

PATENT SPECIFICATION

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(54) MINIMIZING FINE CRYSTALS IN CONTINUOUS CRYSTALLIZATION-BY-COOLING PROCESS

(71) We, HERCULES INCORPORATED, a corporation organised under the laws of the State of Delaware, United States of America, of 910 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is in the chemical arts. It relates to crystallization.

Crystallization, as is well known, is the change of crystallizable material from the dissolved, molten, liquid or gaseous state to a crystalline solid state. This invention pertains to the change of crystallizable material from the dissolved state to a crystalline solid state, in other words, to solution crystallization.

Solution crystallization takes place only after a solution comprising the crystallizable material (herein solute) and a solvent for the solute becomes supersaturated, that is, contains more solute than the solvent normally can dissolve at the prevailing temperature of the solution.

Supersaturation is followed by nucleation and crystal growth. Nucleation, i.e. the formation of nuclei, can be effected by adding fine crystals of the solute or other crystalline material to the solvent, or it can be spontaneous. Crystal growth is the development of crystals from the nuclei. It is dependent on how long the solution remains supersaturated and on how long the nuclei and developing crystals remain in contact with the solution while it is supersaturated.

Supersaturation of solution can be accomplished by changing the temperature of the solution to a temperature at which the solute is less soluble in the solvent (for most solvents and solutes this means cooling the solution), by evaporating solvent from the solution to concentrate the solute, or by conjointly changing the solution temperature and evaporating solvent. This invention is directed to solution crystallization in which supersaturation

is achieved at least by cooling the solution.

Solution crystallization by cooling can be carried out as a batch process or as a continuous process. In the batch process, generally the solution is cooled at a rate or rates selected to establish and maintain the solution in a supersaturated condition until maximum crystallization has been achieved, whereby after nucleation the desired extent of crystal growth is obtained. In the continuous process the hot, concentrated feed is mixed with a large volume of recirculated slurry at the final temperature under conditions that result in a small increase in temperature and concentration for the recirculated material. Supersaturation is achieved by exposing this mixture to a lower vapor pressure in the body which cools the mixture by evaporation of solvent. Thus, one continuous crystallization-by-cooling process (sometimes referred to as the forced circulation process) involves a body (herein crystallizer body) comprising crystallized solute and mother liquor (liquid portion of solution after crystallization of solute takes place), and a high flow rate circulation stream to and from the crystallizer body. The body is established and maintained in a high degree of agitation either by mechanical agitation or, as is the usual case, by hydraulic agitation as by tangentially introducing the circulation stream into the crystallizer body, tangentially withdrawing the circulation stream from the crystallizer, or both with the withdrawal being in the direction of rotational flow in the body. The degree of agitation is such that the body is a slurry. The feed stream of hot solution is introduced into the circulation stream while slurry is withdrawn as a discharge stream either from the body or from the circulation stream. In one embodiment of the process the ambient pressure of the body is selected to result in evaporation of solvent from the crystallizer body and thereby to establish and maintain the temperature of the body substantially below the temperature of the feed stream. The flow rate of the

circulation stream is high enough that upon entry of the feed stream into the circulation stream it cools adiabatically to the temperature of the crystallizer body and circulation stream.

5 Compared to batch crystallization, continuous crystallization has a number of advantages. However, when the above-described continuous crystallization-by-cooling process
10 is applied to solutions involving solvents that are substantially more volatile than water, and temperatures substantially higher than the boiling points of the solvents in the solution at atmospheric pressure, there is one major
15 disadvantage. The discharge streams have concentrations of fine crystals that are too high for efficient separation of crystals from the mother liquor.

20 The problem to which this invention provides a solution is how to minimize the production of fine crystals in such instances.

Excessive production of fine crystals in such instances is believed to be due to solvent flashing just before the point where the feed stream enters the substantially cooler circulation stream. Solvent flashing is thought to
25 cause spontaneous nucleation. The cooling effect of the circulation stream upon the feed stream also causes spontaneous nucleation. However, because of the spontaneous nucleation caused by solvent flashing, not only is there an excessive number of nuclei on which
30 to grow crystals, but the amount of solute available for crystal growth is reduced. The result is an excessive amount of fine crystals. The reason why solvent flashing occurs is that the hydrostatic pressure or head at the point of introduction of the feed stream into the circulation stream is insufficient to prevent volatilization of the solvent in the feed
40 stream, although it is sufficient to prevent volatilization of solvent in the cooler circulation stream.

