

Nov. 14, 1967

H. H. MOLLS ET AL
APPARATUS FOR THE PRODUCTION OF AQUEOUS DISPERSIONS
OF SOLIDS INSOLUBLE IN WATER

3,352,500

Filed Oct. 7, 1964

2 Sheets-Sheet 1

FIG. 1

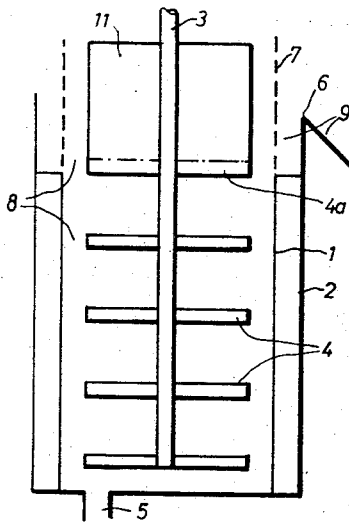


FIG. 2

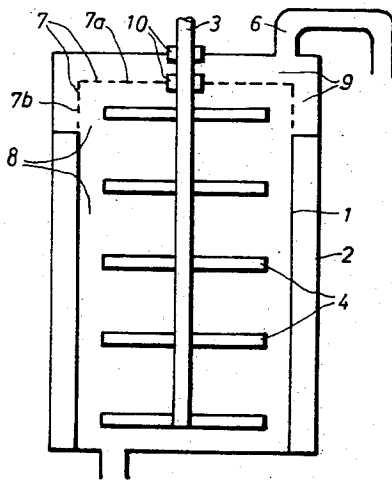
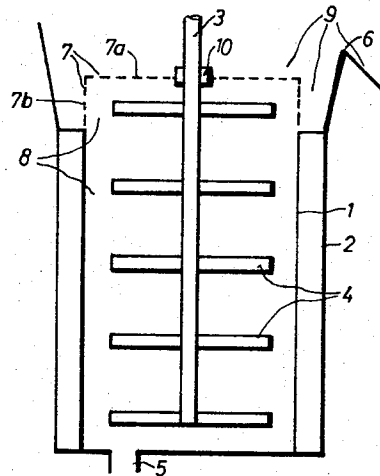


FIG. 3

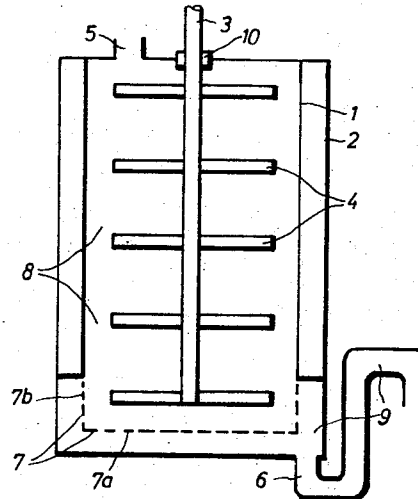


FIG. 4

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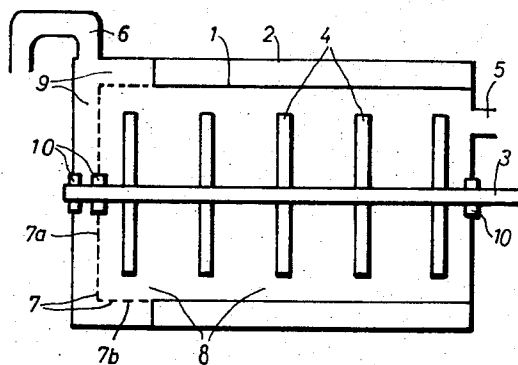


FIG. 5

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A T T O R N E Y

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APPARATUS FOR THE PRODUCTION OF AQUEOUS DISPERSIONS OF SOLIDS INSOLUBLE IN WATER

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Filed Oct. 7, 1964, Ser. No. 402,213

1 Claim. (Cl. 241—74)

It is known that solids, for instance dyestuffs, can be finely subdivided in an aqueous or organic medium by means of agitated rounded grinding elements of quartz, glass, ceramics, metals or plastics, optionally in the presence of dispersing agents (cf. for instance Swiss patent specification No. 132,086; German patent specifications Nos. 619,662 and 915,408 and German published specification No. 1,109,988; Belgian patent specification No. 588,161, British patent specification No. 909,609 and U.S. patent specifications Nos. 2,212,641, 2,361,059 and 2,581,414). The efficiency of a process of this type depends on the kind and intensity of the agitation imparted to the grinding elements, on the relation between the volume of the grinding elements and that of the suspension, on the concentration of the solid in the suspension and on the type and amount of the added tensides (surface active agents). The selection of a suitable dimension for the grinding elements largely depends on the initial particle size of the grinding stock.

