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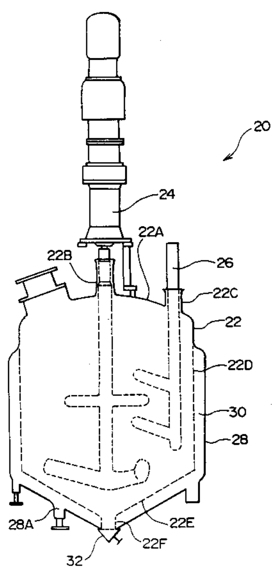
(54) Method of crystallizing organic chemicals.

(57) A method of crystallizing an organic chemical includes a step of starting crystallization that controls a degree of supersaturation of a solution of an organic chemical so as to crystallize platy crystals predominantly, and a step of crystallization which is carried out immediately after the step of starting crystallization, the step of crystallization lowering a temperature of the solution of the organic chemical while changing a composition of solvents so as to lower the degree of supersaturation of the solution of the organic chemical thereby continuing crystallization predominantly of the platy crystals. In the method, the crystals of the organic chemical are crystallized by stirring the solution of the organic chemical such that a flow of crystallized platy crystals is kept in a completely suspended state throughout the step of starting crystallization and the step of crystallization.

FIG. 1



Rank Xerox (UK) Business Services
(3.10/3.09/3.3.4)

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method of crystallizing an organic chemical by cooling a solution of the organic chemical and crystallizing crystals of the organic chemical dissolved in the solution of the organic chemical.

Description of the Related Art

In the production of industrial chemicals, medicines and foodstuffs, since no sufficient purifying effect can be obtained by solution purification, a crystallization step is provided for ensuring the quality of final products.

Fig. 3 shows a method of crystallization in the prior art adopted for the crystallization step in the form of a graph of a solubility curve. A crystallizing operation line is schematically illustrated in Fig. 3. As shown in the figure, in the conventional method, an organic chemical is dissolved in a good solvent to form a solution of the organic chemical, the solution is cooled to lower the liquid temperature, the solution passes through a metastable region and a platy crystal region to form lumpy crystals, and then the solution of the organic chemical is cooled so as to pass through a lumpy crystal region as it is thereby crystallizes out lumpy crystals.

The lumpy crystals have a crystal structure suitable for production since they can easily be put to solid/liquid separation in succeeding steps and have a high crystallization rate. On the other hand, since the crystals are heavy, crystallized lumpy crystals can not be kept suspended in the solution, for example, by a small Phaudla type stirring blade 2 as shown in Fig. 6. Therefore, the degree of supersaturation in a tank 4 loses uniformity as shown in Fig. 6(A), and a great amount of fine acicular crystals of a poor filtering property are crystallized finally in an upper portion of the tank 4 in which the degree of supersaturation is higher, thereby resulting in a slurry of extremely poor flowability (Fig. 6B).

In order to prevent such a drawback, it is necessary to use a device used exclusively for crystallization, which device has a large stirring blade 6 such as an anchor type blade as shown in Fig. 4 and can make the degree of supersaturation uniform in the tank 4 and crystallize only the lumpy crystals. Accordingly, a great restriction is imposed on equipment which can be used for crystallization.

SUMMARY OF THE INVENTION

The present invention has been accomplished in view of the aforementioned, and it is an object thereof to provide a method of crystallization capable of obtaining crystals of a good filtering property and a slurry of a good flowability even at a low stirring efficiency, thereby permitting crystallization which is superbly suited to production, even when a general-purpose device is used.

Another object of the present invention is to provide a method of obtaining crystals which can be easily recovered without using an anchor type blade having high stirring efficiency but by using a general-purpose vessel having a Phaudla type blade which can be used both for reaction and concentration.

As a result of earnest study and research in order to attain the foregoing objects, the inventor of the present application has found that crystallization which is well-suited for production can be conducted even by using a general-purpose device by crystallizing platy crystals.

In a first aspect of the present invention, there is provided a method of crystallizing an organic chemical, which comprises a step of starting crystallization that controls the degree of supersaturation of a solution of an organic chemical so as to crystallize platy crystals predominantly, and a step of crystallization which is carried out immediately after the step of starting crystallization, the step of crystallization lowering the temperature of the solution of the organic chemical while changing the composition of solvents so as to lower the degree of supersaturation of the solution of the organic chemical thereby continuing crystallization predominantly of the platy crystals, wherein the crystals of the organic chemical are crystallized by stirring the solution of the organic chemical such that the flow of the crystallized platy crystals is kept in a completely suspended state throughout the step of starting crystallization and the step of crystallization.

