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54 Method of producing fine particles.

57 This invention relates to a method of reducing the particle size of solid particles and is applicable to the production of very fine particles of a wide variety of solids, including relatively hard solids.

The method comprises milling a liquid suspension of solid particles in an agitated media mill, pumping the milled suspension through a particle size classification device to separate the slurry into a coarse fraction and a fine fraction, the particles of the coarse fraction having a greater median particle size than the particles of the fine fraction, recycling the coarse fraction from the particle size classification device to the input of the mill, and recycling the fine fraction by pumping it to the classification device, wherein recycling of both coarse and fine fractions are continued until solid particles of the desired reduced particle size are produced.

Preferably a single classification device and a single mill can be used, and particles having a median particle size of 0.3 microns or less and a relatively narrow particle size distribution can be produced, even using a hydrocyclone as the classification device.

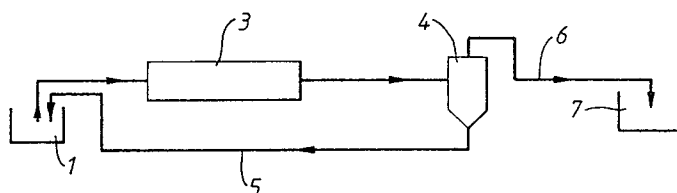


Fig.1.

Description**METHOD OF PRODUCING FINE PARTICLES**

This invention relates to a method of reducing the particle size of solid particles and is applicable to the production of very fine particles of a wide variety of solids, including relatively hard solids.

Very fine inorganic particles, of median particle size of 2 microns or less, are used for various purposes. One application of such particles is as a filler material for plastics compositions, for example in filled cable sheathing compounds. Use of fine powders can also accelerate reaction rates in chemical reactions involving a solid reagent and accelerate dissolution of the solid, metallic or ceramic powders of small particle size are used for processing into components, and some solid catalysts are more effective when of small particle size. In many applications a superior solid product, or superior process using the products may be obtained.

Reduction of solid particles, especially of hard materials, to micron and sub-micron size is generally achieved by means of an attrition mill, such as a bead mill, fed with a dispersion of the coarse particles in a liquid (usually water). The milled particles obtained usually have a wide particle size distribution and to obtain a reasonably uniform small particle size the particles obtained have to be classified.

The Applicants' EP-A-0253635 describes and claims alumina hydrate particles having a high surface area and a narrow particle size distribution, optionally with a low soluble soda content. Such finely divided particles are useful as fillers in paper, rubber and plastics compositions where, not only can they improve the mechanical and electrical properties of such compositions, but also can act both as a fire/flame retardant and as a smoke suppressant. Too wide a particle size distribution can have deleterious effects on filled polymer mechanical properties and residual soda can adversely affect the alumina hydrate's performance in many applications, particularly because of water pick-up.

In the course of developing the novel alumina hydrate particles of that invention, a process was used for producing the particles which appeared to have a very favourable effect on the breadth of the particle size distribution, and is described for this purpose in EP-A-0253635 as the preferred preparative method for such particles. Specifically, the preferred method of producing alumina hydrate particles comprises milling a liquid suspension of larger alumina hydrate particles in a stirred media mill, subjecting the milled suspension to continuous classification to separate the suspension into a coarse fraction of greater particle size and a fine fraction of smaller particle size, recycling the coarse fraction to the mill input and recycling the fine fraction to the continuous classification step, if required subjecting the milled suspension to ion exchange to reduce the content of the soluble soda in the particles, and subsequently drying the suspension.

Because of the particular morphology of the

coarse alumina hydrate particles used, it had been considered that this particular preparative method had applicability only to alumina hydrate particles and would not have the same beneficial effect on particle distribution width with other materials. As a result of further work, however, it has now been found that this preparative method does yield particles with a desirably narrow particle size distribution with a wide range of differing materials.