Solids, for instance dyestuffs, have already been finely subdivided according to the process of U.S. patent specification No. 1,837,772 by stirring the solids in an aqueous or non-aqueous medium, in the presence of a dispersing agent, with solid grinding elements in an open vessel. Anion active dispersing agents such as the sodium salt of dinaphthylmethane-2,2'-disulphonic acid, the sodium salt of sulphite cellulose and its oxidation product, as well as amidated sulphite cellulose and sodium benzylsulphonate have already been employed as the dispersing agents. Compact insoluble powders which are harder than the material to be finely subdivided or dispersed are recommended as the grinding elements, for instance iron powder, zinc powder, copper powder or sand with a maximum particle size of 0.125 mm.

The last mentioned process has not been adopted in practice, and neither have the previously cited processes except that of U.S. patent specification No. 2,581,414, because no appreciable advantages in respect of the fine subdivision of the grinding stocks were evident in comparison with the customary methods of subdivision (for instance without solid insoluble auxiliary grinding elements) in the usual ball mills with grinding elements of a comparable size. The above mentioned processes also do not offer any improvement in respect of a saving in effort (time requirement). The application of the only process adopted in practice (U.S. patent specification No. 2,581,414) is limited to the preparation of dispersed pigments in non-aqueous film forming media. Aqueous pigment pastes, such as are for instance obtained during the manufacture of pigment dyestuffs, cannot be processed according to the process of this patent in order to form finely dispersed dyestuffs.

In all known grinding devices with small grinding elements, the agitation of the grinding mixture leads to the formation of turbulent currents at the interface between the air (or gas) and the dispersion of the grinding stock or the grinding mixture, so that air (or gas) is aspired into the grinding mixture. This circumstance exerts a particularly unfavourable effect on the grinding action or on the dispersion of solids insoluble in water when use is made of those dispersing agents which exhibit a stronger

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tendency towards the formation of foam. Strong formation of foam takes place in particular during grinding with small grinding elements under these conditions, and owing to the resultant air cushion effect the mobility of these small grinding elements is impeded, so as to cause a decrease of the grinding action down to a technically useless value and frequently so as to cause difficulties during the separation of the grinding stock from the grinding elements; flotation of the grinding elements is also often experienced during this operation.

A large number of dispersing agents which exhibit a particularly good dispersing action unfortunately have a tendency to form the kind of foam described above. Such dispersing agents may already have originated from the process for the production of the solids or their presence may also be generally desirable in order to achieve a fine dispersing action by means of suitable devices. Therefore, technologists do not in practice like to dispense with the application of such agents, and as a consequence a large number of devices for the fine subdivision of pigments have not been successfully adopted for this reason alone.

The dispersing devices of U.S. patent specification No. 2,581,414 and of German published specification No. 1,109,988 intended for non-aqueous dispersion are also unsuitable for processing dispersions containing substances which promote strong foaming; they aspire air on the top side of the uppermost disc or of the uppermost ring as well as on the vertical sieve, and this air passes through the whole grinding system within a short time so as to cause appreciable foaming. The reduced separation at the sieve basket and the flotation of the grinding elements causes the foam-charged grinding mixture to spill over the upper edge of the sieve.

Processes and devices for the dispersion in an aqueous medium of organic and inorganic solids insoluble in water have now been found which do not exhibit the disadvantages known to occur during processing in an aqueous medium by means of the devices known as "sand mills" and comparable appliances, and these permit the attainment of optimum results even when strongly foam-forming dispersing agents are applied. The novel process utilises a number of known factors, by agitating an organic or inorganic solid insoluble in water in an aqueous medium with a dispersing agent and a material containing silicon dioxide groups whose specific gravity is greater than 1.5 and which is harder than the product to be dispersed; it is characterised in particular in that rounded elements whose radii do not differ by more than $\pm 40\%$ from the mean radius, which have a smooth surface, whose diameters are from 0.3 to 1.5 mm. and where the particle diameter does not differ by more than 0.5 mm. from the mean value are employed as the material containing silicon dioxide groups, in a proportion of 10 to 300% of the solid volume, referred to the volume of the dispersion of the grinding stock; in that non-ionic, anionic, cationic or betaine-type dispersing agents are employed in a proportion of 0.1 to 200% by weight, referred to the weight of the solid to be dispersed, optionally in conjunction with defoaming agents; and in that the agitation of the grinding mixture is continued until the particle size of the grinding stock is 6μ or preferably less; in the case where use is made of those dispersing agents which increase the volume of the grinding stock during the grinding operation by more than 20%, and in particular by more than 50%, as a consequence of their capacity for the formation of foam, the grinding operation is carried out in an arrangement of apparatus such that no appreciable air (or gas) aspiring currents can possibly be formed at the interface between the air (or gas) and the dispersion of the grinding stock or the grinding mixture.

The terms "grinding stock," "dispersion of the grinding stock," "grinding elements" and "grinding mixture" are

here employed in accordance with the following definitions: the "grinding stock" is the solid to be dispersed; the "dispersion of the grinding stock" is the aqueous dispersion of the grinding stock which may optionally contain dispersing agents; the "grinding elements" are the rounded elements containing silicon dioxide groups; and the "grinding mixture" is the mixture of the dispersion of the grinding stock with the grinding elements.