The present invention provides a method extremely effective for purifying a produced organic chemical in the final step of production thereof. The method of the present invention is applicable to organic chemicals, for example, color couplers for usual photography typically represented by cyan coupler, magenta coupler and yellow coupler, colorants for instant photography and anti-fogging agents. However, the present invention is not limited to these examples and may be applied to any organic compounds having a low melting point (suitably a melting point from about 0 to 50°C).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic structural view of a crystallizing device according to the present invention;

Fig. 2 is a view illustrating a model for the control of crystal forms in a crystallizing method according to the present invention;

Fig. 3 is a view illustrating a model for the control of crystal forms in a crystallizing method of the prior art;

Fig. 4A is a view illustrating the state of crystallization in the crystallizing method of the prior art, showing a state in which lumpy crystals begin to crystallize;

Fig. 4B is a view illustrating the state of crystallization in the crystallizing method of the prior art, showing a state upon completion of crystallization;

Fig. 5 is a view illustrating a model for the control of crystal forms by using a Phaudla type stirring blade in the crystallizing method of the prior art; and

Fig. 6A is a view illustrating a state of crystallization by using a Phaudla type stirring blade in the crystallizing method of the prior art, showing a state in which lumpy crystals begin to crystallize;

Fig. 6B is a view illustrating a state of crystallization by using a Phaudla type stirring blade in the crystallizing method of the prior art, showing a state upon completion of crystallization.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the method of the present invention, the degree of supersaturation of the solution of the organic chemical is at first controlled such that platy crystals are predominantly crystallized (step of starting crystallization). The control can be conducted by any of various methods, for example, a method of dissolving an organic chemical into a good solvent to form a solution of the organic chemical, then adding a poor solvent to the solution of the organic chemical to control the degree of supersaturation of the solution of the organic chemical so as to crystallize the platy crystals predominantly.

"Crystallizing the platy crystals predominantly" or "continuing crystallization predominantly of the platy crystals" mean that the platy crystals are contained by more than 60%, preferably, by more than 80% in the crystallized crystals.

The terms "good solvent" and "poor solvent" are also well-known to those skilled in the art. "Good solvent" means a solvent having a large capability of dissolving a solute, while "poor solvent" means a solvent having a smaller or small capability of dissolving a solute. Typically, a solvent capable of dissolving more than 5 g, preferably, more than 20 g of a solute in 100 g of the solvent at 40°C is a good solvent. A solvent capable of dissolving a solute by less than 10 g, particularly, only by 1 g, in 100 g of the solvent is a poor solvent.

Ethyl acetate is a good solvent for various types of photographic reagents, while methanol, ethanol and water are poor solvents to photographic reagents. In the present invention, two types of poor solvents can be used together. The poor solvents used together can be added successively or may be used by mixing the poor solvents in advance. A combination capable of forming a homogeneous solution after the addition of the poor solvents is preferred.

The degree of supersaturation of the solution of the organic chemical is preferably controlled between 3 to 30. The degree of supersaturation means herein a ratio of an absolute value for the concentration of a solution to the saturated concentration.

In accordance with the method of the present invention, the temperature for the solution of the organic chemical is lowered while changing a solvent composition so as to lower the degree of supersaturation of the solution of the organic chemical, thereby continuing crystallization predominantly of the platy crystals having satisfactory filtering property and satisfactory stirring property (crystallization step). The degree of supersaturation of the solution of the organic chemical may be lowered by any of various methods. Mention can be made, for example, of a method of adding a poor solvent to a solution of an organic chemical in a good solvent thereby controlling the degree of supersaturation, and gradually adding water to the thus controlled solution of the organic chemical to change the composition of the solvents in a homogeneous system.

The crystallized platy crystals are stirred in a completely suspended state throughout the step of starting crystallization and the step of crystallization so that the degree of supersaturation of the solution of the organic chemical does not lose uniformity in the device. The completely suspended state referred to herein means a stirred state in which crystals do not stagnate for more than 1 to 2 seconds at the bottom of a tank.

When the crystallization method according to the present invention is practiced on a large scale, adequate stirring conditions can be determined based on the stirring conditions obtained by an experiment of crystallization conducted by using an experimental device of a smaller scale. For instance, it is effective to adopt, for example, a scaled-up method based on Z factor, described in "Effects of Stirring on Grain Size Analysis in Crystallization of Phenoxy Acetic Acid Compounds", by Momonaga et al, (Chemical Engineering Reports, Vol. 10, No. 2, 1984). In this method, first, minimum stirring conditions capable of satisfying the completely suspended conditions, which are determined under scaled-down conditions with geometrical similarity, are determined. Then, the rotational speed for stirring under the scaled-up conditions can be determined by making the values for the Z factor identical between them.