Furthermore, in EP-A-0253635, no particular classification system or device is described. It has now been realised that the preparative method of EP-A-0253635 is particularly suited to classification devices which have a low separation efficiency, particularly hydrocyclones.

Hydrocyclones are known for dividing a suspension of milled particles into a coarse fraction and a fine fraction, but it has not so far been possible to obtain satisfactory particle size separation for particles smaller than 2 or 3 microns in a single pass through the classifying device. It has been necessary to pass the suspension through a series of classifying devices, which results in an inefficient process having a very poor yield. Furthermore, conventional theory holds that hydrocyclones have little useful separating capacity for particles below about 4 microns, particularly using relatively high slurry loadings.

It has been found, surprisingly, that very efficient separation of particles having a median size of 2 microns or less from larger median size particles and a high overall yield may be obtained by the method of the present invention, which can require for its performance only a single mill and a single classification device, although more than one mill and/or classification device can be used if desired.

According to the present invention, there is provided a method of producing solid particles of reduced median particle size, other than alumina hydrate as claimed in EP-A-0253635, which comprises milling a liquid suspension of solid particles in an agitated media mill, pumping the milled suspension through a particle size classification device to separate the slurry into a coarse fraction and a fine fraction, the particles of the coarse fraction having a greater median particle size than the particles of the fine fraction, recycling the coarse fraction from the particle size classification device to the input of the mill, and recycling the fine fraction by pumping it to the classification device wherein recycling of both coarse and fine fractions are continued until solid particles of the desired reduced particle size are produced.

The agitated media mill may be of known type and may be a stirred media mill in which milling media, such as ceramic balls or rods typically of size 0.5 to 3.0 mm are agitated by means of a rotating shaft. The shaft may be provided with agitating discs. Alternatively the mill may be a vibro energy mill in which the milling medium is agitated by vigorous movement of the milling chamber. In all cases the milling medium

reduces the average particle size of the solid by attrition. The mill is preferably of a type allowing continuous operation, in which the slurry can be continuously fed into the mill, generally pumped into the mill under pressure, and continuously removed at one or more points.

The classification device used may be a continuous centrifugal device or a hydrocyclone which allow particle size classification of the solid suspended in the slurry. A suitable hydrocyclone typically has a maximum internal diameter up to 10 cm.

The concentration of solid in the slurry may vary widely and would normally be within the range of 50% to 65%, preferably 35% to 50% by weight. The preferred concentration generally depends on the use to which the milled slurry is to be put. A high concentration is not usually favourable when the slurry is to be dried to produce a dry solid. A viscosity modifier can be added if desired.

In one method according to the invention the milled suspension discharged from the mill and the fine fraction discharged from the classification device are both conducted to a receptacle for receiving the desired milled product and the contents of the receptacle are recycled to the input of the classification device by a pump intermediate the receptacle and the classification device. In this embodiment the suspension may be pumped from a container for the initial unmilled suspension, passed into the mill at a typical pressure of up to 20 psi, and discharged to the receptacle where it is not under pressure. When a hydrocyclone is used the pump intermediate the receptacle and hydrocyclone may feed the contents of the receptacle to the hydrocyclone at a typical pressure of 50 psi. The coarse fraction is discharged to the container for starting material, and the fine fraction discharged to the receptacle, at substantially zero gauge pressure. As the suspension is repeatedly recycled through the apparatus the median average size of the particles obtained in the receptacle is reduced, and the larger particles eliminated by attrition, so that after a certain time the suspension may have a substantially uniform particle size which is very small.

In another embodiment of the invention the suspension discharged from the mill is conducted, not to the final receptacle for the product, but to an intermediate reservoir, and the contents of the reservoir are pumped to the classification device, from which the coarse fraction is recycled to be passed again through the mill and the fine fraction is delivered to the receptacle. The fine fraction from the receptacle is brought, for example by pumping, to the reservoir so that the fine fraction is recycled through the classification device together with the suspension discharged by the mill. Control of the process of this embodiment is more complex than for the embodiment described above, but the efficiency of the process is greater as only the fine fraction from the classification device is discharged to the receptacle in which the desired suspension of finely divided product eventually accumulates.