The agitation of the grinding mixture during the process according to the invention is effected so that the highest possible velocity gradient exists between the grinding elements without causing the grinding elements to become squashed at any point in the grinding mixture. It should not be possible for the grinding stock to escape from the action of the grinding elements within the grinding device.

By way of grinding appliances which cause an air aspirating turbulence at the surface of the grinding stock or grinding mixture, falling, tumbling and turbine mixers may be employed, such as have for instance been listed in Ullmann: "Encyclopädie der technischen Chemie" (Urban und Schwarzenberg Verlag, Munich-Berlin), 3rd edition, volume I (to be referred to as Ullmann I hereafter) on pages 714-715. In addition, stirrer mixers have been employed, where suitable mixing elements at a low number of revolutions (at circumferential speeds of 1-4 m./sec.) are for instance those specified in Ullmann I on page 707. Owing to the risk of abrasion and the possibility that the grinding elements may be destroyed, only stirrers with plane crossed blades, stirrers with a streamline cross section, stirrer screws and also stirrers with one or several flat or conical compact or perforated circular discs or rings connected to the shaft by spokes are suitable at circumferential speeds greater than 4 m./sec.; the circular discs or rings should be attached vertically to the stirrer shaft and the shaft should pass through their centre. In the case where several mixing elements are employed, they should be spaced at a distance of roughly between their half and their full radii in their attachment to the stirrer shaft. The circumferential speeds should be between 4 and 20 m./sec., preferably between 7 and 13 m./sec. In addition, oscillatory mixers operating at moderate frequencies (Ullmann I, p. 722) and vibrating mills operating at high frequencies such as have for instance been specified in Ullmann I on page 725 are also suitable.

Moreover, the agitation of the grinding mixture can be effected by means of a vibro mixer with the use of one stirrer plate or of several stirrer plates arranged on top of each other as the mixing elements (Ullmann I, p. 702) at frequencies of 50-100 cycles/sec. and an amplitude of preferably 2-3 mm. The diameter of the conical apertures at the narrowest point in the stirrer plates should amount to between 4 and 16 times the mean diameter of the grinding elements. In the case where several stirrer plates are employed, these should be spaced at a distance of roughly between their quarter and their full radii in their attachment to the shaft.

When grinding devices of this type are operated discontinuously, the aspiration of gas or air at the interface between the grinding mixture or grinding stock and the gas or air can sometimes be prevented by carrying out the grinding operation at a reduced pressure of preferably less than 200 mm. Hg.

The formation of foam may also be eliminated during a discontinuous operation by carrying out the process in sealed vessels which are completely filled with the grinding mixture, although this form of execution can only be applied when there is no appreciable resultant deterioration of the grinding action.

The arrangement of apparatus in machines with a continuous operation is such that no appreciable turbulent current of air (or gas) aspiration can occur at the interface between the air (or gas) and the dispersion of the grinding stock or the grinding mixture.

The machines with a continuous operation do not differ from the appliances with a discontinuous operation which have already been mentioned above in respect of their

grinding devices. However, since their operation is continuous, they have an inlet and outlet for the grinding stock. The risk of a formation of foam mainly exists at the side where the grinding stock is discharged from the machine.

A sieve adapted to the required rate of throughput of the grinding stock and to the dimensions of the grinding elements has to be fitted in front of the discharge outlet in order to retain the grinding elements. The prevention of a turbulent current of aspired air or gas can be effected in front of or beyond the sieve, when the constructions represented diagrammatically in FIGURES 1-5 are preferably employed.

In FIGURES 1-5, 1 represents a cylindrical grinding vessel surrounded by a cooling or heating jacket 2; a shaft 3 carrying the mixing elements 4, which have in the given case been drawn in the form of discs, extends concentrically into the grinding vessel. The grinding vessel is provided with an inlet 5 for the coarse dispersion which has to be ground, this being connected to a liquid pump and optionally provided with a device for preventing the backflow of the grinding mixture. The discharge outlet 6, which is an overflow in the case of FIG. 1 and FIG. 2, is provided beyond a sieve 7, in relation to the position of the grinding mixture, and this is preferably adjoining the free side of the grinding vessel. The design of the sieve 7 in FIGURES 2-5 may also be modified in that the part of the sieve which is either perpendicular 7a to the shaft 3 or parallel 7b with it is replaced by a compact surface when in the second case the cooling jacket 2 is raised up to the level of the sieve 7a. The mesh width of the sieve has to be selected so that the smallest employed grinding elements are just prevented from passing through it.

