is caused by some temperature change, perhaps a too rapid chilling of the crystals due to the evaporation of the mother liquor therefrom.

Further, in the drying of the crystals in the ordinary manner, there is a tendency toward a deposition of very fine crystals of the crystal material on the surfaces of the larger crystal. But the most serious difficulty has been the cracking or checking of the crystal surfaces just noted.

I have attempted to avoid these difficulties by blotting the excess mother liquor from the crystals. But I have found this also to result in serious impairment of the mirror-like crystal surfaces.

The present invention provides a highly effective method of avoiding the difficulties heretofore experienced whereby crystals have relatively large unbroken mirror-like surfaces can be readily obtained.

In accordance with my invention, the crystals may be grown from liquid solutions in any conventional manner. But immediately upon removing the crystals from the mother liquor in which they are grown, without permitting substantial evaporation of the solvent, the crystals are submerged in a relatively viscous, film-forming solution and gently agitated therein, so that the residual

mother liquor is washed or diffused away from the crystal surfaces by the film-forming solution. The crystals are thereafter removed from the film-forming solution and permitted to dry slowly. When thoroughly dried, the film thus formed may be stripped from the crystal surface. By this means dry crystals having unimpaired mirror-like surfaces are obtained and no subsequent cracking or checking of the crystals has been observed.

As the film-forming solution, I have used with particular advantage, a 4% solution of collodion in amyl acetate. However, the concentration of this collodion solution may be varied somewhat without greatly impaired results. Collodion solutions of less than 2% concentration are generally insufficiently viscous for my purpose. Best results have been obtained where a very viscous film-forming solution is used but its viscosity must be below that at which the solution ceases readily to wet the crystal surfaces.

In place of the collodion solution, one may use other viscous film-forming materials which set and harden on the crystals to form a non-adhering film which can be readily stripped from the crystal surfaces leaving it dry and clean. Where the crystal is insoluble in water, one may use a viscous aqueous solution of polyviny alcohol or a viscous suspension of gelatin in water as the film-forming material. However, in the following description I shall for brevity sometimes refer to the film-forming material generally as a collodion solution.

The submerging and agitation of the crystals in the film-forming solution and the drying of the film on the crystals are with advantage carried on at room temperature. Under adverse atmospheric conditions, the film may with advantage be dried on the crystal under a bell jar with controlled atmosphere. But this is usually unnecessary.

The agitation of the crystals in the collodion solution may be merely that sufficient to displace the mother liquor from the crystal surfaces and bring the collodion solution into intimate contact therewith. Holding a crystal with tweezers and rapidly moving it through the viscous solution is usually adequate for this purpose.

Where the amount of crystals to be treated is relatively large with respect to the amount of collodion solution or where for other reasons the amount of mother liquor introduced into the collodion solution with the crystals is relatively large, the collodion solution may become excessively contaminated by the mother liquor. Under such circumstances, the crystals are with advantage removed from the first collodion solution and agitated, in the manner previously described, in a fresh collodion solution substantially free from mother liquor. This step may be repeated as often as necessary to obtain on the crystal surfaces a residual coating of the collodion solution substantially free from mother liquor. Usually three such washings are sufficient, even under most adverse conditions.

The film may be removed from the crystal surface as soon as it has thoroughly set and dried or may be allowed to remain on the crystal to protect its surfaces up to the time of use.

As a specific illustration of the invention, I have grown crystals of ammonium dichromate having excellent mirror-like surfaces by the following procedure. An aqueous solution of ammonium dichromate (C. P. grade) saturated at 75° C. was heated in an oven at 90° C. and permitted to cool slowly overnight in the oven. Of the crystals thus formed those having mirror-like surfaces of adequate size were selected and removed from the remaining solution one-by-one with the aid of tweezers and immediately immersed in about 25 cc. of a 4% solution of collodion in amyl acetate in a beaker and

moved back and forth through the liquid until the crystal was thoroughly wetted by the collodion solution. The crystal was then removed from the solution and immediately immersed in 25 cc. of a fresh 4% collodion solution in amyl acetate in a second beaker. After gentle agitation, as before, the crystal was removed to a 3d bath of collodion solution, of a volume and concentration just described, and after gentle agitation was removed therefrom and permitted to dry slowly in air at room temperature until the collodion film was thoroughly set and dry. The collodion film was then stripped from the crystal, and examination indicated that no cracking or marring of the crystal surfaces had occurred.