In a further embodiment, instead of pumping the suspension to be treated through the mill under positive pressure the suspension is aspirated

through the mill by a pump arranged between the mill and the classification device, the pump feeding the milled suspension from the mill to the classification device under positive pressure. With this arrangement the pump can feed the milled suspension to a hydrocyclone at the desired relatively high pressure, typically about 50 psi, and the pressure difference across the mill may approach atmospheric pressure (about 15 psi) which may be sufficient to allow efficient operation of the mill. The coarse fraction from the classification device is again recycled to pass through the mill and the fine fraction, discharged to the receptacle, may be returned to the feed line for the classification device at a point between the mill and the pump, so that the pump aspirates the suspension from the receptacle also. With this arrangement only one pump is required to operate the process. In a variant of this embodiment, a further pump is provided to pump the fine fraction from the receptacle to the line feeding the classification device, the fine fraction from the receptacle being delivered to the classification device feed line at a point between the classification device and the pump feeding suspension from the mill to the device. In this variant the efficiency of the mill may be increased as the pump aspirating suspension through it does not have the additional function of aspirating the fine fraction from the receptacle.

The mill used in the method of the invention may be a bead mill of the known "Eiger" type, loaded with zirconia beads of diameter about 0.8 mm. The classification device may be a hydrocyclone of a known type, such as the "Mozley" hydrocyclone.

Methods of reducing the median particle size of particles according to particular embodiments of the invention will now be described with reference to the accompanying drawings in which:

Figure 1 is a flow diagram showing a method according to the prior art,

Figures 2-5 are flow diagrams of methods according to the invention,

Figure 6 is a diagram of a bead mill which may be used in the invention.

In the prior art arrangement of Figure 1 a liquid slurry of particles to be treated is fed from a container 1 to a bead mill 3 which grinds the slurry and discharges the ground slurry to hydrocyclone 4 which separates it into a coarse and a fine fraction. The coarse fraction is returned through line 5 to container 1 for recycling through the mill and hydrocyclone and the fine fraction is delivered through line 6 to receptacle 7.

It is found that the method of Figure 1 is incapable of producing a fine fraction having a very low average particle size, as the slurry delivered to receptacle 7 still has a high proportion of relatively coarse particles. When a slurry of solid particles is treated with this arrangement it has not been found possible to obtain a fine fraction of median particle having a size of 2 microns or less.

In the arrangement of Figure 2, the slurry containing the solid particles is fed from container 11 to pump 12 which delivers the slurry at a pressure of up to 20 psi to the input of bead mill 13, which is of

the type described below with reference to Figure 6. The slurry is ground in the mill and discharged to receptacle 14.

The slurry in receptacle 14 is then fed to pump 15 which feeds it at a pressure of about 50 psi to hydrocyclone 16, which separates the slurry into a coarse fraction which is returned by line 17 to container 11, and a fine fraction which is sent by line 18 to the receptacle 14.

When the embodiment of Figure 2 is used, a batch of slurry is supplied, one half to container 11 and the other half to receptacle 14, and the pumps, mill and hydrocyclone are run until the median particle size of the product batch which accumulates in receptacle 14 has the desired value.

The method described with reference to Figure 2 allows the mill to be operated under favourable grinding conditions, that is with a slurry having a relatively high solids content (up to 65% by weight) and a high flow rate. The slurry is fed to the mill under positive pressure. The rate of flow is easily adjusted by adjusting the rate of operation of pump 12 so that the rate of flow of the slurry through the mill is matched to the requirements of the hydrocyclone. Pump 15 may be used simply to maintain the feed pressure for hydrocyclone 16; thus the method is simply controlled by adjusting pump 12 according to the respective levels of the slurry in container 11 and in receptacle 14. When operated with an aqueous slurry of a solid particles the method is capable of yielding particles of a median particle size of 0.3 microns or less, using only one mill and only one hydrocyclone.