The inner surfaces of the grinding vessel 1 and of the sieve 7 enclose the grinding space 8, although the construction according to FIG. 1 constitutes an exception in that the horizontal plane extending from the upper edge of the overflow represents the upper limit of the grinding space in this non-enclosed system. The grinding space is completely filled with the grinding mixture when the dispersion of the solid which has to be ground is pumped through it. The grinding space and where required the external surfaces are sealed by means of seals 10 at the locations where the shaft 3 penetrates through them, and these may also act as bearings. The seal 10 may for instance be of rubber, metal, graphite, plastics or sealing liquid, and in the last case the dispersion of the grinding stock rising above the upper surface of the sieve 7a may also act as the seal, as may the grinding mixture itself in a suitable construction, for instance if a sieve or pipe is passed round the shaft.

The grinding mixture is agitated by stirring (rotation) or by vibration. When the agitation is effected by stirring, the grinding space contains 30 to 70, and preferably 40 to 60, percent of the solid volume of the grinding elements in relation to the free volume; in that case, the stirrer mixers mentioned in column 3 are employed as the mixing elements, when the distance between the mixing element and the grinding vessel in each case depends on the diameter of the grinding elements and should amount to between 3 and 30 times the diameter of the grinding elements.

The aspiration of air or gas into the grinding mixture at the interface between the grinding mixture or the dispersion of the grinding stock and the air or gas 9 which occurs to an extremely marked extent in the normal constructions of high speed stirred ball mills with circular discs or rings on spokes is prevented in the case of the form of execution according to FIG. 1 by replacing the uppermost stirrer element 4a by a compact cylinder 11 whose radius is of about the same magnitude and by placing the overflow 6 for the dispersion of the grinding stock at an appreciably higher level than the lower side of the sieve 7. The lower surface of the cylinder 11

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should be at the level of the lower edge of the sieve 7 or below it; the upper surface of the cylinder 11 should extend above the upper edge of the overflow 6.

In the case of the form of execution according to FIG. 2, only the dispersion of the grinding stock passing through the sieve 7 or 7a or 7b sealed on the shaft or closely adjoining the shaft comes into contact with the surrounding gas. The rate of discharge of the dispersion of the grinding stock is selected so that the turbulence transmitted to it by the stirring operation has been damped to the extent that an aspiration of gas will have been eliminated. The upper edge of the overflow 6 is preferably at least 3 cm. above the upper extremity of the sieve. This type of execution is especially suitable for viscous dispersions of the grinding stock.

In the case of the forms of execution according to FIGURES 3 to 5, the air or gas aspiring turbulence of the grinding mixture is eliminated by limiting the extent of the interface between the dispersion of the grinding stock 9 and the air or gas to the interfacial area at the discharge outlet; moreover, the flow of the dispersion of the grinding stock counteracts the aspiration of gas or air.

When the agitation is effected by vibration, the grinding space contains 10 to 50, and preferably 15 to 40% of the solid volume of the grinding elements, and use is made of the stirrer plates normally encountered in vibro mixers, where the discs 4 should be fitted so that the narrow ends of the conical apertures point towards the charge inlet, i.e. their effect opposes the direction of the throughput. The distance between the mixing elements and the grinding vessel once again depends on the diameter of the grinding elements in each case and generally amounts to between 3 and 10 times the diameter of the grinding elements.

The following may inter alia be mentioned as materials containing silicon dioxide suitable as the grinding elements: quartz, for instance any type of sand which satisfies the above criteria in respect of dimensions and shape such as Ottawa sand, and also glass and ceramic masses provided that their surface is not porous, such as porcelain and steatite, and other sintered metal silicates insoluble in water such as aluminum silicate.

The diameter of the coarse fraction of the solids to be dispersed should not in general exceed 30% of the mean diameter of the grinding agents and it should preferably be less than 10% of the mean diameter. The following may be mentioned, inter alia, as solids insoluble or barely soluble in water which can be dispersed: inorganic solids such as flowers of sulphur, red phosphorus, kaolins and other soft silicates, inorganic catalysts such as vanadium pentoxide and manganese dioxide, inorganic pigments such as iron oxides, titanium dioxide and cadmium sulphides, organic compounds such as intermediate products insoluble in water before or during a reaction, in particular coupling components for the preparation of azo dyestuffs insoluble in water, organic pest control agents and plant protection agents, organic pharmaceuticals such as analgesics, sulphonamides, antibiotics and contrast agents. The process is of particular interest for grinding organic dyestuffs, such as pigments, dispersion dyestuffs and vat dyestuffs, as well as organic whiteners insoluble in water.

In order to supplement the stability of the dispersion or to promote the grinding action, the following surface active agents are added in a proportion of 0.1 to 200%, referred to the weight of the solid, to the 1 to 80%, and preferably 10 to 50% aqueous suspensions or extruded pastes of the solids. In the case where grinding is carried out in machines in which a strong air or gas aspiring turbulence is caused at the interface between the dispersion of the grinding stock or the grinding mixture and the air or gas, it is convenient to employ the alkali metal or alkaline earth metal salts of dinaphthylmethane-2,2'-disulphonic acid, of p-toluene-sulphonic acid and of polystyrene-sulphonic acid (molecular weight 10,000-15,000) and polyvinyl-pyrrolidone (molecular weight 10,000-

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30,000) as the surface active agents. Provided that this will not interfere with the further application of the dispersion of the solids, these may also be processed with up to 10%, calculated on the amount of solid to be dispersed, of the alkali metal salts of spent sulphide cellulose liquor and its amine condensation products or with the condensation product from cresol-formaldehyde resin and the ω -sulpho acid obtained from 2,6-naphthol-sulphonic acid in combination with 1 to 2% of a defoaming agent, referred to the amount of solid.