The present invention provides an apparatus for the continuous crystallization of crystallizable solute from a solution thereof in a solvent substantially more volatile than water and at a temperature substantially above the boiling point of said solvent at atmospheric pressure, in which crystallization is effected by cooling said solution, which apparatus comprises vessel means for containing a crystallizer body having a normal effective liquid level, which vessel means comprise a slurry outlet for a stream of slurry from said body, and a mixed stream inlet for a stream into said body below said normal effective liquid level, circulation stream conduit and pump means in combination with
60 said slurry outlet and said mixed stream inlet for withdrawing at a high rate as a withdrawal stream a stream of slurry through said slurry outlet and returning at least a substantial portion of it as a circulation stream to said
65 body through said mixed stream inlet, means

for effecting cooling of at least one of said body and said circulation stream, discharge stream means for removing as a discharge stream a stream of slurry from one of said body and said withdrawal stream, and feed stream means for introducing a feed stream of said solution into said circulation stream, means for establishing and maintaining the hydrostatic pressure of said circulation stream at the point said feed stream means introduce said solution into said circulation stream conduit and pump means at least equal to the difference between the vapor pressure of the solvent in said feed stream and the vapor pressure of the solvent in the circulation stream arriving at said point.

The present invention also provides a process for effecting crystallization of crystallizable solute from a solution of it in a solvent substantially more volatile than water and at a temperature substantially above the boiling point of said solution at atmospheric pressure by cooling of said solution which comprises passing a feed stream of said solution into a circulation stream running to and from a crystallizer body, said feed stream being at a temperature substantially greater than the temperature of said circulation stream, and passing a discharge stream from one of said body and said circulation stream, wherein the excessive formation of fine crystals is minimized by establishing and maintaining the hydrostatic pressure of said circulation stream, at the point it is joined by said feed stream, at least equal to the difference between the vapor pressure of the solvent in said feed stream and the vapor pressure of the solvent in said circulation stream arriving at said point.

According to this invention production of fine crystals is minimized by establishing and maintaining the hydrostatic pressure or head of the circulation stream at the point of introduction of the feed stream at least equal to and preferably greater than the difference in the vapor pressure of the solvent in the incoming feed stream and the vapor pressure of solvent at the temperature of the circulation stream arriving at that point. The vapor pressure of the solvent in a stream depends upon the concentration of solute in that stream and upon its temperature. It can readily be determined by procedures and equations well known in the art.

In one embodiment of the process and apparatus of this invention, particularly, although not limited thereto, when cooling of the solution is effected by cooling the crystallizer body or circulation stream by cooling coils or a heat exchanger the required hydrostatic pressure is established and maintained by placing the crystallizer body under ambient pressure corresponding to that hydrostatic head.

In another embodiment of the process of

this invention, particularly, although not limited thereto, when cooling is effected by solvent evaporation, the crystallizer body is placed at that elevation above the point of introduction of the feed stream into the circulation stream at which the hydrostatic pressure required by this invention is established and maintained.

In one embodiment of the apparatus of this invention, particularly, although not limited thereto, when cooling is effected by solvent evaporation, the vessel means for the crystallizer body are positioned at that elevation above the junction of the feed stream conduit means with the circulation stream conduit means at which the required hydrostatic pressure is obtained under normal operative conditions.

In other embodiments of the process and apparatus of this invention both ambient pressure and elevation of the crystallizer body are employed to establish and maintain the required hydrostatic pressure at the point of feed stream introduction.

In those situations in which maximum crystallization is desired, and the point of feed stream introduction is at or near the ground or floor, the height of the crystallizer body from the floor or ground required to obtain at least a substantial proportion of desired hydrostatic pressure at the point of feed stream introduction can be too much to be practical. In such situations, according to this invention, the crystallization is carried out in two or more stages. In the first stage the crystallizer body is placed at a practical height above the point of feed stream introduction into the circulation stream, and the body and circulation stream are established and maintained at that temperature at which the vapor pressure of the solvent in the circulation stream is equal to, and preferably greater than, the difference between the vapor pressure of the solvent in the incoming feed stream and the hydrostatic head of the circulation stream at that point. Under these conditions, only partial crystallization of the solute occurs in the first stage. In the second stage, a second stage crystallizer body is placed at a practical height above the point of introduction of the feed stream for the second stage, which is the first stage discharge stream, and the body and circulation stream are established and maintained at that temperature at which the vapor pressure of the solvent in the second stage circulation stream is equal to, and preferably greater than, the difference between the vapor pressure of the solvent in the incoming second stage feed stream and the hydrostatic head of the second stage circulation stream at that point. Under these conditions more solute is crystallized. If not all of the desired amount of solute is crystallized in the second stage, a

third stage or more can be used to effect the desired maximum extent of crystallization.