The method illustrated by Figure 3 is similar to that of Figure 2 and common components are shown by the same reference numerals. Pump 12, mill 13, pump 15, and hydrocyclone 16 operate in the same way as in Figure 2 and the coarse fraction from the hydrocyclone is again recycled to container 11 through line 17, the fine fraction being delivered to receptacle 14 through line 18. However in this arrangement the output of slurry from the mill 13 is fed not to receptacle 14, but to a reservoir 20 from which it is fed by pump 15 to the hydrocyclone 16, and a further pump 21 returns the fine fraction from receptacle 14 to reservoir 20.

This arrangement is more complex than that of Figure 2 in that an extra container (reservoir 20) is required and an extra pump (21) is needed to transfer the fine fraction from receptacle 14 to the reservoir 20. However the efficiency of this embodiment is rather greater as the coarse fraction from the mill 13 is fed to the hydrocyclone 16 without passing through the receptacle 14 which receives the fine fraction.

Figure 4 shows an arrangement in which only one pump is required. In this case the slurry from container 11 is again fed to bead mill 13 and passes from the mill 13 to hydrocyclone 16 which divides it into a coarse fraction which is returned to container 11 through line 17 and a fine fraction which is sent through line 18 to receptacle 14. However in this case a single pump 20 both delivers the slurry to the hydrocyclone 16 at a pressure of about 50 psi and draws the slurry through mill 13 by suction. The

pressure difference urging the slurry through mill 13 is thus generated by aspiration by pump 20 and it may correspond substantially to atmospheric pressure, that is about 15 psi. If a higher input pressure for the mill 13 is required, container 11 may be a closed tank and the tank may be pressurised. In this arrangement the slurry discharged to receptacle 14 is recycled through line 21 to a point between mill 13 and pump 20, and the slurry is drawn through line 21 by the aspiration of the pump 20. A valve 22 is inserted in line 21 to control the rate of recycling of the slurry from receptacle 14 and the process is controlled by adjustment of pump 20 and valve 22 as required.

Figure 5 shows a variant of the process of Figure 4. In this variant the slurry is again aspirated through mill 13 and fed to hydrocyclone 16 by pump 20, the coarse fraction is again recycled through line 17 and the fine fraction of the slurry is recycled from receptacle 14 to the hydrocyclone 16. However in this instance line 21 returns the fine fraction to a point between the pump 20 and the hydrocyclone 16 and is impelled by a further pump 23 provided in line 21. Pump 23 delivers the recycled fine fraction to the hydrocyclone 16 at a pressure of about 50 psi and the process is controlled by adjusting both pumps 20 and 23. This variant allows pump 20 to aspirate slurry from container 11 through mill 13 more efficiently.

In all the arrangements of Figures 3, 4 and 5 all the material present in receptacle 14 has been passed through the hydrocyclone at least once, and in practice often many hundreds of times, thereby increasing the overall efficiency of the process. When starting up, the suspension to be treated is generally divided up equally between the various containers and receptacles.

One type of attrition mill which may be used is the "Eiger" bead mill shown diagrammatically in Figure 6. The mill comprises a tubular vessel 31 containing an agitator 32 comprising paddles extending radially from a shaft which is driven in rotation by motor 33. The vessel contains a screen 34 to prevent discharge of gross oversize particles from the mill and the vessel contains, around agitator 32, beads of hard material which grind the liquid suspension. The suspension is fed into the mill at inlet 35, the suspension passes through the mill and is discharged at 36 after passing through the screen 34.

It has been found, surprisingly, that when a slurry is milled and classified by the methods described above the classification device can yield a fine fraction of narrow particle size distribution down to a very small average particle size, down to 0.4 microns or even lower. With hitherto known milling and classifying methods, a hydrocyclone classifying device does not produce any useful separation of particle size fractions at particle sizes as small as this.