In the types of apparatus in which an interference by gas aspiration into the grinding mixture has been eliminated, the following may be added as the surface active products: All types of non-ionic emulsifying agents, such as polyalkoxylated carboxylic acids, alcohols, phenols, amines and mercaptans with a higher molecular weight, as well as anionic dispersing agents such as the alkali metal, ammonium and in some cases also the alkaline earth metal salts of carboxylic acids, sulphonic acids and sulphuric acid esters with a higher molecular weight, and also cationic emulsifying agents such as the salts of primary, secondary and tertiary amines of higher molecular weight with hydrohalide acids and sulphuric acid and in particular their quaternary ammonium compounds; it is also possible to employ surface active agents of the betaine type such as aminosulphonic acids with a higher molecular weight, where the carbon skeleton in their hydrophobic portion with a higher molecular weight may be interrupted by heteroatoms.

The following examples are given for the purpose of illustrating the invention.

Example 1

A homogeneous paste is prepared from 250 g. of coarsely ground flowers of sulphur, having a particle distribution with a main fraction of diameters at about 50μ , larger fractions at about 15μ and smaller fractions at about 6μ and 80μ respectively, by stirring them with 100 cc. of water and 50 g. of the sodium salt, of dinaphthylmethane-2,2'-disulphonic acid as the dispersing agent. This paste is mixed with 970 g. of glass balls (specific gravity 2.97) of diameter 0.45 to 0.75 mm. each of which does not differ in its radius by more than $\pm 1\%$ from the mean radius of the balls, as the grinding elements in the following device. The latter consists of a vertical cylindrical vessel closed at the bottom, open at the top and externally cooled, with a diameter of 10 cm. and a height of about 20 cm. (internal dimensions) into which a stirrer shaft extends vertically and centrally, three plane circular discs of thickness 0.5 cm. and with a diameter of 7.6 cm. being fitted horizontally to the shaft on top of each other at a spacing of 2.7 cm. as the mixing elements. The free clearance between the lowest disc and the bottom is 1 cm. and the rate of rotation is 3000 revolutions per minute. After it has been in operation for 1 hour, the particle distribution of the flowers of sulphur in the paste, which is separated from the grinding elements by means of a sieve, comprises a main fraction at 1 to 2μ , a larger fraction at 0.3 to 1μ and a smaller fraction at 2 to 3μ . The increase in volume of the dispersion of the grinding stock owing to foam amounts to about 40%.

When flowers of sulphur are subdivided with glass balls in the range of 1.8 to 2.2 mm. as the grinding elements under conditions which are otherwise the same, the resultant particle distribution of the flowers of sulphur has a main fraction at 2 to 3μ and moderate fractions at 1 to 2μ and at 3 to 5μ .

When the glass balls have a diameter of 2.7 to 3.1 mm., the main fraction is at 5 to 6μ , moderate fractions are at 6 to 10μ and only small fractions at less than 2μ .

When a mixture of equal parts of glass balls with diameters of about 1, 2, 3, 4, 5, 6, 7 and 8 mm. is employed as the grinding element, the particle distribution of the flowers of sulphur achieved under conditions which are otherwise the same has a main fraction at 2 to 5μ , moder-

ate fractions at 5 to 10 μ , small fractions at about 1 μ and individual particles at up to 15 μ .

Example 2

When flowers of sulphur are subdivided by the use of Ottawa sand as the grinding element under conditions which are otherwise the same as in Example 1, the sand having rounded edges and individual grains whose radii differ by ± 2 to $\pm 25\%$ from the mean radius of the separate particles but its size being the same as that of the glass balls, the resultant particle distribution of the flowers of sulphur has a main fraction at 1 to 2 μ , large fractions at 0.5 to 1 μ and at 2 to 3 μ , and a small fraction at 3 to 4 μ .

When quarry sand with sharp edges and with individual grains whose radii differ by ± 8 to $\pm 40\%$ from the mean radius of the separate particles is employed as the grinding element, grinding becomes impossible since the grinding mixture sets solid. Grinding only becomes possible again when about 100 cc. of water are added.

Example 3

When flowers of sulphur are subdivided under the same conditions as those described in Example 1 except for the use of 50 g. of the sodium salt of polystyrene-sulphonic acid (molecular weight about 13,000) as the dispersing agent, the increase in the volume of the dispersion of the grinding stock due to foam amounts to about 10 to 15% and the particle distribution of the flowers of sulphur is almost entirely at less than 1 μ , with very small fractions at 1 to 4 μ .