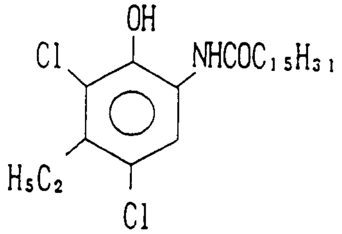
According to the method of crystallizing an organic chemical of the present invention, crystals having a good filtering property and a slurry having good flowability can be obtained even when stirring efficiency is low, so that crystallization well-suited to production can be carried out also by using a general-purpose device. Further, in accordance with the present invention, a scaling-up method which can be applied from an experimental device to an actual production facility is provided.

EXAMPLES

The present invention will now be explained with reference to preferred examples of the invention. However, it should be noted that these examples are merely exemplary, and the present invention is not restricted only to these examples.

Example 1

For obtaining crystals of a cyan coupler (1) having the following structural formula (I), the method of the present invention was carried out in a flask experiment.



(I)

As an experimental device, a 500 ml separable flask having a diameter of 80 mm, and a small-sized Phaudla blade having a stirring blade of 45 mm diameter were used.

After charging 79 g of the cyan coupler (1) into the separable flask containing 43 ml of ethyl acetate, the cyan coupler and the ethyl acetate were dissolved under heating at 40°C. Then, 192 ml of methanol (poor solvent) was gradually added to the solution while stirring with the liquid temperature being maintained at 40°C. Further, seed crystals were added to the solution and 213 ml of water (another poor solvent) was added while stirring, and then the temperature was lowered to 20°C for 4 hours. In this process, crystallization of the platy crystals was observed, and the stirring speed was controlled such that the crystallized platy crystals were kept in a completely suspended state. The rotational speed for stirring was 400 rpm. The degree of supersaturation was 20 to 25 in the temperature lowering step starting from 40°C and reaching 20°C.

After reaching 20°C, stirring was performed continuously for one hour, and then the temperature was rapidly lowered to 5°C to ensure the yield of crystallization.

The thus formed slurry had a good flowability, and the crystallizates and the mother liquid were separated by filtration.

The crystallizates were platy crystals of 5 μm x 30 μm and the yield of crystallization was 92%. The above-mentioned crystallization method was applied to actual production.

The vessel used in this experiment was a 4000 liter-volume glass-lined vessel, and the stirring blade was a Phaudla type stirring blade of 900 mm diameter. Fig. 1 shows a schematic structure of a crystallization device 20 having the vessel and the stirring blade.

The crystallization device 20 has a vessel 22 described above, a stirrer 24 having three Phaudla blades (rod-shaped blades) as described above, and an upwardly inclined baffle 26 having a substantially F-shaped cross section. The vessel 22 has an opening 22B formed at a substantial center of a ceiling 22A, and the Phaudla blade of the stirrer 24 is held in the vessel 22 through the opening 22B. The rotational speed of the stirrer 24 is variable from a maximum of 95 rpm to a minimum of 27 rpm. Another opening 22C is also formed near the outer circumference of the ceiling 22A, and the baffle 26 is held through the opening 22C in the vessel 22. The vessel 22 has a cooling tank 28 formed around the periphery of a side wall 22D and a bottom 22E of the vessel 22 for cooling the solution in the vessel 22. The cooling tank 28 has a coolant inlet 28A for introducing a coolant 30 into the cooling tank 28 and a coolant exit (not illustrated) for discharging the coolant 30. The coolant inlet 28A and the coolant exit are connected by way of pipelines (not illustrated) with a heat exchanger (also not illustrated), and the coolant is circulated between the heat exchanger and the cooling tank 28. The vessel 22 has a discharge port 22F formed at a substantially central portion of the bottom 22E of the vessel 22 for discharging slurry obtained by cooling the solution. Discharge of the slurry is controlled by way of a valve 32. The crystallizer 20 also has a solution port for charging the solution into the vessel 22 and a thermometer for measuring the temperature in the vessel 22. Further, 80 mm of clearance is defined between the stirring blade of the stirrer 24 and the deepest central portion at the bottom of the vessel 22 so that crystals stagnating at the bottom are suspended easily.

In this example, brine was used as the coolant.