The invention may be applied to a very wide variety of solids which may be slurried with a wide range of liquids. Solids which may be milled include iron oxide, talc, silica and other minerals like chalk, zinc oxide, boric oxide, borax, zinc borate, pigments, carbon black, various metals, solid organic com-

pounds, e.g. terephthalic acid, and mixtures thereof. The liquid may be chosen from water, volatile non-aqueous liquids such as hydrocarbons, tetrahydrofuran, dioxan, alcohols and esters, and non-volatile solvents such as phthalates, polyvinylchloride plastisols and waxes. Non-volatile liquids may be used when the slurry is to be used subsequently in liquid form, without drying, for example as plastisols or in certain pharmaceutical preparations. The slurry may include one or more additives to aid milling, such as a dispersant, or to assist later processing, for example a stearate which forms a coating on the particles.

Possible applications for the milled solid include ceramics, catalysts, plastics fillers, fire/flame retardants, smoke suppressants and powder metallurgy.

In the methods mentioned above the classification device may be operated continuously or it may be operated intermittently to give quasi-continuous operation, so as to balance the flow of coarse fraction from the classification device with the mill input. The overall process is generally operated as a batch process, i.e. with 100% recycle of both coarse and fine particle fractions since generally the efficiency of the separation device is too low for continuous operation to yield particles of the desired average particle size and breadth of particle size distribution.

The method of the invention may be operated at a range of temperatures according to the nature of the solid and/or liquid being processed. An operating temperature down to -20°C is generally feasible.

Example 1

49.5 kg of zinc borate (crystalline form 2335) available from U.S. Borax were dispersed into 150 litres of water. This material had a median particle size of 6 microns. It was processed in accordance with the preferred process of this invention as shown diagrammatically in Fig. 2 for three hours. The grinding device was a 20 litre capacity "Eiger" bead mill and the classification device was a "Mozley" hydrocyclone of 2 inch (5.08 cm) nominal diameter.

After three hours the product taken from receptacle 14 was then analysed using the "Malvern" laser photon correlating spectrometer and was found to have a median particle size of 0.28 microns and a polydispersity of 0.23. Polydispersity is a measure of the narrowness of a particle size distribution and is represented by the magnitude:

$$-\frac{1}{2} \left(\frac{\ln(d) - \ln(d_{50n})}{\sigma} \right)^2$$

wherein

$\ln$ = natural logarithm

$$f(d) = N \cdot \frac{1}{\sqrt{2\pi} \cdot \sigma \cdot d} \cdot e$$

d_{50n} = number median particle size

N = number of particles

σ = width parameter, that is the log standard deviation

$$\frac{d_{84}}{d_{50}} \quad \text{or} \quad \frac{d_{50}}{d_{16}}$$

of the particle size

Further information about polydispersity can be found in the reference "The Coulter Nano-Sizer" published by Coulter Electronics Limited in January 1980.

Example 2

50 kg of terephthalic acid available from ICI were dispersed into 100 litres of water and milled as Example 1 above for a total of 15 hours. In order to maintain a working viscosity during grinding a further 400 litres of water were added at intervals during the 15 hours together with 2 litres of "Teepol" surfactant available from Shell. The feed material prior to grinding had a specific surface area of 0.18 m²/g as determined by the standard Strohlein method as described in "Particle Size Measurement", p. 390, Terence Allen, Chapman and Hall Ltd. 1975, a median particle size of 83 microns as determined by Coulter counter, and a particle size mode of 90 microns as determined by Coulter counter. After completion of grinding the product taken from receptacle 14 had a surface area of 3.9 m²/g, a median particle size of less than 1.2 microns, and particle size mode of 1.1 microns as evaluated by the same methods.