On the other hand, when the operation is carried out by employing as the dispersing agent the reaction product of hydroxydiphenyl and benzyl chloride to which 12 to 14 moles of ethylene oxide had been added per mole, on average, the increase in volume of the dispersion of the grinding stock due to foam amounts to about 100%, and the particle distribution of the flowers of sulphur has a main fraction at 4 to 5 μ and moderate fractions at 2 to 4 and at 5 to 10 μ .

Example 4

When grinding of the flowers of sulphur is carried out with the ethylene oxide addition product of hydroxydiphenyl by the method described in Example 5 except that the operation is conducted in an appliance which corresponds to that in Example 1, though in this case a lightweight plate sealed on the shaft and on the grinding vessel is placed over the grinding mixture so as to prevent the entry of air, the resultant particle distribution of the flowers of sulphur has a main fraction at less than 1 μ and only small fractions at 1 to 5 μ .

Example 5

400 g. of a 36% aqueous suspension of the vat dyestuff Indanthrene Brown R (Schulz, Farbstofftabellen, 7th edition, No. 1227) present in a state of subdivision with a main fraction at 3 to 8 μ , with a large fraction at 8 to 40 μ and a small fraction at 1 to 3 μ and which contains 10%, referred to the dyestuff, of the sodium salt of polystyrene-sulphonic acid with a molecular weight of about 13,000, are mixed during 15 minutes with 970 g. of glass balls having diameters of 0.6 to 0.9 mm. in a device like that described in Example 1. The state of fine subdivision of the dyestuff in the resultant dispersion of the grinding stock consists of a main fraction at 2 to 3 μ , a large fraction at 1 to 2 μ and a small fraction at 3 to 4 μ .

Example 6

370 g. of a 35% aqueous dispersion of copper phthalocyanine in the α -modification, prepared in accordance with German patent specification No. 1,136,303 at a state of subdivision with a main fraction of particles at 7 to 25 μ , and which contains 10%, referred to the weight of the pigment, of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid, are mixed with 970 g. of glass balls

with the dimensions of 0.7 to 1 mm. as the grinding elements in the following device. The latter consists of a vertical cylindrical vessel, closed at the bottom, open at the top and externally cooled, with a diameter of 10 cm. and a height of about 20 cm. (internal dimensions), into which a stirrer shaft extends vertically and centrally which carries a vertical flat paddle stirrer of height 10 cm. and width 7 cm. as the mixing element. The free clearance from the bottom is 1 cm. and the rate of rotation is 1000 revolutions per minute. After it has been in operation for 30 minutes, the particle distribution of the pigment comprises a main fraction at 0.5 to 1 μ , large fractions at less than 0.5 μ and at 1 to 2 μ , and a small fraction at 2 to 5 μ .

When the pigment is ground in the device described in Example 1 under conditions which are otherwise the same, i.e. with 3 horizontal stirrer discs as the mixing elements and at a rate of rotation of 3000 revolutions per minute, the final resultant particle distribution is almost entirely the same as that during the above experiment.

Example 7

200 cc. of an aqueous suspension of 30 g. of copper phthalocyanine in the α -modification, prepared in accordance with Example 1 of German patent specification No. 1,136,303, whose main fraction consists of particles at 7 to 25 μ , are mixed for 1 hour at a frequency of 100 cycles per second and an amplitude of 3 mm. together with 9 g. of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid and with 300 g. of glass balls with a diameter of 0.5 to 0.75 mm. in a cylindrical vessel, open at the top, with a diameter of 7 cm. and a height of 15 cm. (internal dimensions) with the aid of a vibro mixer having a perforated circular disc of thickness 2.4 mm. and of diameter 5.4 cm. provided with 20 conical drillings uniformly distributed throughout the disc, their largest diameter being 9.0 mm. and their least diameter being 5.2 mm. The main fraction of the particles in this pigment is at less than 3 μ , and a few individual particles at up to 6 μ are also present.

Example 8

250 g. of a 30% aqueous suspension of the organic substance obtained in accordance with Example 1 of German patent specification No. 1,080,963, which is hardly soluble in water and has a particle distribution with a main fraction at 10 to 15 μ , a large fraction at 1 to 6 μ and a small fraction at 15 to 40 μ , and containing 20%, referred to the weight of the dyestuff, of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid are ground for 1 hour with 500 g. of glass balls with diameters of 0.65 to 0.9 mm. as the grinding elements in a vessel of 1 litre capacity which is placed on a vibrating mill (Ullmann's Encyclopädie der technischen Chemie, 3rd edition, volume I, page 725). The resultant state of fine subdivision comprises a main fraction at 1 to 2 μ and a large fraction at 3 to 4 μ .

When use is made of balls at 4.8 to 5.3 mm., the resultant state of subdivision only comprises a main fraction at 4 to 10 μ , larger fractions at 2 to 4 μ and at 10 to 14 μ and merely small fractions at less than 2 μ .