The best mode now contemplated of carrying out the invention is illustrated by the drawing which forms a material part of these disclosures and which, in brief, depicts diagrammatically a preferred embodiment of a two-stage evaporative cooling crystallization system of this invention.

In greater detail, the drawing illustrates diagrammatically a first crystallization stage 10 and a second crystallization stage 12.

The first crystallization stage comprises a crystallizer vessel 14 adapted to contain a crystallizer body 16 at an ambient pressure greater than atmospheric pressure. The vessel has a domed top with a solvent vapor outlet connected to a vapor discharge conduit 18 which comprises a flow rate and vessel pressure control valve 20. The vapor discharge conduit 18 leads to a condenser 22. Condenser vapor is removed from the condenser 22 by way of a condensate conduit 24 which in this instance leads to an inlet in the crystallizer vessel 14. The vessel 14 has an outlet for tangentially withdrawing a stream of slurry from the bottom region of the crystallizer body 16, and a mixed stream inlet for tangentially introducing, in the direction of rotational flow or swirl of the body 16, a stream into the upper portion of the body below, but in the region of, the dynamic top surface of the body 16 under normal operative conditions. In combination with the outlet and the mixed stream inlet of the crystallizer vessel 14 are circulation stream conduit and pump means. These means comprise a slurry withdrawal conduit 26, a pump 30 and a return conduit 32. The slurry withdrawal conduit 26 extends downwardly from the slurry withdrawal outlet in the crystallizer vessel 14 to the intake of the pump 30, while the return conduit 32 extends from the discharge of the pump upwardly to the mixed stream inlet of the vessel 14. Connected to the return conduit 32 is a feed stream conduit 34, with a flow rate control and shutoff valve 36. The point at which the feed stream conduit 34 joins the return conduit 32, the point of feed stream introduction, according to this invention, is where under normal operative conditions the hydrostatic pressure of the mixed stream in the return conduit 32 is at least equal to, and preferably greater than, the difference between the vapor pressure of the solvent in the incoming feed stream and the vapor pressure of the solvent in the circulation stream at that point. In the embodiment shown, this hydrostatic pressure is obtained by positioning the crystallizer vessel 14 so that the effective liquid level (average level of the dynamic top surface of the body 16) in the vessel, under normal operative conditions, is at the height H above the point of feed stream introduction, at

which height a column of the mixture of feed stream solution and circulation stream slurry has, at the bottom thereof, said hydrostatic pressure. As a result, the return conduit 32 has an upwardly extending section 38 from the point of feed stream introduction to the level at which the mixed feed stream and circulation stream are introduced into the crystallizer vessel 14, which can be regarded as a hydrostatic leg.

Slurry is removed from the first crystallization stage 40, leading from the stage discharge conduit 40, leading from the slurry withdrawal conduit 26 to the second crystallization stage 12. The first stage discharge conduit 40 has a flow rate control and shut off valve 42.

The second crystallization stage 12 comprises a second stage crystallizer vessel 44 adapted to contain a crystallizer body 46 at an ambient pressure less than atmospheric pressure. The vessel 44 has a domed top with a solvent vapor outlet joined to a vapor discharge conduit 48. The vapor discharge conduit 48 leads to a condenser 52. Condensate formed in the condenser 52 is conveyed from the condenser through a condensate conduit 54 which, in this embodiment, leads to an inlet in the crystallizer vessel 44. In combination with the condensate conduit 54 is a vacuum conduit 55 fitted with a vacuum control and shut-off valve 57, which leads to a vacuum source 59. The crystallizer vessel 44 has an outlet for tangentially withdrawing a stream of slurry from the bottom region of the crystallizer body 46, and a mixed stream inlet for tangentially introducing, in the direction of rotational flow or swirl of body 46, a stream into the upper portion of the body below, but in the region of the dynamic top surface of the body 46 under normal operative conditions. In combination with the outlet and the mixed stream inlet of the crystallizer vessel 44 are circulation stream conduit and pump means. These means comprise a slurry withdrawal conduit 56, a pump 60 and a return conduit 62. The slurry withdrawal conduit 56 extends downwardly from the slurry withdrawal outlet in the crystallizer vessel 44 to the intake of the pump 60, while the return conduit 62 extends from the pump discharge upwardly to the mixed stream inlet of the vessel 44. Connected to the return conduit 62 is the first stage discharge conduit 40. The point at which the first stage discharge stream conduit 40 joins the return conduit 62, the point of feed stream introduction in the second stage 12, according to this invention, is where, under normal operative conditions, the hydrostatic pressure of the mixed stream in the return conduit 62 is at least equal to, and preferably greater than, the difference between the vapor pressure of the solvent in the incoming first stage discharge stream and the vapor pressure of