Claims

1. A method of producing solid particles of reduced median particle size, other than alumina hydrate as claimed in EP-A-0253635, which comprises milling a liquid suspension of solid particles in an agitated media mill, pumping the milled suspension through a particle size classification device to separate the slurry into a coarse fraction and a fine fraction, the particles of the coarse fraction having a greater median particle size than the particles of the fine fraction, recycling the coarse fraction from the particle size classification device to the input of the mill, and recycling the fine fraction by pumping it to the classification device,

wherein recycling of both coarse and fine fractions are continued until solid particles of the desired reduced particle size are produced.

2. A method according to claim 1, in which the particle size classification device comprises a hydrocyclone. 5

3. A method according to claim 1 or 2, in which the milled suspension and fine fraction are pumped continuously to the particle size classification device. 10

4. A method according to claim 1 or 2, in which the milled suspension and fine fraction are pumped to the particle size classification device for intermittent periods such that over a period of time the flow from the coarse fraction of the classification device balances the flow through the mill. 15

5. A method according to any preceding claim, in which the milled suspension discharged from the mill and the fine fraction discharged from the classification device are both conducted to a receptacle and the contents of the receptacle are pumped to the inlet of the classification device. 20

6. A method according to any one of claims 1 to 4, in which the milled suspension discharged from the mill is conducted to a reservoir, the fine fraction discharged by the classification device is conducted to a receptacle, the contents of the receptacle are conducted to a reservoir, and the contents of the reservoir are pumped to the input of the classification device. 25

7. A method according to any one of claims 1 to 4, in which the milled suspension discharged from the mill is pumped to the classification device by a pump intermediate the mill and the classification device, the suspension is aspirated through the mill by said pump, the fine fraction discharged by the classification device is conducted to a receptacle and the contents of the receptacle are aspirated to a point intermediate the mill and the pump to be recycled through the classification device. 30

8. A method according to any one of claims 1 to 4, in which the milled suspension discharged from the mill is pumped to the classification device by a first pump intermediate the mill and the classification device, the suspension is aspirated through the mill by the first pump, the fine fraction discharged by the classification device is conducted to a receptacle and the contents of the receptacle are pumped by a second pump to a point intermediate the first pump and the classification device to be recycled therethrough. 40

9. A method according to any preceding claim, in which the slurry contains from 5 to 65% by weight of solid. 45

10. A method according to claim 9, in which the slurry contains from 35 to 50% by weight of solid. 50

11. A method as claimed in any preceding claim, in which a single classification device is used. 55

12. A method as claimed in any preceding 60

claim, in which a single mill is used.

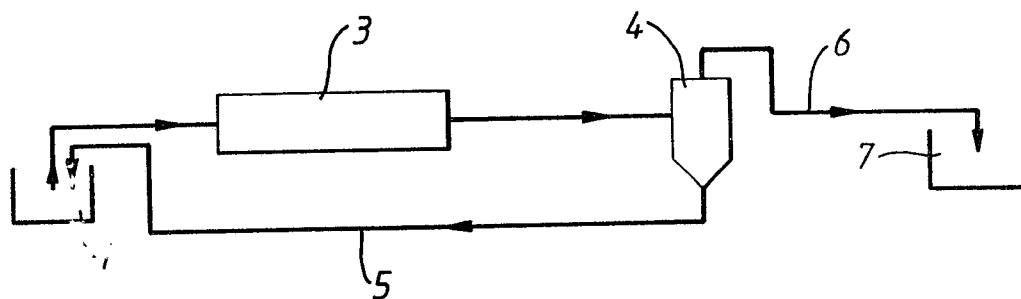


FIG. 1.