Example 9

240 g. of the compressed filter cake which contains 50 g. of the azo pigment dyestuff from 2,4,5-trichloroaniline and naphthol AS-D are stirred intensively in a cylindrical mixing vessel having a useful volume of 1 litre with 75 g. of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid and treated with 300 g. of glass balls with a diameter of 0.6 to 0.8 mm. The mixing vessel is now placed into a vibrating mixer "Turbula" System Schatz (described in Pharmaceutika Acta Helvetia 37 [1962], pp. 529-543) and shaken for 2 hours. The dyestuff had a particle distribution at 2 to 10 μ prior to the treatment, with small fractions at 20 μ . After the treatment, the

particle distribution of the dyestuff was between 0.3 and 3 μ .

Example 10

20 kg. of a 10% aqueous paste of the dispersion dyestuff obtained by the mixed bromination of 1,5-diamino-4,8-dihydroxy-anthraquinone in accordance with German patent specification No. 1,029,506 at an initial particle distribution with a main fraction at 8 to 15 μ , large fractions at 2 to 8 μ and at 5 to 50 μ , and a very small fraction at 1 to 2 μ and which contains 150%, referred to the weight of the dyestuff, of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid as the dispersing agent are stirred with 50 kg. of glass balls with a diameter of 0.9 to 1.2 mm. for 6 hours in a mixer of the following construction. The latter consists of a closed cylindrical vessel inclined to the horizontal at an angle of 15° and having a diameter of 60 cm. and a height of 70 cm. (internal dimensions) which has been provided on its internal wall with two mixing fins of height 10 cm. and length 70 cm. positioned opposite each other, parallel with the axis and pointing towards the axis; its rate of rotation is 20 revolutions per minute. The subsequent fine subdivision of the dyestuff is at less than 4 μ .

Example 11

The organic substance obtained in accordance with Example 1 of German patent specification No. 1,080,963 which is hardly soluble in water and has a particle distribution with a main fraction at 10 to 15 μ , a large fraction at 1 to 6 μ and a small fraction at 15 to 40 μ is pumped in the form of its 40% aqueous suspension, with a content of 20%, referred to the weight of solid to be subdivided, of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid and 1%, referred to the weight of solid to be subdivided, of a silicone defoaming agent, at a uniform speed of 100 litres per hour through the following device. The latter is constructed in accordance with FIGURE 1, where the mixing elements 4 and 4a are plane circular discs, the cylinder 11 being missing, and the discharge level is at the level of the lower edge of the sieve. The dimensions of the grinding vessel are height 100 cm. and diameter 26 cm. (internal dimensions), and those of the discs are diameter 21 cm. and thickness 1 cm. The lowest disc is spaced 2 cm. clear of the bottom and the uppermost disc 4a is at the level of the lower edge of the sieve, with 9 other discs spaced at equal distances between them in their attachment to the shaft. The shaft rotates at a rate of 1000 revolutions per minute, and the grinding vessel contains 67 kg. of glass balls with a diameter of 0.5 to 0.75 mm. After it has been passed through twice, the resultant particle distribution comprises a main fraction with particles at 1 to 1.5 μ , larger fractions at 0.5 to 1 μ and at 1.5 to 2 μ , as well as traces at 2 to 2.5 μ .

Example 12

A 35% aqueous suspension of C.I. Pigment Yellow 3 (Colour Index, 2nd edition, 11, 710) which conveniently contains 0.04% of polyglycol-modified oleic acid (12-16 moles of ethylene oxide per mole of acid) and 0.36% of the sodium salts of sulphochlorination products of higher hydrocarbons originating from the preparation of the pigment, which has a particle distribution with a main fraction at 1 to 3 μ , large fractions at 3 to 7 μ , small fractions at 0.5 to 1 μ and at 7 to 40 μ , and which has been treated with 10%, referred to the weight of the pigment, of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid, is pumped through the following device at a uniform rate of throughput amounting to 27 litres per hour. The latter is constructed in accordance with FIGURES 2 to 5, where the grinding vessel has a diameter of 15 cm. and a height of 28 cm. (internal dimensions) and the sieve 7b has a height of 3 cm.; in the case of a construction according to FIG. 2, the lowest point of the overflow 6 is 3 cm. above the sieve 7a. 7 circular discs with a diameter of 12 cm. and a thickness of 0.6 cm. are fitted as the mixing elements at equal distances to the shaft 3 of thickness 2.6 cm. so that

the disc next to the charge inlet 5 is spaced 1 cm. clear from the bottom and so that the disc next to the sieve 7a has a clearance of 3 cm. from the latter. The seals 10 are slip rings. The shaft rotates at 1650 revolutions per minute. The grinding vessel 1 contains 7 kg. of glass balls with diameters of 0.55 to 0.85 mm. The sieves 7a and 7b have a free mesh width of 4 mm. The paste free from foam which is thereby obtained and can therefore be readily further processed contains the pigment in a state of fine subdivision with a main fraction at 1 to 2 μ , large fractions at 0.5 to 1 μ and at 2 to 4 μ , and small fractions at 4 to 5 μ .

