

[54] **SOLID-LIQUID CONTINUOUS
COUNTERCURRENT PURIFIER
METHOD AND APPARATUS**

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[58] Field of Search62/58; 23/273 F, 273

[56] **References Cited**

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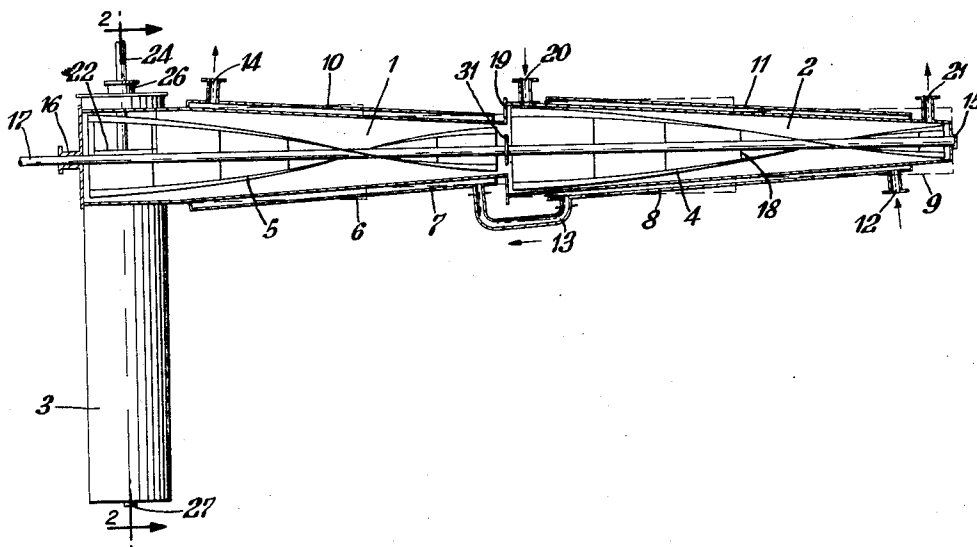
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[57] **ABSTRACT**

At least one component of a multicomponent molten mixture is separated from the mixture and purified by introducing the mixture into the recovery section of an array of apparatus comprising a recovery section, a refining section and a purifying section. The recovery and purifying sections each have helical scraper-conveyors to move crystals through them, increasing cross sectional areas in the direction of crystal progression and downward temperature gradients in the direction of liquid and reflux movement which is countercurrent to the crystal progression. The feed mixture is introduced to the recovery section near its junction with the refining section and flows in the countercurrent or reflux direction. Crystallization occurs at a certain temperature encountered in the recovery section and the crystals grow and are purified as they are moved by the scraper-conveyors through the recovery and refining sections and into the purifying section and purify by gravitational movement through the countercurrent molten reflux. At the end of the progression through the purifier, the crystals are remelted and withdrawn as substantially pure preselected component.