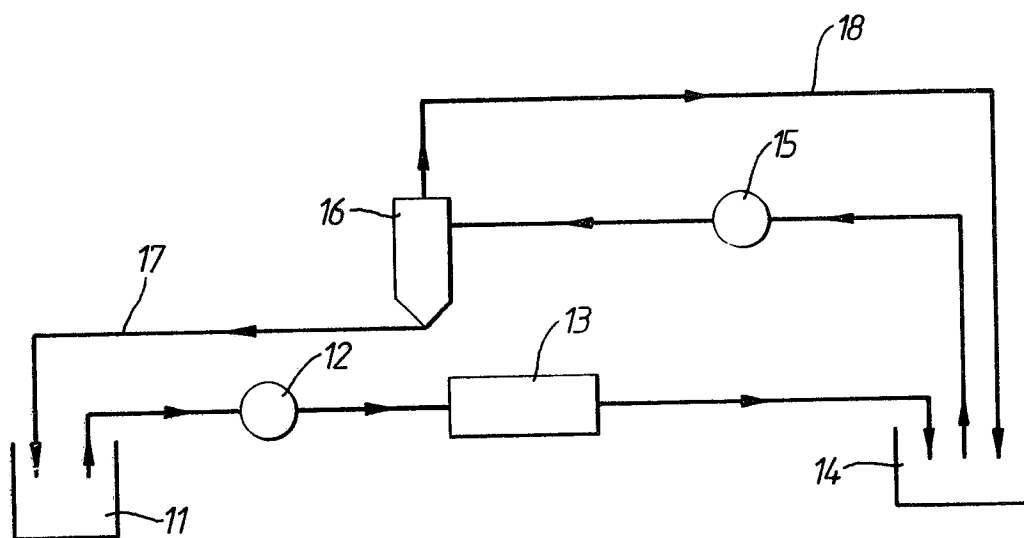
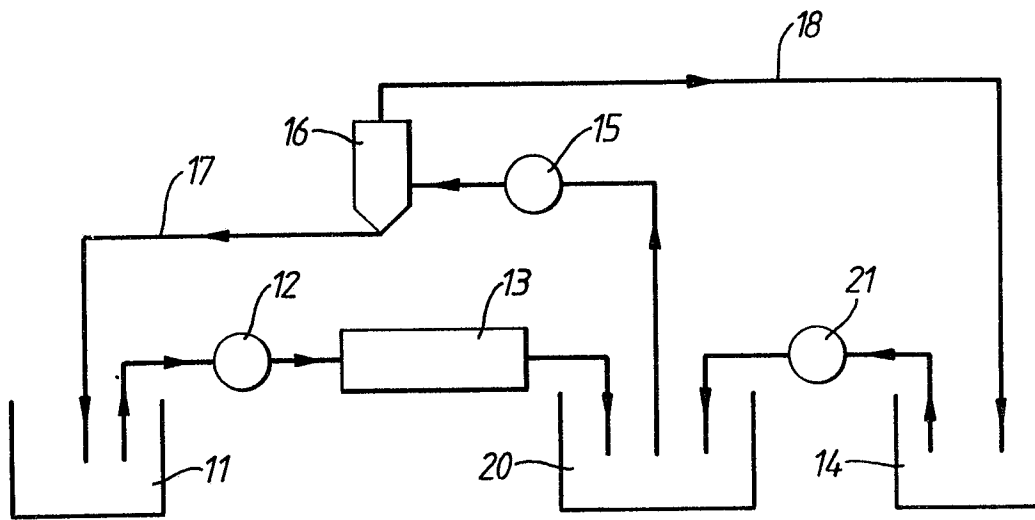
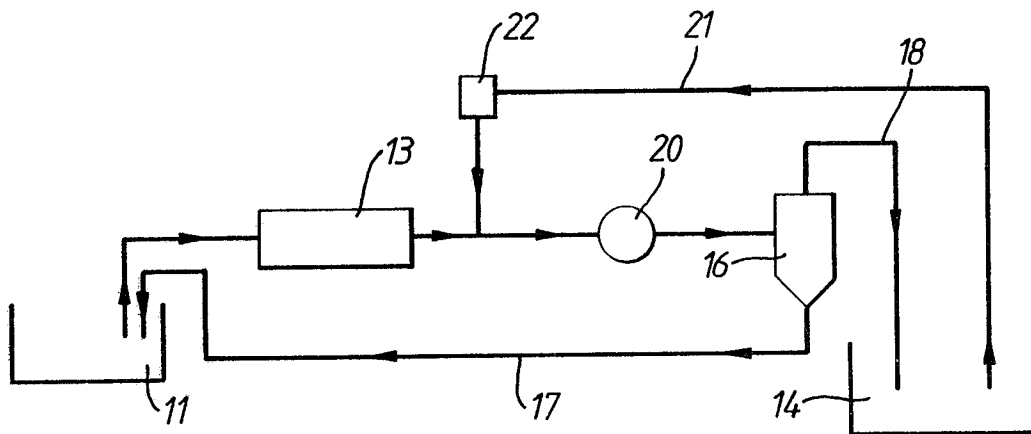