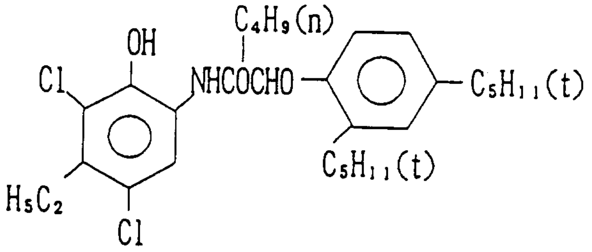
After charging 780 kg of the cyan coupler (1) into the vessel 22 containing 426 liter of ethyl acetate, the cyan coupler (1) and the ethyl acetate were dissolved while stirring with the temperature of the liquid maintained at 40°C. Then, 1919 liter of methanol was gradually added to the solution while stirring with the liquid temperature being maintained at 40°C. Further, seed crystals were added to the solution and 2132 liter of water were added while stirring, and the temperature was lowered to 20°C for 4 hours. The stirring speed was controlled such that platy crystals crystallized in this step came into a completely suspended condition. The rotational speed of stirring was 48 rpm. After the temperature was lowered to 20°C, stirring was further continued for one hour, and after rapidly lowering the temperature to 5°C, the crystals and the mother liquid were separated through filtration by a centrifugator.

The slurry in this step had a satisfactory flowability, and platy crystals identical to those obtained in the flask experiment were obtained as crystallizates.

Fig. 2 shows solubility curves and a schematically represented crystallizing operation line. Each solubility curve represented by a broken line shows a solubility curve of the solution before addition of the poor solvent, while a corresponding solubility curve represented by a solid line shows a solubility curve after addition of the poor solvent. The solubility curve represented by the broken line is lowered to the solubility curve represented by the solid line to facilitate the crystallizing operation in the platy crystal region.

Example 2

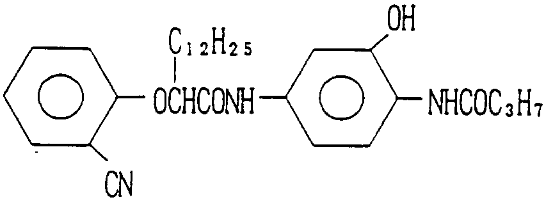
When a cyan coupler (2) having the following structural formula (II) was crystallized under the same scaled-up conditions as those in Example 1, platy crystals having a good filtering property were obtained.



(II)

Example 3

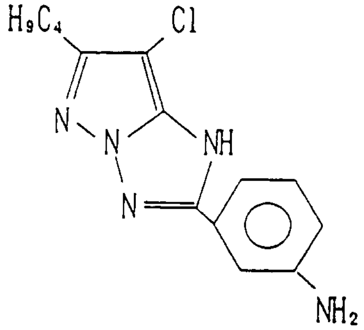
When a cyan coupler (3) having the following structural formula (III) was crystallized under the same scaled-up conditions as those in Example 1, platy crystals having a good filtering property were obtained.



(III)

Example 4

When a magenta coupler intermediate product having the following structural formula (IV) was crystallized under the same scaled-up conditions as those in Example 1, platy crystals having a good filtering property were obtained.



(IV)

Claims

1. A method of crystallizing an organic chemical, comprising:

   a step of starting crystallization that controls the degree of supersaturation of a solution of an organic chemical so as to crystallize platy crystals predominantly, and

   a step of crystallization which is carried out immediately after said step for starting crystallization, said step of crystallization lowering the temperature of the solution of the organic chemical while changing the composition of solvents so as to lower the degree of supersaturation of the solution of the organic chemical, thereby continuing crystallization predominantly of the platy crystals,

   wherein the crystals of the organic chemical are crystallized by stirring the solution of the organic chemical such that the flow of the crystallized platy crystals is kept in a completely suspended state throughout said step of starting crystallization and said step of crystallization.

2. A method of crystallizing an organic chemical according to claim 1, wherein the method further comprises a step of dissolving the organic chemical in a good solvent to form a solution of the organic chemical and then adding a poor solvent to the solution of the organic chemical, thereby controlling the degree of supersaturation of the solution of the organic chemical such that platy crystals are predominantly crystallized.

3. A method of crystallizing an organic chemical according to claim 1, wherein the degree of supersaturation after the control is from 3 to 30.

4. A method of crystallizing an organic chemical according to claim 1, wherein the organic chemical is selected from the group of color couplers for photography, colorants for instant photography and anti-fogging agents.

5. A method of crystallizing an organic chemical according to claim 2, wherein a good solvent is ethyl acetate.

6. A method of crystallizing an organic chemical according to claim 2, wherein poor solvents are methanol, ethanol and water.

7. A method of crystallizing an organic chemical according to claim 1, wherein the crystallized platy crystals are stirred such that said crystals do not stagnate for more than 1 to 2 seconds at the bottom of the tank throughout said step of starting crystallization and said step of crystallization.