This procedure has been applied with like results to crystals of copper sulfate, aluminum potassium sulfate, aluminum ammonium sulfate and the like.

The invention is applicable generally to the growing of salt and other crystals from liquid solutions. However, the film-forming solution must be so chosen with respect to the composition of the particular crystal that the crystal is not soluble therein. Thus, the collodion solution noted above is eminently adapted to use in treating crystals of water-soluble materials, for instance, sodium chloride or potassium nitrate. Where the crystal is insoluble in water, one may, as previously noted, use a film-forming material in aqueous solution instead of collodion solution. Aqueous solutions of polyvinyl alcohol or aqueous suspensions of gelatin may be used with advantage in such instances.

It will be understood that the invention is not restricted to the particular film-forming solutions specifically named herein but contemplates the use of any viscous solution in which the crystal is insoluble and which sets and hardens to form a film which is readily stripped from the crystal.

The invention, in its broader aspect, also contemplates the preserving of crystal surfaces which have been etched by means of a selective solvent in accordance with the procedure more fully described in my above noted copending application. By removing the etched crystal from the selective solvent and immediately submerging and agitating the crystal in the viscous film-forming solution, for instance a 4% solution of collodion in amyl acetate, the adhering selective solvent, containing portions of the dissolved crystal material, is quickly removed from the etched crystal surface and the deposition of small crystals on the etched surface, cracking and the like, which otherwise would result in a distortion of the relief matrix, is prevented.

I claim:

1. A method of protecting the surfaces of individual soluble salt crystals against the development of cracks and imperfections apparent on electron microscope examination, upon removing the crystal from a bath of liquid in which there is dissolved material the same as that constituting the crystal, said method comprising the following steps, immediately upon removing the crystal from the bath and while it still has liquid of the bath on its surface, washing the liquid solution from the crystal by submerging and agitating the crystal in a bath of a viscous film-forming solution in which the crystal is insoluble until the liquid of the bath has been removed from the crystal and the crystal surface to be preserved is uniformly wetted with the film-forming solution, removing the crystal from the bath of film-forming solution and slowly drying the adhering film-forming solution on the crystal surface.

2. In the growing of individual soluble salt crystals suitable for electron microscopy from liquid solutions of the material constituting the crystal, the steps of removing the crystal from the mother liquor and immediately, and while it still has mother liquor on its surface, washing the mother liquor from the crystal by submerging and agitating the crystal in a bath of a viscous film-forming solution in which the crystal is insoluble until the mother liquor has been removed from the crystal and a continuous film of the film-forming solution is formed on the crystal surfaces, removing the crystal from the bath of film-forming solution and slowly drying the adhering film-forming solution on the crystal surfaces.

3. The method of claim 2 in which the crystal is water-insoluble and the viscous solution is an aqueous solution of polyvinyl alcohol.

4. The method of claim 2 in which the crystal is water-insoluble and the viscous solution is an aqueous suspension of gelatin.

5. The method of claim 2 in which the crystal is ammonium dichromate and the viscous solution is a 4% solution of collodion in amyl acetate.

6. In the growing of individual water-soluble crystals suitable for electron microscopy from liquid solutions of the material constituting the crystal, the steps of removing the crystal from the mother liquor and immediately, and while it still has mother liquor on its surface, washing the mother liquor from the crystal by submerging and agitating the crystal in a bath of viscous solution of collodion in amyl acetate until the mother liquor has been removed from the crystal and a continuous film of the collodion solution is formed on the crystal surfaces, removing the crystal from the bath of collodion solution and slowly drying the adhering collodion solution on the crystal surfaces.

7. The method of claim 6 in which the viscous solution is a 4% solution of collodion in amyl acetate.

8. In the growing of individual soluble salt crystals suitable for electron microscopy from liquid solutions of the material constituting the crystals, the steps of removing the crystal from the mother liquor and immediately, and while the crystal still has mother liquor on its surface, washing the crystal by submerging and agitating the crystal in a bath of a viscous film-forming solution in which the crystal is insoluble, removing the crystal from the bath of film-forming solution and immediately rewashing the crystal by submerging and agitating the crystal in a second bath of a viscous film-forming solution, repeating the last step until the residual film-forming solution adhering to the crystal is substantially free from mother liquor and removing the crystal from the final bath of film-forming solution and slowly drying the adhering solution on the crystal surfaces.

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