12 Claims, 6 Drawing Figures



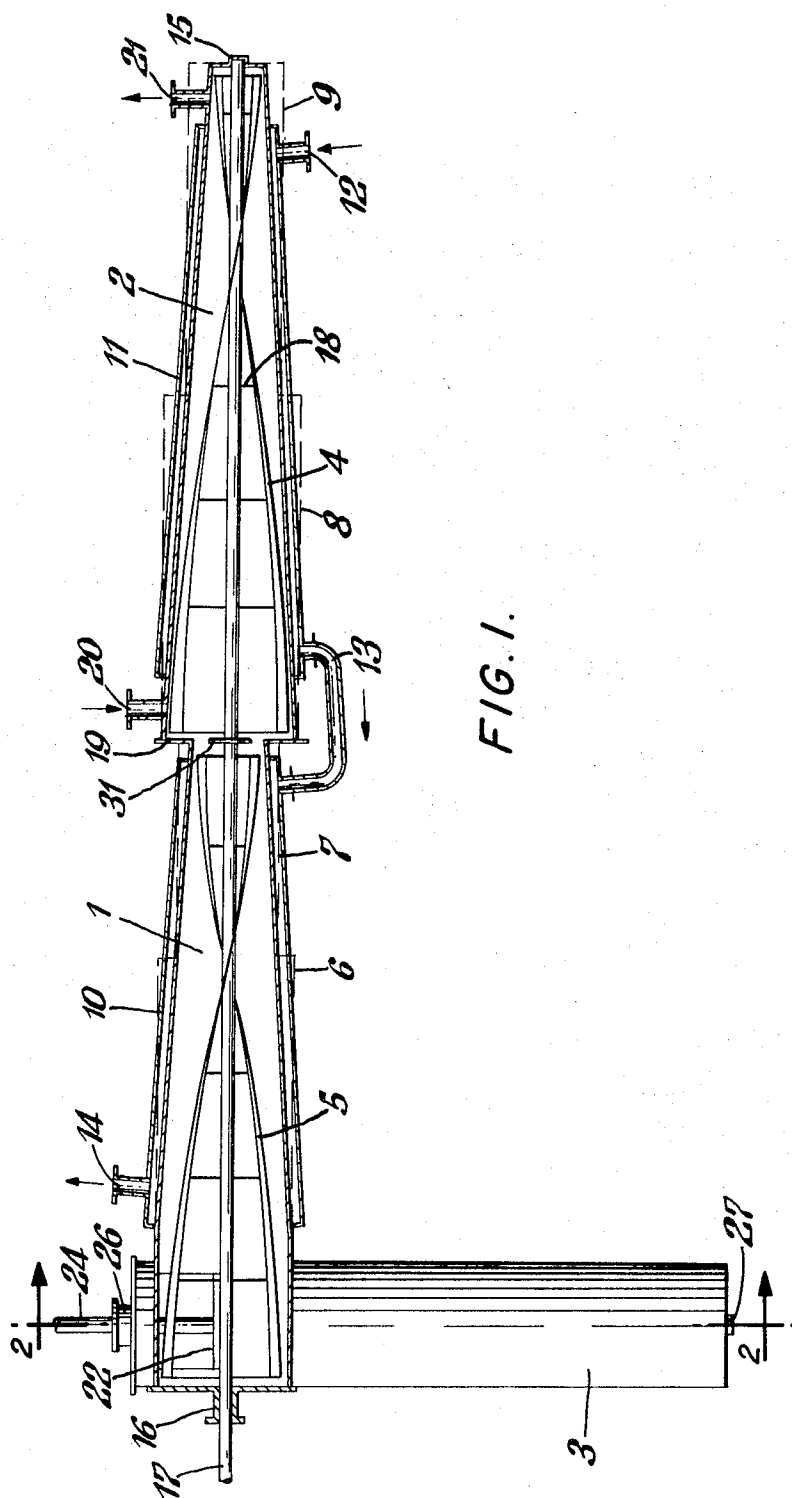
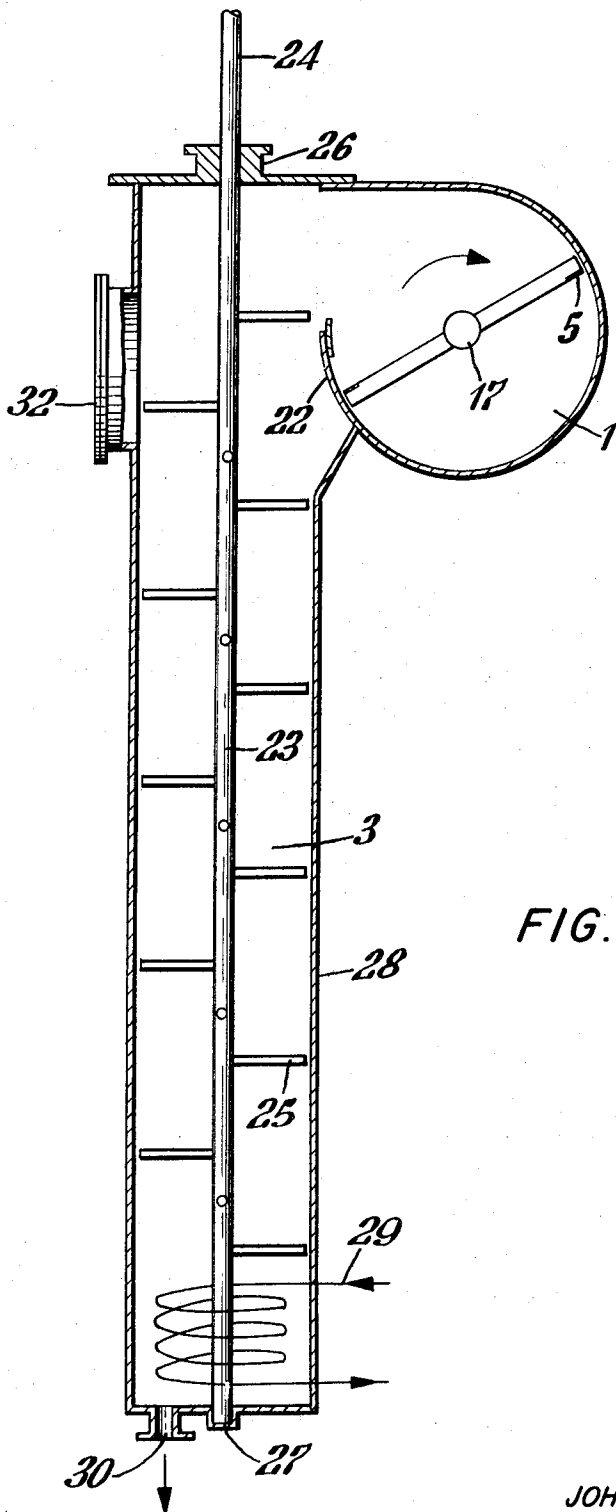
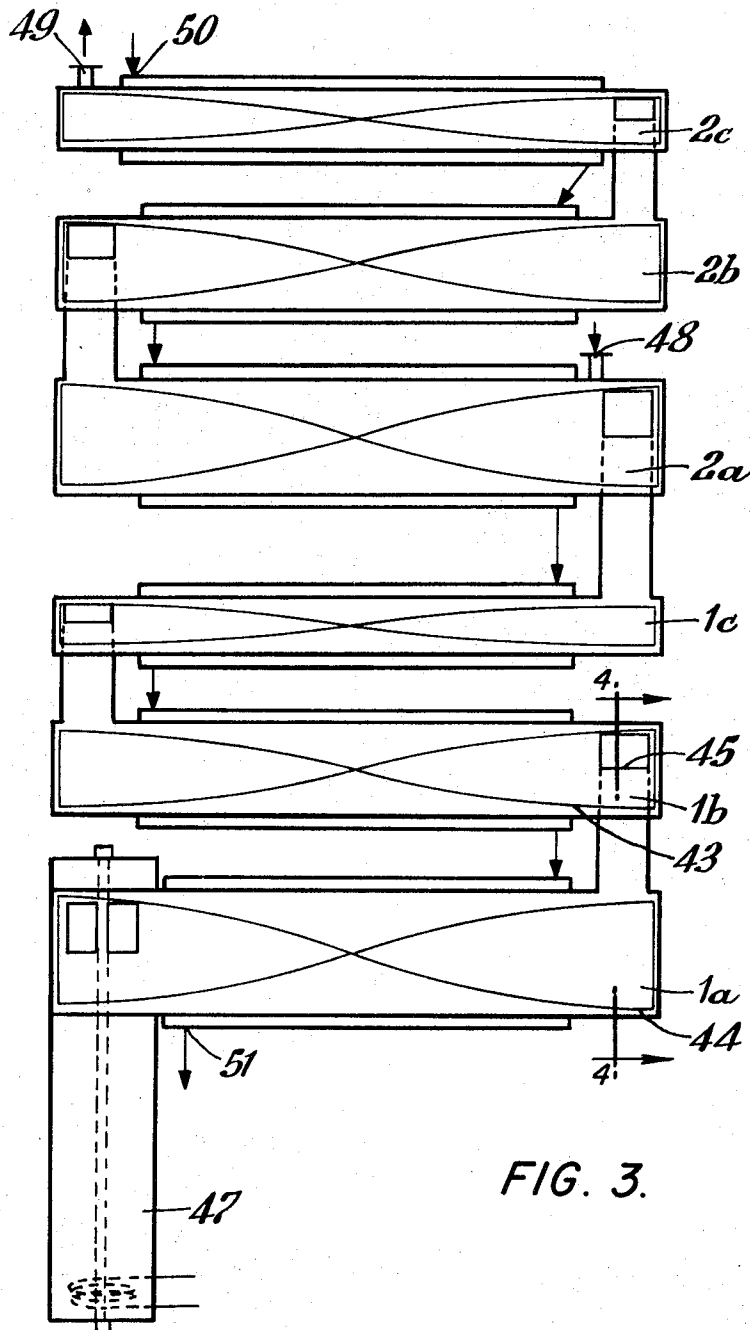


FIG. 1.