the solvent in the circulation stream at that point. In the embodiment shown, this hydrostatic pressure is obtained by positioning the crystallizer vessel 44 so that the effective liquid level (average level of the dynamic top surface of the body 46) in the vessel, under normal operative conditions, is at the height H' above the point of feed stream introduction, at which height a column of the mixture of the first stage discharge stream slurry and second stage circulation stream slurry has at the bottom thereof said hydrostatic pressure. As a result, the return conduit 62 has an upwardly extending section 68 from the point of first stage discharge stream introduction to the level at which the mixed first stage discharge stream and second stage circulation stream are introduced into the crystallizer vessel 44, which likewise can be regarded as a hydrostatic leg.

Slurry is removed from the second crystallization stage 12 by means of a second stage discharge conduit 70 with a flow rate control and shutoff valve 72.

This conduit, in some embodiments, leads to one or more additional crystallization stages. However, in the embodiment shown, it leads to a crystal separation stage 74 in which crystals 76 and mother liquor 78 are separated.

To operate the two-stage crystallization system depicted in the drawing, the feed stream of hot solution at a temperature substantially in excess of the atmospheric pressure boiling point temperature of the solvent therein is introduced by way of the feed stream conduit 34 into the first stage return conduit 32. The feed stream promptly cools adiabatically to the prevailing temperature of the circulation stream flowing through the return conduit 32. Because of the hydrostatic head or pressure at the point of feed stream introduction into the circulation stream, no flashing of the solvent in the feed stream occurs. Any nucleation that occurs in the mixed stream that results from the joining of the feed stream with the circulation stream is a result of cooling of the feed stream. Hence, the conditions for crystal growth are maximized. When the mixed stream enters the crystallizer body 16, evaporation of solvent takes place and heat is thereby removed from the crystallizer body 16. The extent of evaporation, and thus the amount of heat removed (and in turn the temperature of the crystallizer body 16), is controlled by regulating the release of solvent vapor through the vapor discharge conduit 18, and thus the pressure inside the crystallizer vessel 14. By thus controlling the pressure, the extent of evaporation of solvent from the crystallizer body is controlled, and thus the temperature of the crystallizer body is controlled. Slurry is withdrawn from the crystallizer body via the slurry withdrawal

conduit 26 at a rate, controlled by the capacity of the pump 30 and regulation of the speed of the pump 30, at which the flow rate of the circulation stream flowing through the pump 30 and return conduit 32 is such that it is substantially at the temperature of the crystallizer body 16, and the mixture of feed stream and circulation stream flowing upwardly through the hydrostatic leg 38 is at substantially the temperature of the crystallizer body 16. Temperature of the crystallizer body 16 is established and maintained at the temperature at which the vapor pressure of the solvent in the circulation stream is at least equal to and preferably greater than the vapor pressure of the solvent in the incoming feed stream in the feed stream conduit 34, less the hydrostatic pressure at the bottom of the hydrostatic leg 38.

Part of the slurry withdrawn from the crystallizer body through the slurry withdrawal conduit 26 is conducted by way of slurry discharge stream conduit 40 into the second crystallization stage. In this stage the crystallization body 46 is established and maintained under subatmospheric pressure. By regulating, with the vacuum conduit valve 57, the amount of vacuum applied, the pressure of, the extent of evaporation of solvent form, and thus the temperature of the crystallizer body 46 are controlled. Slurry is

withdrawn from the crystallizer body 46 by way of the second stage slurry withdrawal conduit 56 at a rate, controlled by the capacity of the pump 60 and regulation of the speed of the pump 60, at which the flow rate of the circulation stream flowing through the pump 60 and the return conduit 62, and the mixture of first stage discharge stream and the second stage circulation stream flowing through the hydrostatic leg 68 are at substantially the same temperature as the crystallizer body 46. The temperature of the crystallizer body 46 is thereby established and maintained at a value at which the vapor pressure of the solvent in the circulation stream arriving at the point of entry of the first stage discharge stream is at least equal to and preferably greater than the vapor pressure of the solvent in the first stage discharge stream in the conduit 40, less the hydrostatic pressure at the bottom of the hydrostatic leg 68.