FIG. 1

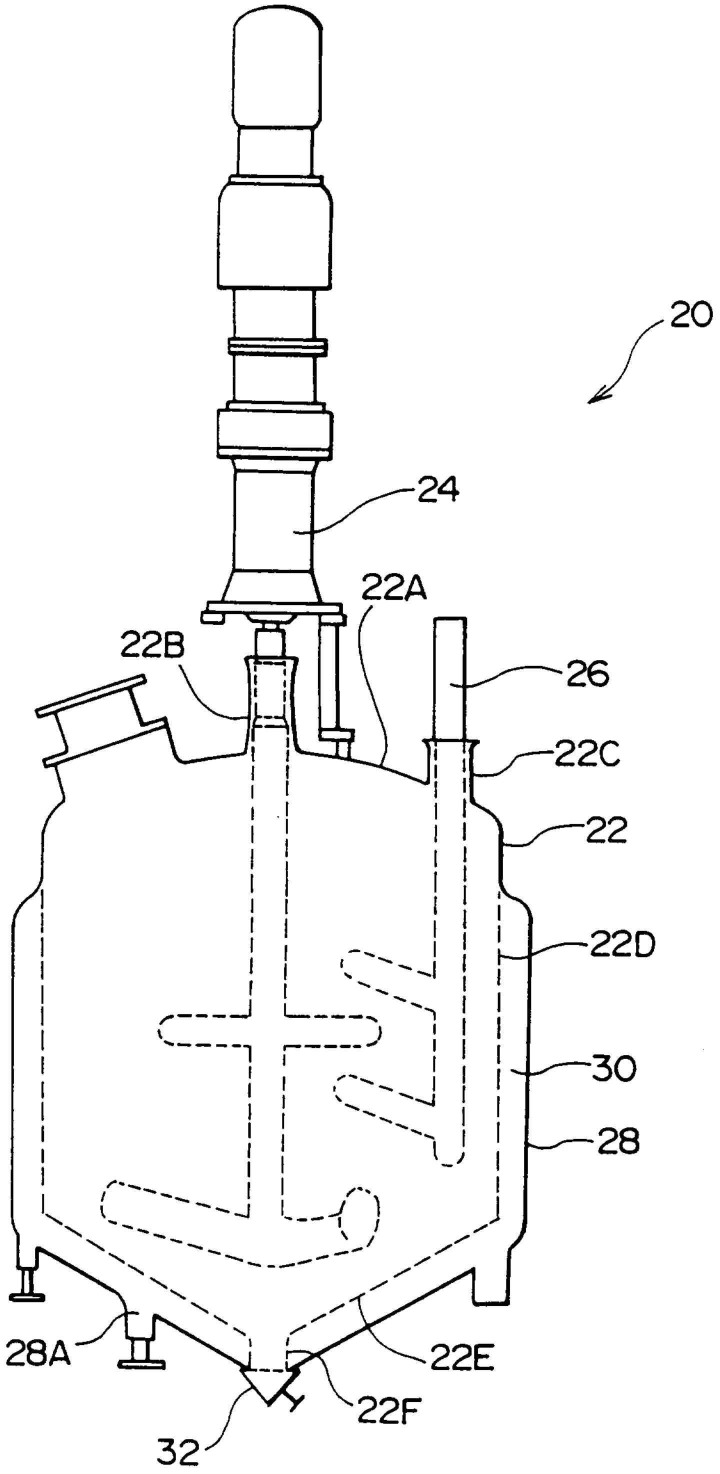


FIG. 2

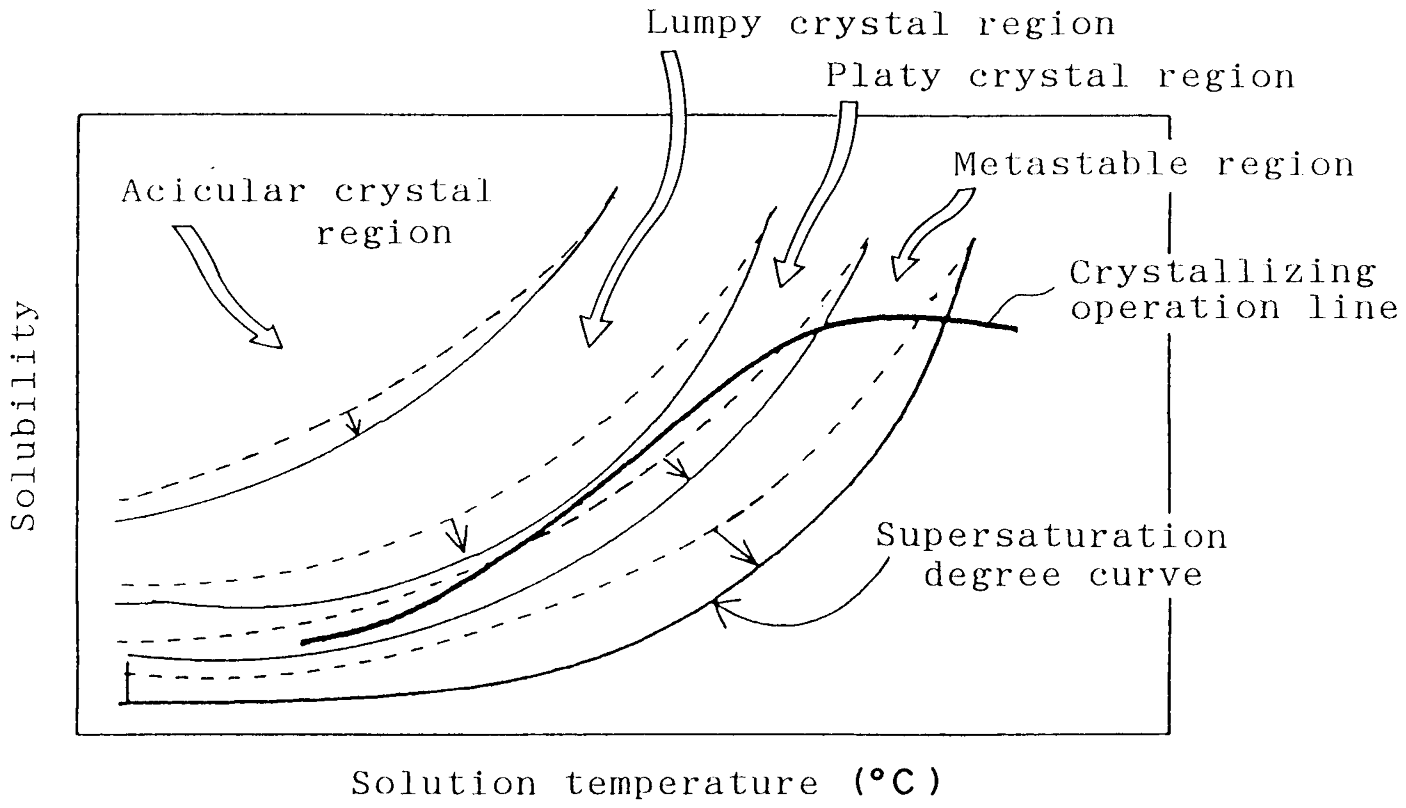

Lumpy crystal region
Platy crystal region
Metastable region
Acicular crystal region
Crystallizing operation line
Supersaturation degree curve
Solubility
Solution temperature (°C)