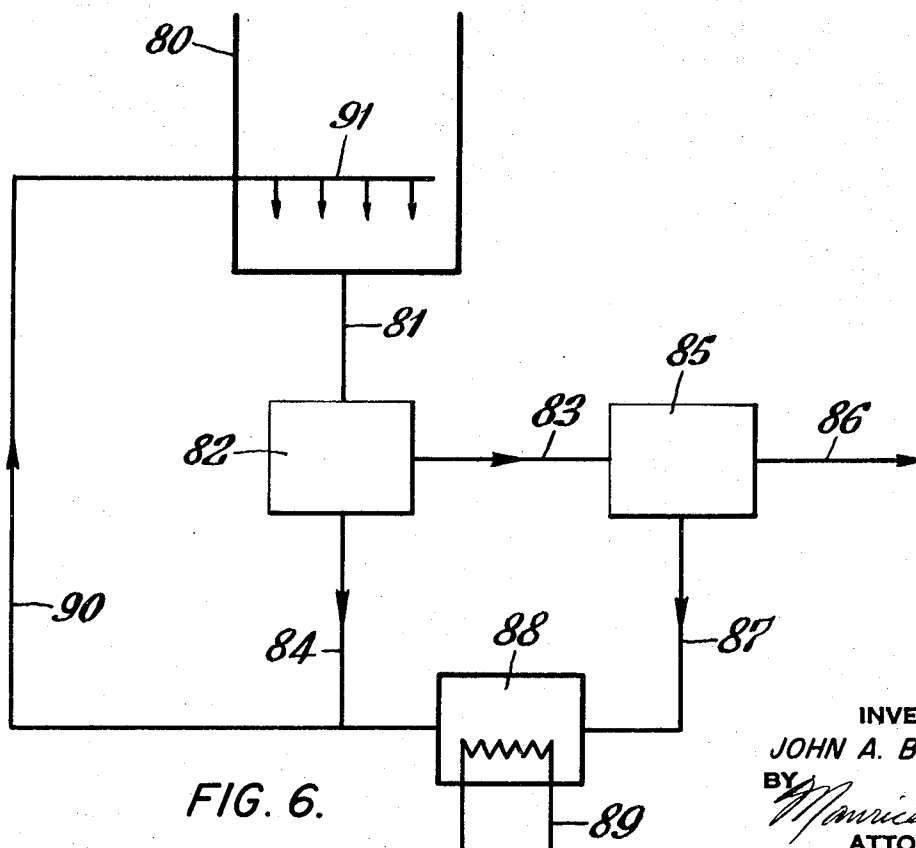
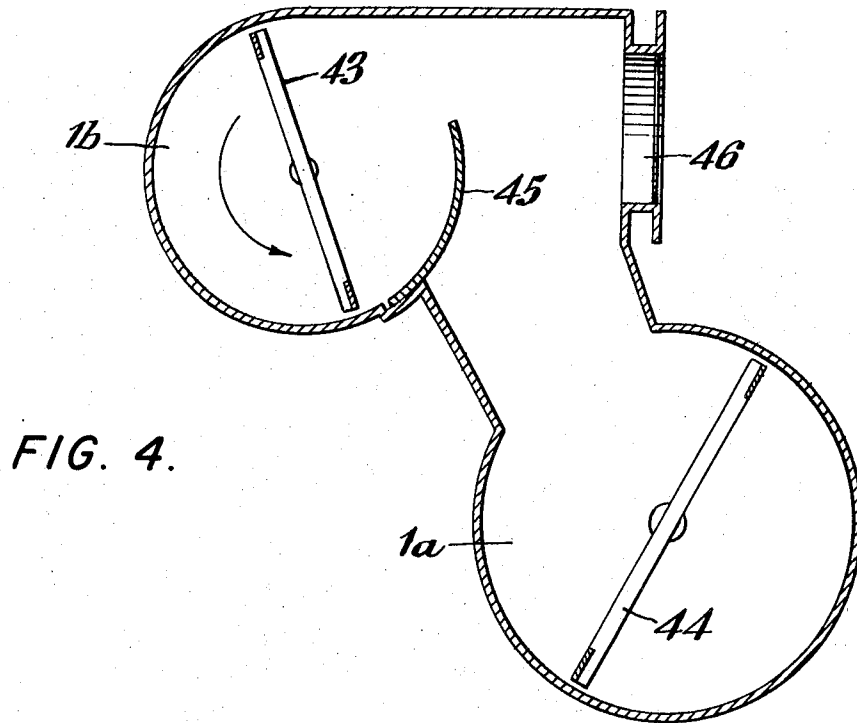
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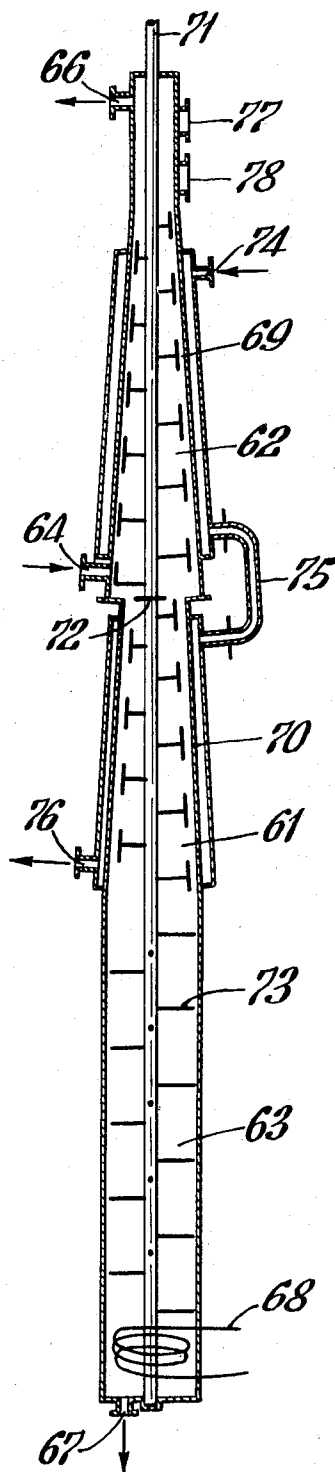


FIG. 5.

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SOLID-LIQUID CONTINUOUS COUNTERCURRENT PURIFIER METHOD AND APPARATUS

This invention relates to a solid-liquid continuous counter-current separation and purification method and apparatus employing crystallization phenomena.

It is known in the materials separation arts that where close boiling points of materials in mixture make for great difficulty in separating such materials by distillation techniques, provided the melting points of the materials in mixture are sufficiently spaced to render it feasible, resort to crystallization procedures may permit separation of a solid phase from a liquid phase with greater facility than and often with great advantage over distillation techniques.

An elaborate technology has evolved utilizing combinations of crystallizers and purifiers, and with the optional addition of solvent materials, to achieve separations with crystallizing procedures. Resort has been made to sieves or screens, to porous pistons, to pulsed operation and to a variety of other devices for moving crystals and liquids. While significant advances have been made in such technology, no completely satisfactory crystallization process has been made available to industry. It is known for instance to those skilled in the art that the achievement of a 99 percent pure desired product is often relatively simple compared with the critical operation and effort required to achieve 99.99 percent purity in commercial operation with economic throughput. Indeed, there are a number of reports in the relevant literature indicating that scale-up from bench size to pilot plant installations is far from easy, and thus far some of the problems have proved insuperable.