With the foregoing crystallization system, a desired maximum crystallization of solute from the initial feed stream can be effected with a minimum production of fine crystals.

A typical application of this two-stage crystallization system is in the crystallization of dimethyl terephthalate (DMT) from methanol. The following table gives solubility data for DMT in methanol, and methanol vapor pressure data at various temperatures.

Temp. °C.	Solubility gms. DMT/100 gms. soln.	Methanol Vapor Pressure	
		mm Hg abs.	m. of methanol abs.*
40	2.1	255	4.4
50	3.5	400	6.9
60	5.7	620	10.7
70	9.8	940	16.2
80	16.0	1,350	23.2
90	27.0	1,900	32.7
100	44.0	2,600	44.8
110	70.0	3,550	61.1

*Assuming a constant density of methanol of 0.79 g./ml. and neglecting solution effects.

From these data, it can be calculated that for a single stage crystallization system according to this invention, with the feed stream being a saturated methanolic solution of DMT at 100°C., and with the crystallizer body temperature being 50°C., the crystallizer body must be at such an elevation that the height of the effective liquid level of the crystallizer body under normal operative conditions must be at least 37.9 meters, or about 124 feet, above the point of introduction of the feed stream into the circulation stream. With the body temperature being 42°C., the height of the effective liquid level of the crystallizer body under normal operative conditions must be at least (by interpolation of the above data plotted on a logarithm of the pressure versus reciprocal of the absolute temperature basis) 39.9 meters, or about 131 feet, above the

point of introduction of the feed stream into the circulation stream. Mounting of crystallizer vessels at elevations at which the crystallizer bodies have these normal effective liquid level heights generally is not practical. Consequently, under such circumstances a multistage crystallization system is preferred. Typical normal operating conditions for the crystallization of a saturated methanol solution of dimethyl terephthalate in the two-stage continuous crystallization system depicted in the drawing are as follows:

Temperature of feed stream 34=100°C.
Ambient pressure of crystallizer body 16=1000 mm. Hg abs.
Temperature of crystallizer body 16=71.2°C.

H=27.5 m. (90.2 feet) minimum
 Ambient pressure of crystallizer body
 46=280 mm. Hg abs.
 Temperature of crystallizer body 46=
 5 42.0°C.
 H'=12.5 m. (41.0 feet) minimum

Under these conditions excessive formation of fine DMT crystals is minimized.

WHAT WE CLAIM IS:—

10 1. An apparatus for the continuous crystallization of crystallizable solute from a solution thereof in a solvent substantially more volatile than water and at a temperature substantially above the boiling point of said
 15 solvent at atmospheric pressure, in which crystallization is effected by cooling said solution, which apparatus comprises vessel means for containing a crystallizer body having a normal effective liquid level, which
 20 vessel means comprise a slurry outlet for a stream of slurry from said body, and a mixed stream inlet for a stream into said body below said normal effective liquid level, circulation stream conduit and pump means in combina-
 25 tion with said slurry outlet and said mixed stream inlet for withdrawing at a high rate as a withdrawal stream a stream of slurry through said slurry outlet and returning at least a substantial portion of it as a circulation
 30 stream to said body through said mixed stream inlet, means for effecting cooling of at least one of said body and said circulation stream, discharge stream means for removing as a discharge stream a stream of slurry from
 35 one of said body and said withdrawal stream, and feed stream means for introducing a feed stream of said solution into said circulation stream, means for establishing and maintaining the hydrostatic pressure of said circulation
 40 stream at the point said feed stream means introduce said solution into said circulation stream conduit and pump means at least equal to the difference between the vapor pressure of the solvent in said feed stream and the
 45 vapor pressure of the solvent in the circulation stream arriving at said point.

2. An apparatus as claimed in claim 1 in which crystallization is effected by evaporation of solvent from the solution, and comprising a solvent vapor outlet for a stream of vapor of solvent evaporated from said body and means for withdrawing solvent vapor through said outlet.