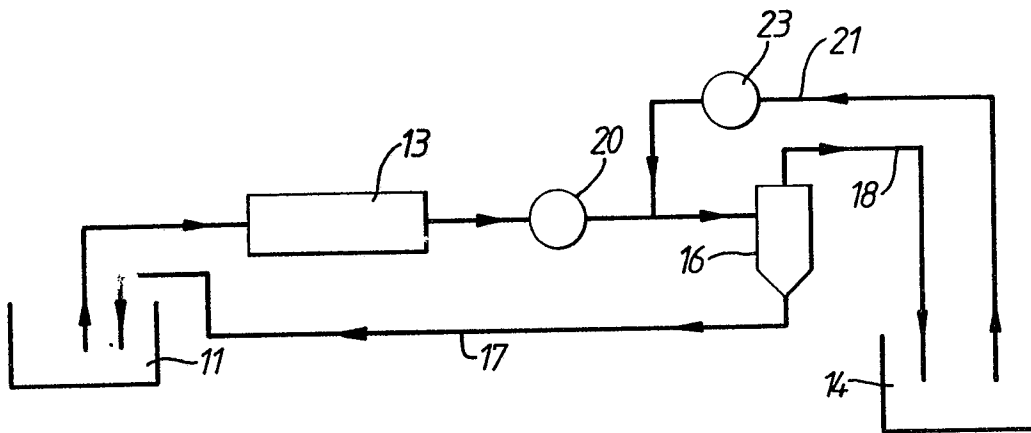
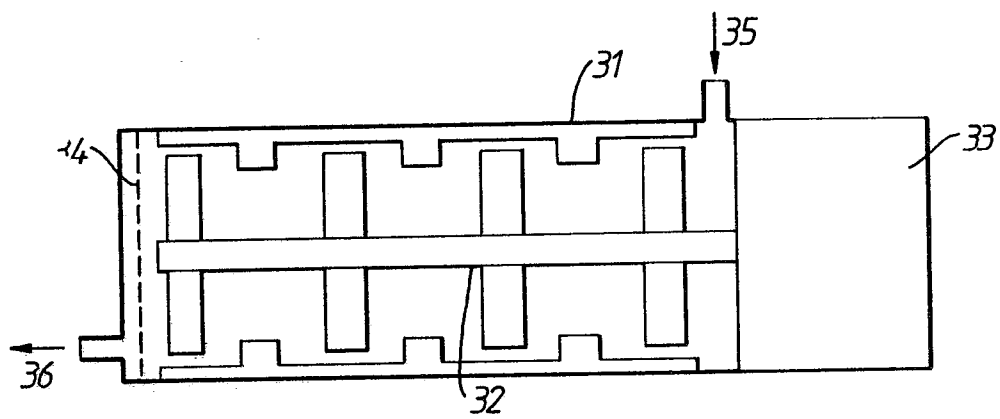


FIG. 2.

*FIG. 3.**FIG. 4.*

*FIG. 5.**FIG. 6.*