With this then being the state of art, the present invention was made to provide a process and means to achieve separations of components from multicomponent mixtures through crystallization procedures.

It is an advantage of the present invention that by it commercial operation to give purities in excess of 99.99 percent can be achieved.

It is a further advantage of the present invention that it is operated with high thermodynamic efficiency, notwithstanding the fact that the equipment is of comparatively simple construction. Said high purity and high efficiency are believed to arise from the novel features of the process reflected in the equipment design, which depart significantly from those taught by the prior art.

It is a still further advantage of the invention that the design and operating parameters are so related that they may be readily adapted to computerized control if desired, though it must be recognized that considerable change in certain design parameters of equipment will be necessary if there is a radical change in feed stocks or products. Where feed stocks suffer from minor fluctuations, operating parameters can be adjusted to achieve equilibrium operation; larger fluctuations may be dealt with by minor changes, such as alteration of point of feed stock entry, or the incorporation of comparatively simple surge absorbing zones. Gross changes will call for design variation, which however need not involve major rebuilding, as will become apparent hereafter in the discussion of forms of equipment that can be employed in practicing the invention.

Another advantage of the present invention lies in the fact that it allows a complete separation of one of the components of the feed stock, within the limits set by an eutectics, in one totally sealed continuous piece of equipment. This is of extreme importance where hazardous or toxic substances are involved.

While the invention is primarily described as separating mixtures of organic materials, it can be adapted to solutions wherein an equilibrium liquid phase is substituted by a saturated solution, which may include an aqueous solution of a substantially nonfusible inorganic salt.

In general according to the invention there is provided a process and apparatus for the separation in very pure form of at least one component of a multicomponent mixture whereby

the mixture is fed into a solid-liquid continuous countercurrent purifier, which includes of a purifying section, a refining section and a crystal-forming recovery section, all in series. The mixture is fed into the recovery station at a point near the junction of the recovery section and the refining section. A continuous downward temperature gradient is provided from the junction of the refining section with the purifying section to the end of the recovery section remote from the purifying section by continuous heat extraction throughout the length of said sections which are fitted with cooling jacket or the like means. A liquid phase velocity at any point in a direction opposite to the direction of crystal movement is maintained which velocity is greater than the back mixing velocity of liquid at said point under the influence of agitation, crystal transport, and convection instability. The crystal phase is maintained in suspension in the liquid phase in each section in a state intermediate between sedimentation and fluidization by the control of agitating means and liquid flow velocity. Where necessary to prevent crystal buildup on unscrapped surfaces in the recovery and refining sections, all such unscrapped surfaces are provided with a sufficient small positive heat input. The purifying section is operated under essentially adiabatic conditions modified only by a small heat input throughout its length to keep the temperature of its wall and agitating means just above the crystallizing point of the liquid immediately adjacent thereto. Crystals are transferred slowly from the crystal forming recovery section through the refining section to the purifying section to maximize equilibrating crystal contact with the countercurrent flow of liquid and to cause adequate growth and purity of crystals finally fed into the purifying section.

The arrangement of a purifying section a refining section and a crystal forming recovery section in series, with a feed point near the junction of the refining section and the recovery section, a pure product output at the end of the purifying section remote from said feed point and a second product or mother liquor output at the end of the recovery section remote from said feed point represents a development of the center-fed type crystallization apparatus. Its construction and operation have distinct differences from known types end-fed crystallization apparatus which generally feature a crystal forming section and purifying section operating without the limitations and structures of the process of the present invention. In particular it is to be noted that the end-fed crystallization apparatus usually employ flash chillers to cool the mix introduced to the purifying section, said chillers having their coolant circulation so arranged that there exists an upward temperature gradient from the junction of the chiller with the purifying section to the feed point remote from the purifying section; that is, the end-fed crystal forming section operates with a low-temperature feed to the refining or purifying section.

It is an important feature of the present invention that it operates with a continuous downward temperature gradient (not necessarily linear) from the junction of the refining section with the purifying section to the feed input point and continuing from the feed input point through the length of the recovery section to the liquid discharge point at the end of the recovery section most remote from the purifying section. Thus the countercurrent purifier of this invention operates with a feed at a temperature practically identical to the temperature obtaining in the apparatus where it enters close to the junction of the refining and recovery sections, which temperature is intermediate of that of the low temperature liquid discharge from the remote end of the recovery section and the maximum temperature in the refining section where reflux liquid enters from the purifying section. It is further to be understood that this downward temperature gradient through the length of the refining section, when associated with the slow crystal transport and maximized equilibrating contact provided by the invention, means that crystals transported through the refining section pass in succession through a series of equilibrating stages characterized by increasing temperature: consequently

the length of the refining and recovery sections and the temperature difference between their remote ends will determine the number of "equivalent plates" available in these sections for the purification of a mixture in terms of a liquid-solid composition whose temperature and composition can be represented on an associated phase diagram.

In the practice of the invention, the downward temperature gradient in the direction of liquid flow within the sections of the apparatus requires that the coolant circulation moves in a direction opposite to that of the flow of the liquid phase of the mix with the consequent benefit of enhanced thermodynamic efficiency. One or more coolant circuits may be employed, according to required temperature and heat loads required. Separate control of the countercurrent coolant to the refining and recovery sections, for instance, makes it possible to attain preselected temperature gradients downwards from the end of the refining section contiguous to the purifying section and upwards from the remote or liquid discharge end of the recovery section so that the two gradients meet at the point of feed stock inlet to produce a temperature there equal to the crystallization point of the product of interest. In operation, the liquid phase flow is in a direction opposite to that of crystal movement, and of a velocity that exceeds the back mixing velocity of the liquid under the influence of agitation, crystal transport and convection instability. Known devices employ agitators or conveying means which operate at relatively high speeds. This causes turbulence and a back-mixing effect which tends to negate the progress in purification achieved in the crystal phase. Since the passage of the scraper-conveyor blades through the liquid crystal mixture inherently causes a certain amount of backmixing and, further, since there is always a tendency for a liquid to adhere in layer formation to crystals suspended in it, backmixing cannot be completely avoided. Again, in some crystallization separation processes there is the possibility that a feed stock, denuded of one component by crystallization and perhaps also affected by a temperature reduction, may have a higher density than the original or initially introduced form or a partially denuded form thereof. Such more dense liquid may, in certain arrangements of apparatus, tend to gravitate undesirably into zones holding comparative pure product.