55 3. An apparatus as claimed in claim 1 and 2, wherein said vessel means are at a height above the junction of said feed stream means with said circulation stream conduit and pump means in which the hydrostatic pressure of said circulation stream at said junction is at least equal to the difference between the vapor pressure of said solvent in said feed stream and the vapor pressure of
 60 said solvent in said circulation stream arriving at said point.

said solvent in said circulation stream arriving at said point.

4. An apparatus as claimed in claim 3, wherein said circulation stream conduit and pump means comprise pump means below said vessel means, withdrawal stream conduit means from said slurry outlet to the intake of said pump means, and slurry return conduit means from the discharge of said pump means to said mixed stream inlet, said feed stream being in combination with said return conduit means.

5. An apparatus as claimed in claim 3 or 4, wherein said discharge stream means comprise conduit means in combination with said slurry withdrawal conduit means.

6. An apparatus as claimed in claim 3, 4 or 5, which comprises second vessel means for containing a second crystallizer body having a normal effective liquid level, which second vessel means comprise a solvent vapor outlet for a stream of vapor of solvent evaporation from said second crystallizer body, a slurry outlet for a stream of slurry from said second crystallizer body, and a mixed stream inlet for a stream into said second crystallizer body below its normal effective liquid level, means for withdrawing said stream of solvent vapor through said solvent vapor outlet of said second vessel means, second circulation stream conduit and pump means in combination with said second vessel means slurry outlet and said second vessel means mixed stream inlet for withdrawing at a high rate as a second withdrawal stream a stream of slurry through said second vessel means slurry outlet and returning at least a substantial portion of it as a second circulation stream to said second crystallizer body through said second vessel mixed stream inlet, said discharge stream means being in combination with said second stream conduit and pump means for introducing said discharge stream into said second circulation stream, said vessel means being at a height above the junction of said discharge stream means with said second circulation conduit and pump means at which the hydrostatic pressure of the second circulation stream in said second circulation stream conduit and pump means at said junction is at least equal to the difference between the vapor pressure of said solvent in said discharge stream and the vapor pressure of said solvent in said second circulation stream arriving at that point, and second discharge stream means for removing as a discharge stream a stream of slurry from one of said second crystallizer body and said second withdrawal stream.

7. An apparatus as claimed in claim 6, wherein said second circulation stream conduit and pump means comprise second pump means below said second vessel means, second slurry withdrawal conduit means from said second vessel means slurry outlet to the intake



H=27.5 m. (90.2 feet) minimum
Ambient pressure of crystallizer body
46=280 mm. Hg abs.
Temperature of crystallizer body 46=
42.0°C.
H'=12.5 m. (41.0 feet) minimum

Under these conditions excessive formation of fine DMT crystals is minimized.

WHAT WE CLAIM IS:—

10 1. An apparatus for the continuous crystallization of crystallizable solute from a solution thereof in a solvent substantially more volatile than water and at a temperature substantially above the boiling point of said solvent at atmospheric pressure, in which crystallization is effected by cooling said solution, which apparatus comprises vessel means for containing a crystallizer body having a normal effective liquid level, which vessel means comprise a slurry outlet for a stream of slurry from said body, and a mixed stream inlet for a stream into said body below said normal effective liquid level, circulation stream conduit and pump means in combination with said slurry outlet and said mixed stream inlet for withdrawing at a high rate as a withdrawal stream a stream of slurry through said slurry outlet and returning at least a substantial portion of it as a circulation stream to said body through said mixed stream inlet, means for effecting cooling of at least one of said body and said circulation stream, discharge stream means for removing as a discharge stream a stream of slurry from one of said body and said withdrawal stream, and feed stream means for introducing a feed stream of said solution into said circulation stream, means for establishing and maintaining the hydrostatic pressure of said circulation stream at the point said feed stream means introduce said solution into said circulation stream conduit and pump means at least equal to the difference between the vapor pressure of the solvent in said feed stream and the vapor pressure of the solvent in the circulation stream arriving at said point.

2. An apparatus as claimed in claim 1 in which crystallization is effected by evaporation of solvent from the solution, and comprising a solvent vapor outlet for a stream of vapor of solvent evaporated from said body and means for withdrawing solvent vapor through said outlet.

3. An apparatus as claimed in claim 1 and 2, wherein said vessel means are at a height above the junction of said feed stream means with said circulation stream conduit and pump means in which the hydrostatic pressure of said circulation stream at said junction is at least equal to the difference between the vapor pressure of said solvent in said feed stream and the vapor pressure of

said solvent in said circulation stream arriving at said point.