FIG. 3

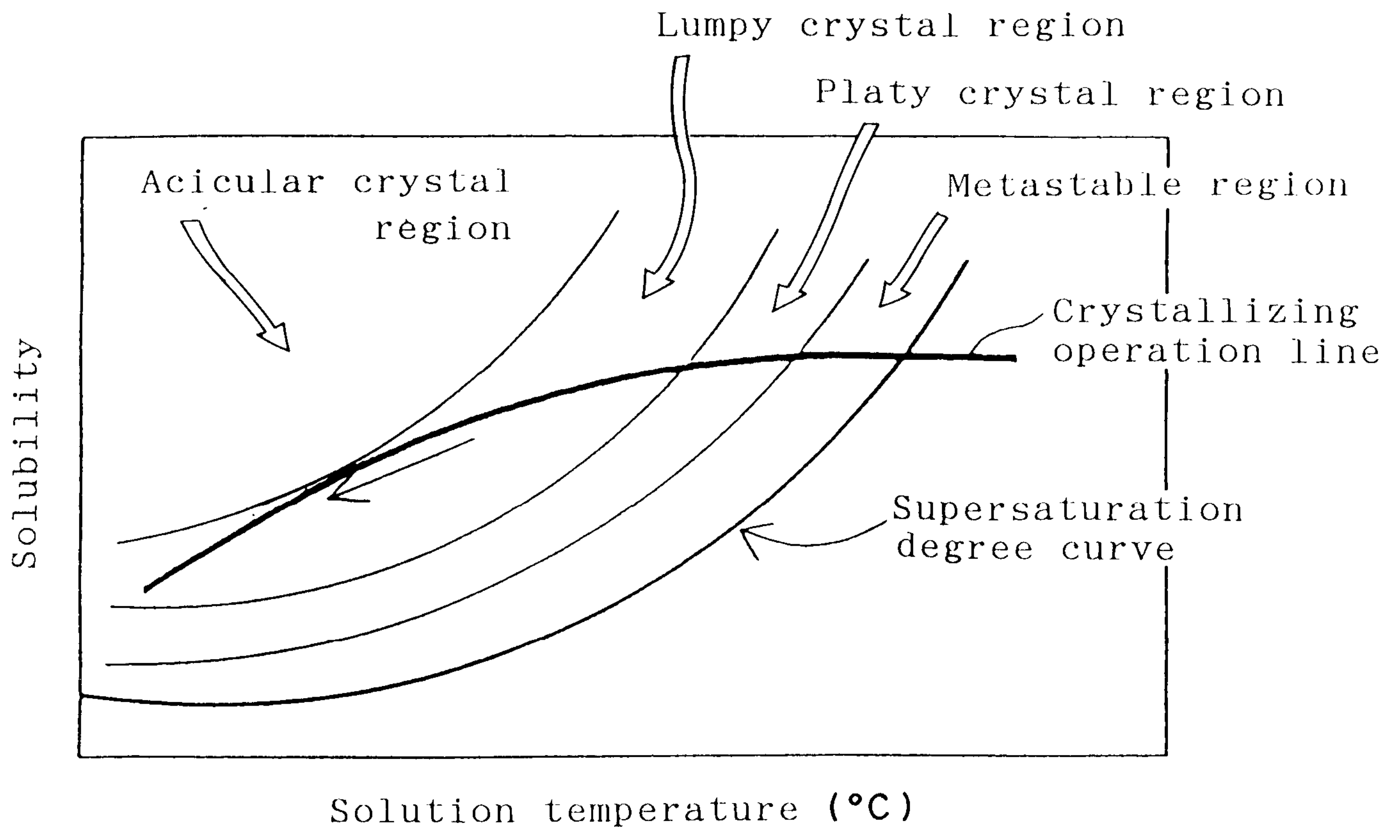

Lumpy crystal region
Platy crystal region
Acicular crystal region
Metastable region
Crystallizing operation line
Supersaturation degree curve
Solubility
Solution temperature (°C)