The selection of agitator and scraper-conveyor rotational speeds with attendant control of liquid phase flow velocities however, as provided by the present invention, minimizes these undesirable backmixing tendencies.

There is, however, one difficulty in insuring that the liquid phase velocity shall always exceed a certain minimum figure. The crystal-liquid mixture must have crystal removed from it for the process to operate and the liquid phase is continually reduced by deposition of crystals therefrom under the influence of lower temperature.

The apparatus of the invention is therefore designed, fabricated and operated to insure that the desired liquid phase velocity can be maintained throughout the length of the refining section and the recovery section. This is achieved by providing refining and recovery sections each having decreasing cross sectional areas in the direction of fluid flow. Each such section may be made in tapered form or, alternatively of a series connected array of cylindrical elements each having a cross-sectional area smaller than the preceding element along the fluid flow direction. The larger cross sectional areas in each of such sections are associated with relatively higher temperatures relatively larger liquid-crystal mix volumes while the smaller cross sectional areas are associated with relatively lower temperatures, and relatively smaller liquid-crystal mix volumes.

It is of importance in practicing the invention that equilibration must be maximized. Therefore, in addition to control of liquid back mixing, means for the control of the crystal phase is provided. If the crystal phase sediments, there is inadequate exchange and equilibration with the liquid phase. If the crystal phase becomes fluidized, there will be excessive back-mixing of crystal, and loss of through-put. It is known that there is a

condition with solid-liquid systems which is intermediate between sedimentation and fluidization, where the bed of solid particles swells, but the solid particles are not able to move freely through the expanded solid bed. It is therefore necessary to control the agitating and scraper-conveyor means and the liquid flow velocity in each of the recovery, refining and purifying sections 50 that the crystal phase is held in suspension in the liquid phase in a state intermediate between sedimentation and fluidization. In conformity with this requirement, an agitator and/or scraper conveyor may in a given case operate at the slow speed of half a revolution per minute, which contrasts strongly with agitator speeds described in some of the prior art.

One particular form of crystal agglomeration is encountered where crystal masses grow on unscrapped surfaces, such as shaft bearings, sections of agitator shafts, the flat sides of scraper-conveyor blades as these are cooled by thermal conduction to other sections of the apparatus at lower temperatures, or, in the case of scraper-conveyor blades, as these are cooled by mechanical contacts with the cooled surfaces of vessel walls or layers of crystalline solids attached thereto. All such accumulations hinder the proper operation of the equipment employed in the invention, and since it is important that agitators and scraper-conveyors move slowly, it is unlikely should such crystal masses disengage that they will be broken up in order to effect equilibration.

A significant integer of the invention is therefore the requirement that the operation shall allow, where necessary to prevent such crystal buildup, a small evenly distributed heat input to such unscrapped surfaces. Electrical tracing with power led in through an agitator shaft is an effective means of achieving such heat input.

It is known to generate a reflux in a vertical purifying section by applying heat to the discharge end of such purifying section, to cause melting withdrawing a proportion of melt and returning the balance of said melt countercurrent to a descending bed of crystals as a reflux. Some end-fed crystallization columns of the prior art discharge such reflux below the top of the purifying section by means of sieves or porous pistons. The present invention operates by returning reflux to the refining section. Certain end-fed crystallization columns of the prior art employ a low temperature feed to the purifying section. The present invention employs a high temperature feed to the purifying section. Certain end-fed crystallization columns of the prior art compact the crystal bed in the purifying section with pistons, and others apply pulsed agitation. The present invention maintains a crystal bed in the purifying section in a state intermediate between sedimentation and fluidization, preferably allowing the crystal bed to form under gravity, and to reform after the small disturbance produced by a very slowly revolving agitating means and the countercurrent flow of liquid reflux. The present invention further provides that the purifying section operates adiabatically, modified only by a small heat input at least to keep the temperature of the wall and agitating means above the crystallizing point of adjacent liquid. This includes compensation for heat lost by conductivity along the purifying section wall and agitating means.

A gravity-operated purifying section performs best with a comparatively large crystal size. In general, large crystals are not grown by shock cooling or steep temperature/time gradients. For a given rate of crystal transport, a temperature/time gradient can be transformed into a temperature/length gradient. In the practice of the present invention therefore, crystals which form in the recovery section pass only slowly through it and the refining section. This insures that the crystals are subjected to a relatively small temperature/time gradient. Where necessary, the recovery and refining sections are designed to be sufficiently long so that maximized equilibrating contact of crystal and liquid through these zones of relatively small temperature/time gradients is achieved. The consequent melting, recrystallization, remelting and further recrystallization steps then insure a feed of

adequate crystal purity and size passing into the purifying section from the refining section.

It is known in the crystallization separation art that impurities are carried on crystal surfaces both by occlusion in crystal surface faults and by migration into dendritic or the like features in crystal facia. It will be readily apparent to persons familiar with the art that the present invention as thus far described provides inherently for the removal of such impurities with consequent enhancement of crystal purity through the optimum time shearing action obtaining between the liquid and crystal phases in counterflow relationship.

The point of entry for the multicomponent feed stock is selected so that its entry into the system effects minimum thermodynamic disturbance. This involves a comparison of the composition-temperature conditions obtaining within the continuous countercurrent purifier, and the composition-temperature conditions in the feed stock when entering the purifier. Thermal stock of the system by the entering feed stock will thus be minimized.

The invention will now be described with greater particularity and with reference to the drawings wherein:

FIG. 1 is a partly sectionalized elevational view showing an apparatus arrangement which includes a recovery section, a refining section and a purifying section according to the invention.

FIG. 2 is a sectional view taken along the line 2—2 of FIG. 1, showing the interiors of the purifying section and the refining section at its junction with the purifying section.

FIG. 3 shows an alternative partially sectionalized arrangement of apparatus utilizing a multiplicity of cylindrical elements each to constitute the recovery and refining sections according to the invention.

FIG. 4 is a sectional view taken along the line 4—4 of FIG. 3 showing the interiors of two elements of the refining section of the apparatus of FIG. 3.

FIG. 5 is an elevational sectionalized view of an alternative arrangement of apparatus according to the invention involving a completely vertical disposition of the recovery, refining and purifying sections.

FIG. 6 is a schematic or block diagram illustrating a variation of apparatus elements according to the invention.

One arrangement of the equipment of this invention is illustrated in FIGS. 1 and 2.

A refining section 1 and a recovery section 2 arranged end to end on one substantially horizontal axis are coupled to a vertical purifying section 3. Helical scraper-conveyors 4 and 5 are provided in the recovery section and refining section respectively, and slowly revolve to urge precipitated crystals towards the purifying section, while producing minimum back-mixing of liquid which moves in a direction countercurrent to the crystal progression from the purifying section 3 through the refining section 1, and, together with some feedstock from its admission point, through the recovery section 2. Both the refining section 1 and the recovery section 2 are shown as uniformly tapered cylindrical vessels, but in alternative form they each may be built of a succession of cylindrical vessels of decreasing diameter as outlined at 6, 7, 8 and 9.