4. An apparatus as claimed in claim 3, wherein said circulation stream conduit and pump means comprise pump means below said vessel means, withdrawal stream conduit means from said slurry outlet to the intake of said pump means, and slurry return conduit means from the discharge of said pump means to said mixed stream inlet, said feed stream being in combination with said return conduit means.

5. An apparatus as claimed in claim 3 or 4, wherein said discharge stream means comprise conduit means in combination with said slurry withdrawal conduit means.

6. An apparatus as claimed in claim 3, 4 or 5, which comprises second vessel means for containing a second crystallizer body having a normal effective liquid level, which second vessel means comprise a solvent vapor outlet for a stream of vapor of solvent evaporation from said second crystallizer body, a slurry outlet for a stream of slurry from said second crystallizer body, and a mixed stream inlet for a stream into said second crystallizer body below its normal effective liquid level, means for withdrawing said stream of solvent vapor through said solvent vapor outlet of said second vessel means, second circulation stream conduit and pump means in combination with said second vessel means slurry outlet and said second vessel means mixed stream inlet for withdrawing at a high rate as a second withdrawal stream a stream of slurry through said second vessel means slurry outlet and returning at least a substantial portion of it as a second circulation stream to said second crystallizer body through said second vessel mixed stream inlet, said discharge stream means being in combination with said second stream conduit and pump means for introducing said discharge stream into said second circulation stream, said vessel means being at a height above the junction of said discharge stream means with said second circulation conduit and pump means at which the hydrostatic pressure of the second circulation stream in said second circulation stream conduit and pump means at said junction is at least equal to the difference between the vapor pressure of said solvent in said discharge stream and the vapor pressure of said solvent in said second circulation stream arriving at that point, and second discharge stream means for removing as a discharge stream a stream of slurry from one of said second crystallizer body and said second withdrawal stream.

7. An apparatus as claimed in claim 6, wherein said second circulation stream conduit and pump means comprise second pump means below said second vessel means, second slurry withdrawal conduit means from said second vessel means slurry outlet to the intake

of said second pump means, and second slurry return conduit means from the discharge of said pump means to said second vessel mixed stream inlet, the first mentioned discharge stream means being in combination with said second slurry return conduit means.

8. An apparatus as claimed in claim 6 or in which said second discharge stream means comprise conduit means in combination with said second slurry withdrawal conduit means.

9. An apparatus as claimed in claim 1 and substantially as hereinbefore described with reference to the accompanying drawings.

10. A process for effecting crystallization of crystallizable solute from a solution of it in a solvent substantially more volatile than water and at a temperature substantially above the boiling point of said solution at atmospheric pressure by cooling of said solution which comprises passing a feed stream of said solution into a circulation stream running to and from a crystallizer body, said feed stream being at a temperature substantially greater than the temperature of said circulation stream, and passing a discharge stream from one of said body and said circulation stream, wherein the excessive formation of fine crystals, is minimized by establishing and maintaining the hydrostatic pressure of said circulation stream, at the point it is joined by said feed stream, at least equal to the difference between the vapor pressure of the solvent in said feed stream and the vapor pressure of the solvent in said circulation stream arriving at said point.

11. A process as claimed in claim 10, wherein cooling of said solution is effected by evaporative cooling so that a vapor stream of solvent is evaporated from the crystallizer body.

12. A process as claimed in claim 11, which comprises passing said discharge stream into a second circulation stream running to and from a second crystallizer body at an ambient pressure at which solvent evaporates from said second crystallizer body, whereby a second stream of vapor of solvent evaporates from said second crystallizer body, said second crystallizer body being at that elevation above the point at which said discharge stream joins said second circulation stream at which the hydrostatic pressure at that point is at least equal to the difference between the vapor pressure of the solvent in said discharge stream and the vapor pressure of the solvent in said second circulation stream arriving at said point, and passing a second discharge stream from one of said second crystallizer body and said second circulation stream.

13. A process as claimed in claim 12, wherein the first mentioned discharge stream is from the first mentioned circulation stream, and said second discharge stream is from said second circulation stream.

14. A process as claimed in any of claims 10 to 13, wherein said solute consists essentially of dimethyl terephthalate, and said solvent is methanol.

15. A process as claimed in claim 10 and substantially as hereinbefore described with reference to the accompanying drawings.

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