FIG. 4 A

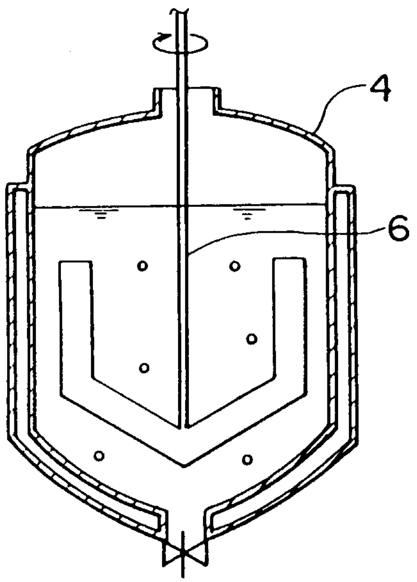


FIG. 4 B

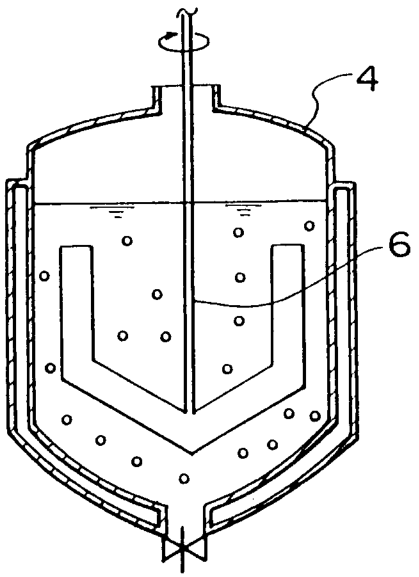
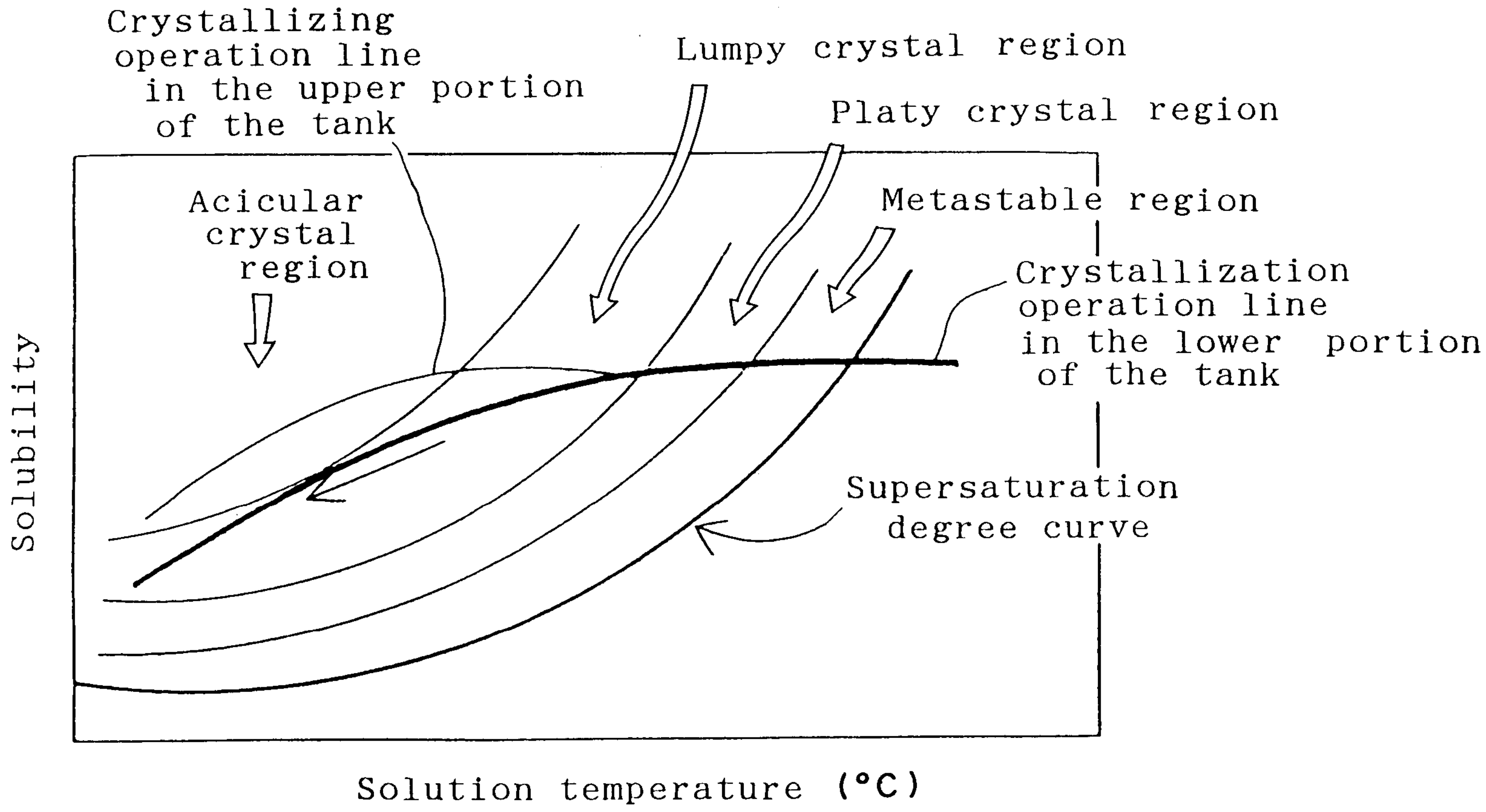


FIG. 5


Crystallizing operation line in the upper portion of the tank
Lumpy crystal region
Platy crystal region
Metastable region
Acicular crystal region
Crystallization operation line in the lower portion of the tank
Supersaturation degree curve
Solubility
Solution temperature (°C)

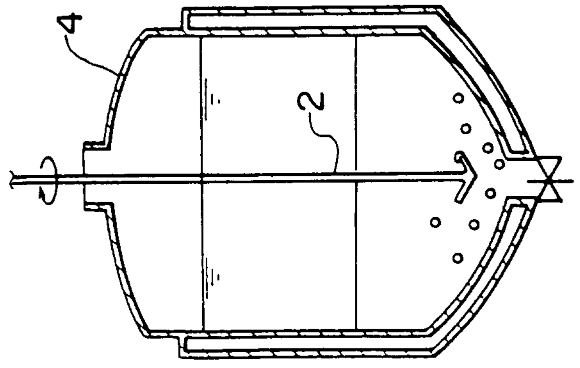


FIG. 6A

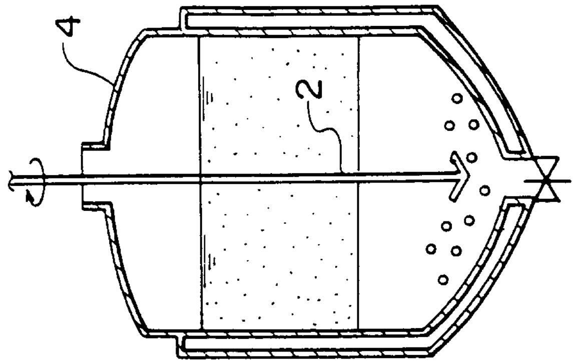


FIG. 6B