Cooling jackets 10 and 11 are provided for the refining section 1 and the recovery section 2, the coolant entering at 12 into the jacket 11, thereafter passing into jacket 10 via the bridging connection 13, and leaving jacket 10 at 14.

The helical scraping-conveyors are mounted on a shaft 17 supported by bearings 15 and 16, and articulated at 31, and provision is made to supply a small heat input to the shaft 17, the scraper-conveyor blades 4 and 5 and the spokes 18 to prevent crystal buildup on these unscrapped surfaces.

The discontinuity in diameter which marks the junction 19 of the recovery section 2 and the refining section 1 is designed for maximum performance to be adjacent to the feed inlet point 20. A liquid product is discharged at 21 at a relatively low temperature achieved in the operation of the equipment. Although as illustrated in the drawings the apparatus is for a liquid feed stock, feed stocks which are themselves crystalline

can be processed according to the invention. For a liquid feed as shown, the feed stock enters the apparatus at inlet point 20 on the recovery section. Should a crystal feed be used, the inlet point 20 would be located on the refining section 1, again just adjacent the refining section/recovery section junction 19.

The purifying section 3 is contiguous to and connected with the larger end of the refining section 1. A weir 22 which may be provided with means to adjust its height relative to the shaft 17 serves to retain in the refining section 1 a body of crystals which are slowly transferred to the purifying section 3 as the scraper-conveyor 5, rotating clockwise as shown in FIG. 2, raises the crystals to the edge of weir 22, over which they fall into the purifying section 3.

The purifying section is fitted with a slowly rotating stirrer 23 mounted on a shaft 24 supported in bearings 26 and 27 carrying blades 25 which are designed to prevent agglomeration of the crystal bed forming in the body of the purifying section 3 while minimizing turbulence and back-mixing. The insulated wall 28 incorporates heating means to provide a small heat input just sufficient to keep the wall temperature at each point above the melting point of the crystals accumulated adjacent thereto in effect compensating for the conduction of heat upward through the vessel wall toward the colder end 26 of the purifying section and offsetting heat losses through the outer insulation.

Similarly through the shaft 24 there are incorporated heating means to provide a small heat input to the shaft 24 and the blades 25 of the stirrer 23 for the same purpose.

One or more inspection ports 32 are an advantage in the purifying section construction.

Heating means 29 are provided at the base of the purifying section 3 to provide the heat of fusion for the melting of the mass of crystals which continuously reach the base of the purifying section. A portion of the molten material can be withdrawn through an outlet 30, the balance of the molten material being displaced upward through the purifying section 3 by the descending mass of crystals of higher specific gravity. The heat furnished by heating means 29 must be sufficient to melt the crystals adjacent thereto at the bottom of the purifying section and thus permit liquid product withdrawn through outlet 30 but must not be so great as to cause increase in the relative velocities of the descending crystals and/or the rising liquid reflux stream at any point in the purifier section.

This arrangement of the equipment operates in the following manner.

Coolant at an appropriate temperature and in appropriate quantity is caused to pass through the jacket system 12—11—13—10—14. The multicomponent feedstock enters the recovery section 2 at the point 20, and under equilibrium conditions it is preferred that the feedstock temperature be at the crystallizing point if liquid or for a crystal feed at the melting point, which temperature in either case should closely approximate the temperature of the solid-liquid mixture within the apparatus adjacent to the feed inlet point 20. This provision will prevent partial melting of the already-formed crystals and avoid shock cooling and excessive fine nucleation at the point of feedstock entry.

The feedstock will tend initially to pass toward the end 15 of the recovery section, and because of the temperature gradient will deposit an increasing amount of solid crystal which will be conveyed toward the refining section, leaving a reduced amount of liquid to pass to the discharge point 21.

There will be an optimal interrelation of the heat transfer, the liquid-solid ratio and the taper of the recovery section for each multicomponent system fed into such equipment.

The refining section 1 receives the crystal deposited in the recovery section 2 by reason of the rotation of the scraper-conveyor 4. The refining section also receives a liquid component of high purity returning from the purifying section 3 over the weir 22. The temperature gradient through the refining section from 19 to 16 causes the crystals being carried by the scraper-conveyor 5 to be subject to melting or partial melting; on the other hand, the same temperature gradient

causes the liquid component returning from the purifying section 3 over the weir 22 into the refining section 1 to be subject to crystallization.

In the end result, the temperature gradient of the refining section together with the reflux into the refining section from the purifying section combine to produce a quality gradient in the refining section.

It is further to be noted that the arrangement described whereby the coolant passes countercurrent to the liquid moving through the refining and recovery sections permits high thermal efficiency, and in practice is the opposite of most systems of the prior art.

The crystals lifted over the weir 22 by operation of the conveyor-scraper 5 fall by gravity through the purifying section 3 and the blades 25 of the stirrer give a slowly, falling unagglomerated crystal bed through the depth of the purifying section, the level of crystal bed being maintained just below weir 22.

For liquid-solid systems in which the solid is of lower specific gravity than the liquid, i.e., in which the solid floats in the liquid, it will be sufficient to make a few minor modifications in adapting the apparatus just described. The purifying section will rise above the refining section, the weirs will control a bed of crystals floating on liquid.

As an alternative to the end-to-end arrangement of refining and recovery sections, a cascade arrangement is shown in FIGS. 3 and 4. In this arrangement, the succession of three jacketed cylinders 1a, 1b and 1c of reducing diameters constitutes the refining section, and the succession of three jacketed cylinders 2a, 2b and 2c also of reducing diameters constitutes the recovery section. FIG. 4 represents a cross section in the plane of the line 4—4 of FIG. 3 showing the connection between the cylinders 1b and 1a. A scraper-conveyor 43 lifts crystals from the cylinder 1b over an adjustable weir 45, whence they fall downward into the cylinder 1a, to be conveyed by the scraper-conveyor 44 toward the purifying section 47. An inspection port 46 is provided.

The feedstock 48 inlet is placed in proximity to the junction of the refining section 1c and the recovery section 2a. The liquid discharge point 49 is provided at the end of the recovery section 2c. The direction of coolant flow is from the entry point at 50 in the direction marked by the arrow connecting the jacket elements to the discharge point at 51.

Equivalent provisions are made for small heat input to unscrapped surfaces, and to compensate for conduction losses in the purifying section, as have been described for the first arrangement illustrated in FIGS. 1 and 2. A small evenly distributed heat input may also be applied advantageously to the unscrapped surfaces of the passages between these cylinders.