When a subdivision of the yellow pigment is attempted in a device of the same dimensions but where the construction is in accordance with FIGURE 1, when the mixing element 4a also represents a circular disc of diameter 12 cm. whilst the cylinder 11 is missing, the discharge level is at the level of the lower edge of the sieve and the sieve has a height of 12 cm. the operation proves to be impossible since the grinding mixture (dispersion of the grinding stock and the grinding balls) spills over the upper edge of the sieve after a short while owing to the resultant stable foam.

When silicone defoaming agents were added, it was still impossible to achieve a satisfactory result of the experiment.

Example 13

A 62.5% aqueous suspension of flowers of sulphur at a particle distribution with a main fraction at about 50 μ , larger fractions at about 15 μ and smaller fractions at 6 μ and at 80 μ , which contains 20%, referred to the weight of the sulphur, of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid is pumped at a uniform rate of throughput of 15 litres per hour through devices like those described in Example 12 and constructed in accordance with FIGURES 2-5. The resultant state of fine subdivision of the sulphur comprises a main fraction at 2 to 4 μ , large fractions at 0.5 to 2 μ and at 4 to 5 μ , and small fractions at 5 to 6 μ .

When the same experiment is carried out in a device with the same dimensions but where the construction is in accordance with FIGURE 1, when the mixing element 4a also represents a circular disc of diameter 12 cm. whilst the cylinder 11 is missing, the discharge level is at the level of the lower edge of the sieve and the sieve has a height of 12 cm., the resultant increase in the volume of the discharged dispersion of the grinding stock is 35%, compared with that of the charged dispersion of the grinding stock, even when 1% of a silicone defoaming agent has been added (calculated on the sulphur content). The resultant particle distribution of the sulphur has a main fraction at 7 to 10 μ , large fractions at 5 to 7 μ and at 10 to 15 μ , and small fractions at 1 to 5 μ and at 15 to 25 μ .

Example 14

When a subdivision of the flowers of sulphur is carried out under the same conditions as described in Example 13 in a device with the same dimensions but where the construction is in accordance with FIGURE 1 when the cylinder 11 has a diameter of 12 cm. and a height of 10 cm., its lower surface being at the level of the lower edge of the sieve 7, the sieve 7 has a height of 12 cm. and the highest point of the overflow 6 is 5 cm. above the lower edge of the sieve 7, the increase in volume of the discharged dispersion of the grinding stock due to the foam amounts to 15 to 20% of the volume of the charged dispersion of the grinding stock. The resultant state of fine subdivision of the sulphur comprises a main fraction at 5 to 6 μ , larger fractions at 2 to 5 μ and at 6 to 8 μ , and small fractions at 1 to 2 μ and at 8 to 10 μ .

Example 15

A 30% aqueous suspension of copper phthalocyanine in the α -modification, prepared in accordance with German patent specification No. 1,136,303 at a particle distribution with a main fraction at 7 to 25 μ and which contains

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20%, referred to the pigment content, of the sodium salt of dinaphthylmethane-2,2'-disulphonic acid and 50%, referred to the pigment content, of the sodium salt of the aniline condensation product of lignin-sulphonic acid is pumped through devices like those described in Example 12 and constructed in accordance with FIGURES 2-5, at a uniform speed of 15 litres per hour. The resultant state of fine subdivision of the pigment comprises a main fraction at 0.5 to 2 μ , large fractions at 0.3 to 0.5 μ and at 2 to 5 μ , and small fractions at 5 to 6 μ .

When the same experiment is carried out in a device with the same dimensions but where the construction is in accordance with FIGURE 1, when the mixing element 4a also represents a circular disc of diameter 12 cm. whilst the cylinder 11 is missing, the discharge level is at the level of the lowest edge of the sieve and the sieve has a height of 12 cm., the resultant increase in the volume of the discharged dispersion of the grinding stock is 110%, compared with the volume of the charged dispersion of the grinding stock. The resultant particle distribution of the pigment comprises a main fraction at 4 to 10 μ , large fractions at 2 to 4 μ and at 10 to 13 μ , and small fractions at 1 to 2 μ and at 13 to 15 μ .

What we claim is:

Apparatus for continuously dispersing solids in a liquid medium which comprises a hollow vessel having a sieve therein, which sieve divides said vessel into a grinding

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zone and a residence zone; an inlet opening in said hollow vessel in the grinding zone portion thereof and an outlet at the residence zone portion thereof; wherein said residence zone is defined by said sieve, said outlet and walls along all other surfaces thereof, whereby to exclude air from contact with the contents of said residence zone; said outlet being disposed at a point of said apparatus which is the highest point in said residence zone and higher than said inlet and being operatively associated with an outlet tube having a multiple bend therein, which tube has an exit which is disposed at a point lower than said outlet, but higher than said inlet.

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