A third arrangement is illustrated by reference to FIG. 5. A refining section 61, a recovery section 62 and a purifying section 63 are assembled in line on a vertical axis. The feedstock entry point is at 64, the liquid discharge point is at 66, and the melted solid product discharge is at 67, below the heating element 68.

Since the crystals deposited are conveyed from the recovery section through the refining section to the purifying section by gravity, a modified scraper system 69, 70 is provided to maintain heat transfer through the walls of the recovery and refining sections. To facilitate assembly a common shaft 71 driving the scrapers 69 and 70 and the agitator 73 is provided with articulating means at 72.

Coolant flow enters the recovery section jacket at 74, passes to the refining section jacket through the bridging connection 75, and is discharged at 76. Here again, separate control of coolant flow temperature to the jackets of the refining and recovery sections may be of advantage.

This vertical form of the equipment of this invention operates with a substantially continuous crystal bed extending from a level just above the heating element 68 in the purifying section upward through the refining section 61 and into the recovery section 62, the upper level of the crystal bed being a variable determined by variation of the heat input and heat

removals, the upper level of the crystal bed being maintained between the sight glasses or other level detecting devices associated with the inspection ports 77 and 78.

In the above described three arrangements of equipment, the crystal mass reaching the base of the purifying section is melted by heating means provided within the base of the purifying section to allow withdrawal of part of the melt as product.

While FIGS. 1, 3 and 5 as presented show recovery sections and refining sections of approximately equal length, in practice this relation will be varied. A feedstock rich in the desired higher melting component will in general require a shortened refining section and lengthened recovery section. A feedstock poor in that material will require a shortened recovery section and a lengthened refining section. A crystal feedstock may require a crystal-forming recovery section of minimum cross section. As the liquid component of the feedstock becomes weaker in the desired high melting component, the recovery section becomes shorter, until when said liquid component reaches eutectic composition the recovery section disappears to be replaced by some auxiliary crystal forming means. An important feature of the invention is that it can accept a feed of any concentration within the limits set by the phase diagram, in liquid, crystal or slurry form, and can make a complete separation within the same limits.

A variation applicable to any one of these three arrangements is illustrated by the block diagram of FIG. 6. From the base of the purifying section 80 crystal is withdrawn through a rotary valve or equivalent 81 and passes to a separating device 82 serving to separate crystal 83 from adhering liquid 84. The crystal mass is divided by a splitter 85 into crystal product 86 which is drawn off and a return fraction 87. The return fraction 87 passes to a heat exchanger 88 with heat input means 89 and is thereby melted. The resultant liquid, together with the liquid stream 84, passes by a return line 90 into the base of the purifying section where it is distributed by a ring jet or equivalent to become the reflux liquid stream passing up through the crystal mass in the purifying section in countercurrent.

EXAMPLE 1

An arrangement of the equipment of this invention in the form shown and described in relation to FIGS. 3 and 4 was used to prepare paradichlorobenzene from a feedstock consisting of mixed dichlorobenzenes containing 75 percent of the para isomer.

The feed was run in at a rate of 60 gallons per hour, and the reflux/product ratio was maintained at 0.5:1.

A tails product containing 75 percent orthodichlorobenzene was withdrawn at a rate of 20 gallons per hour (15 gallons DCB and 5 gallons p DCB).

A very pure paradichlorobenzene assaying 99.99 percent was withdrawn at a rate of 40 gallons per hour.

By application of the design principles described above temperature and quality gradients were established so that at no section of the unit was the liquid subjected to a cooling rate exceeding 3° C. per hour.

By adjustment of the weirs the retention time of crystals conveyed in the refining and recovery sections in countercurrent to the liquid was adjusted so that they increase in temperature at approximately the same rate of 3° C. per hour.

By this means crystals were produced of a size and quality such that a product rate of 35 gallons per hour per sq. ft. of gross purifying section cross section was consistently maintained when producing product of the stated purity at the stated reflux ratio, the average temperature and quality gradient in the purifying section being 0.6° C. per foot of height approximately. On an exponential basis the impurity content of the crystal stream was reduced by 50 percent for each foot of purifying section height.

On a theoretical basis the utility heat required to effect the above almost complete separation within the limits set by the

eutectic (15 percent paradichlorobenzene and 85 percent orthodichlorobenzene) is that required to provide latent heat to melt the product and the reflux, where a molten product is taken off, and that required to melt the reflux only where the product is taken off in crystal form and also in both cases the sensible heat to raise the product temperature from feed temperature to that of the melting point of product material. A practical low-temperature limitation in the coolant refrigeration apparatus alone prevented the complete removal of paradichlorobenzene down to the eutectic.

The heat removed by the coolant is the latent heat required to crystallize the product and the reflux, and to cool the outgoing cold end impurity stream from feed temperature to that of the outgoing stream.

Additional heat is required in practice to maintain the temperature of all internal and external unscrapped surfaces to be just above that of the crystallizing point of the adjacent liquor.

Extra cooling is required for the removal of this additional heat. Extra heating and cooling is also required to offset normal heat losses or gains through external insulation. In a unit of the capacity indicated an efficiency exceeding 50 percent of the theoretical basis described above was obtained.

Because of the extremely low speed of the scraper-conveyors in the refining and the recovery sections the power consumption in the apparatus is extremely low, the connected power being 1.5 hp. per million pound per annum of product including that required for the feed pump and the coolant circulating pump. This does not include power associated with the supply of refrigerant to cool the circulating coolant.

EXAMPLE 2

The plant employed in Example 1 was caused to operate under different rates of feed and product withdrawal.

	1.	2.
Feed rate	76 gal./hr.	95 gal./hr.
Product rate	54 gal./hr.	60 gal./hr.
Reflux ratio	0.25 to 1	0.25 to 1
Product set point	53.1° C.	53.0° C.
Product quality	99.6%	99.5%

The results indicated that quality was beginning to be sacrificed to give the throughput obtained. At the higher throughput the thermal efficiency, expressed as the ratio of the sensible heat and latent heat removed, including reflux heat, to the total heat removed exceeded 60 percent.

EXAMPLE 3

A preliminary experimental run was undertaken with the solid solution system paradibromobenzene - paradichlorobenzene, using a form of equipment with abbreviated recovery and refining sections. Under total reflux steady state conditions were obtained in eleven hours.

Sample analyses showed the paradibromobenzene content to be as follows at the sites indicated:

Feed end, refining section	64.4% wt.
Discharge end, refining section	71.4% wt.
Base, purifying section	97.6% wt.

The foregoing description is for illustrative purposes only and should not be construed in any limiting sense, it being intended to define the invention by the appended claims.

What is claimed is:

1. A process for separation of at least one component of a multicomponent mixture comprising:

- feeding the mixture into a solid-liquid continuous countercurrent purifier comprising in combination a recovery zone, a refining zone and a purifying zone, said recovery zone and refining zone each having decreasing cross-sectional areas in the direction of liquid flow;
- extracting heat continuously throughout the length of said recovery zone and refining zone to generate a con-

tinuous downward temperature gradient from the junction of the refining zone with the purifying zone to the end of the recovery zone remote from the purifying zone;

c. controlling the axial liquid phase velocity at any point in a direction opposite to the direction of crystal movement to generally exceed the liquid dispersion or back-mixing velocity in the opposite direction caused by agitator movement and changes in liquid density by employing in conjunction both the aforesaid variation of cross-sectional area available for crystal and liquid flow as the mass rate of flow of these streams vary along the temperature gradient and also the relationship of feed, reflux, and product withdrawal rates;

d. maintaining the bed of crystals in suspension in the liquid phase in each of said recovery, refining and purifying zones in a state intermediate between sedimentation and fluidization by control of speed of stirrer and conveying means and liquid flow velocity;

e. transporting the crystals formed in the recovery zone slowly through the refining zone to the purifying zone to maximize equilibrating contact of crystal with the countercurrent flow of liquid at all points;

f. maintaining a slow rate of temperature change of the crystal and liquid streams as they pass through the recovery and refining zones to produce a continuing increase in the size of crystals as they move along the upward temperature gradient towards the purifying zone, thus minimizing the reflux required for purification in that zone and the associated heating and cooling requirements;

g. withdrawing portion of the melted crystals produced by the heating element in the purifying zone as pure product, and passing the balance as liquid reflux through the purifying zone and in diminishing quantity through the refining and recovery zones, and withdrawing a mother liquor at the end of the recovery zone remote from the purifying zone.

2. A process according to claim 1 wherein the change in the multicomponent mixture between its crystalline solid state and its liquid state is a change from liquid state to crystalline solid state.

3. A process according to claim 1 wherein the change in the multicomponent mixture between its crystalline solid state and its liquid state is a change from crystalline solid state to liquid state.

4. The process according to claim 1 in combination with the step of adding selective heat inputs to the respective zones sufficient to prevent crystal agglomeration.

5. Apparatus for the separation, purification and recovery of a at least one selected component of a multicomponent mixture of materials, comprising, in combination,

- first enclosure means defining a recovery zone having increasing cross sectional areas from a first end to a second end,
- second enclosure means defining a refining zone having increasing cross sectional areas from a first end which communicates with the second end of the enclosure means defining said recovery zone to a second end,
- third enclosure means defining a purifying zone having a first end communicating with the second end of the enclosure defining said refining zone and a second end,
- stirrer means disposed substantially throughout the respective lengths of each of said enclosure means,
- heating element means in said third enclosure means disposed adjacent the second end thereof,
- inlet means for introducing a multicomponent mixture into the apparatus at a point adjacent the juncture of the second end of said first enclosure means and the first end of said second enclosure means,
- selected component outlet means at the second end of said third enclosure means,
- fluid outlet means at the first end of said first enclosure means,

- i. cooling means operably connected to said first and said second enclosure means adapted to provide a downward temperature gradient along the respective lengths thereof from each said respective second end thereof towards each said respective first end thereof, and
 - j. means for providing a heat input into said stirrer means sufficient to prevent crystal accumulation thereon.
6. Apparatus according to claim 5 wherein the stirrer means in the first enclosure means and the stirrer means in the second enclosure means are adapted to move crystals therein away from each of said respective first ends towards each of said respective second ends.
7. Apparatus according to claim 6 wherein the first enclosure means and the second enclosure means are arranged horizontally and the third enclosure means is arranged vertically.
8. Apparatus according to claim 7 which includes a crystal-movement-restraining weir at the internal junction between the second end of the second enclosure means and the first end of the third enclosure means.
9. Apparatus according to claim 7 which includes crystal-movement-restraining weirs at the internal junctions between each element of said first enclosure means and said second enclosure means.
10. A process in accordance with claim 1, wherein a small positive heat input is provided to all unscraped surfaces in said recovery and refining zones sufficient to prevent crystal buildup on said surfaces, and a small heat input to the stirrer and walls of the said purifying zone throughout its length in order at least to keep the temperature of said stirrer and walls just above the crystallizing point of the liquid immediately adjacent thereto.
11. A process for the separation of at least one component of a multicomponent mixture comprising:
- a. feeding the mixture into a solid-liquid continuous countercurrent purifier comprising in combination a recovery zone, a refining zone and a purifying zone, said recovery zone and refining zone each being disposed horizontally and having decreasing cross-sectional areas in the direction of liquid flow;
 - b. extracting heat continuously throughout the length of said recovery zone and refining zone to generate a continuous downward temperature gradient from the junction of the refining zone with the purifying zone to the end of the recovery zone remote from the purifying zone;

- c. controlling the axial liquid phase velocity at any point in a direction opposite to the direction of crystal movement to generally exceed the liquid dispersion or back-mixing velocity in the opposite direction caused by agitator movement and changes in liquid density by employing in conjunction both the aforesaid variation of cross-sectional area available for crystal and liquid flow as the mass rate of flow of these streams vary along the temperature gradient and also the relationship of feed, reflux, and product withdrawal rates;
 - d. maintaining the bed of crystals in suspension in the liquid phase in each of said recovery, refining and purifying zones in a state intermediate between sedimentation and fluidization by control of speed of stirrer and conveying means and liquid flow velocity;
 - e. defining the depth of the bed of crystals in suspension in the liquid phase in each of said recovery and refining zones;
 - f. transporting the crystals formed in the recovery zone slowly through the refining zone to the purifying zone to maximize equilibrating contact of crystal with the countercurrent flow of liquid at all points;
 - g. maintaining a slow rate of temperature change of the crystal and liquid streams as they pass through the recovery and refining zones to produce a continuing increase in the size of crystals as they move along the upward temperature gradient towards the purifying zone, thus minimizing the reflux required for purification in that zone and the associated heating and cooling requirements;
 - h. withdrawing portion of the melted crystals produced by the heating element in the purifying zone as pure product, and passing the balance as liquid reflux through the purifying zone and in diminishing quantity through the refining and recovery zones, and withdrawing a mother liquor at the end of the recovery zone remote from the purifying zone.
12. A process in accordance with claim 11, wherein a small positive heat input is provided to all unscraped surfaces in said recovery and refining zones sufficient to prevent crystal buildup on said surfaces, and a small heat input to the stirrer and walls of the said purifying zone throughout its length in order at least to keep the temperature of said stirrer and walls just above the crystallizing point of the liquid immediately adjacent thereto.

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