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PREPARATION OF DISPERSIONS

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This invention relates to the production of finely divided materials and in particular it pertains to the production of finely divided, organic materials suitable for use in artificial silk spinning solutions to produce low luster yarn.

Grinding methods are known whereby materials may be ground, in part at least, to particles of small dimensions (below 2-4 microns). Thus, a water slurry of the material may be ground in a pebble mill, a ball mill, or a colloid mill such as a Charlotte mill. Extremely long grinding periods are required to grind substantially all of the particles to dimensions below 2-4 microns. A much more efficient procedure involves grinding for a short period of time, diluting the mill base to a suitable concentration and centrifuging to remove the coarse particles which may then be reground, at a higher grinding rate than before. The product from such a grinding process is a dilute slurry, ill adapted to shipment or storage for long periods of time. The partially ground concentrated slurries cannot be shipped to the point at which they are to be used and then diluted and centrifuged because in such event large quantities of residues must be returned.

Where grinding methods are used for the production of finely divided, organic materials, for example, organic pigments, it is extremely difficult to obtain suitable sub-division particularly when the materials to be ground are organic compounds of definitely crystalline form and for this and other reasons it is extremely difficult to obtain them in the form of stable, aqueous dispersions of particles nearly all of which are under 4 microns in size.

In accordance with the present invention, a method has now been found whereby a concentrated slurry (i. e. a slurry having a concentration above 15% and generally 25-30% of solid matter) containing less than 10% of coarse material, that is, material having a particle size above 4 microns, can be directly produced by a grinding and classifying process. Such a slurry is economical to ship. It may later be diluted and classified again if so desired. Comparatively small amounts of coarse material are then returned for re-grinding.

It is an object of this invention to prepare concentrated slurries, suitable for shipping and storage, of materials with very fine particle size and not more than a few percent of material above 4 microns in diameter. An object is to prepare concentrated slurries and/or dispersions of water-insoluble organic materials suitable for shipment and storage with fine particle size and

not more than a few percent of material above 4 microns in diameter. An object is to prepare concentrated water-dispersions of water-insoluble, polynuclear organic compounds highly deficient in hydrogen, suitable for shipment and storage, with fine particle size and not more than a few percent of material above 4 microns in diameter. Another object is to eliminate excessively long grinding periods in the preparation of such slurries. Another object is to prepare slurries which are substantially non-foaming so that efficient grinding and water classification can be achieved. Other objects of the invention will appear hereinafter.

I have found that grinding slurries can be made up at concentrations of 40-50% of solid matter and after grinding, prior to classifying, be diluted with the fines secured from the grinding and classifying of residues from other grinds. The resulting slurry may be centrifuged at a concentration of 33-35% which will contain 70% or more of the material as fines. The classified slurry will now have a concentration of 25-30% with 90% or more of the solid material below 4 microns in diameter.

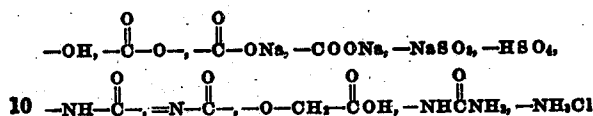
Another method for increasing the concentration of the final slurry is to reclassify or to re-grind and reclassify the residues a second time and to use these fines in diluting one of the first residue grinds prior to classification.

Slurries of fines resulting from the classification of residue grinds can also be used to make up the initial grinding slurries in place of water. Such a practice is not particularly desirable, however, because there is a well known tendency for the presence of fines to reduce the grinding rate.

By the practice of the present invention, it has further been found that concentrated water dispersions containing about 15%, generally 25-30% of solids of solid matter with a particle size distribution 90-100% below 4 microns in diameter and only 0-10% above 4 microns in diameter can be prepared by grinding water slurries of the material with an agent comprising a substantially non-foaming dispersing agent, adding a preservative as desired, and combining the grinding and classifying steps in such a manner that the fines obtained from the grinding and classifying of residues are used in making up and/or diluting the initial grinds prior to centrifuging.

Substantially non-foaming dispersing agents have been found to belong to that class of organic materials with a molecular weight of about 400 and above, and a plurality of hydrophylic groups preferably substantially symmetrically arranged

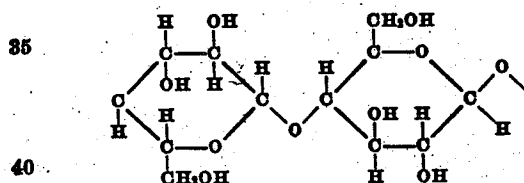
within the molecule. By "hydrophylic groups" are understood groups which are water-soluble or tend to contribute water-solubility to an organic substance. In general, they are polar groups, e. g.



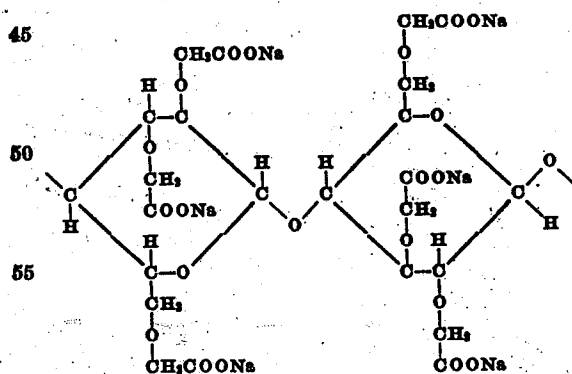
or alkylated derivatives thereof in which one or more of the hydrogen atoms attached to the nitrogen atoms are substituted by alkyl or aryl groups, etc.

Materials which we have found to be substantially non-foaming include such things as peptized casein, alkali metal salts of the formaldehyde condensation product of naphthalene sulfonic acids such as those described in U. S. Patent No. 1,696,199, starch acetate, starch, cellulose glycolic acid, gelatin, agar-agar, sulphite cellulose and viscose. Such materials have their polar groups substantially symmetrically arranged in contrast to soap-like dispersing agents in which the polar groups are located at one end of the molecule. The former agents are substantially non-foaming in grinding and classifying operations, whereas the soap-like agents foam seriously. This difference may be illustrated by the following structural formulas:

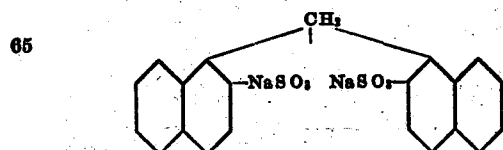
I. Structural unit for starch



II. Structural unit for the sodium salt of cellulose glycolic acid



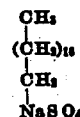
III. The sodium salt of the formaldehyde condensation product of naphthalene-beta-sulfonic acid



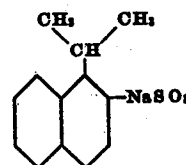
IV. Sodium stearate (foams severely)



V. Sodium salt of stearyl sulfate (foams severely)



VI. Isopropyl naphthalene sodium sulfonate (foams severely)



While the exact structure for casein is unknown, it yields many different amino acids on hydrolysis. These are held together by numerous hydrophylic/polypeptide linkages in the casein molecule. Any single amino acid constitutes but a small proportion of the protein molecule, so that casein contains a "plurality of hydrophylic groups, substantially symmetrically arranged within the molecule".

I have found that casein is one of the most satisfactory agents for use in this invention. The foaming of its solutions decreases as the pH is lowered. I prefer to use solutions with a pH between 5 and 7. Such a solution is made up by known methods according to the following formula:

Casein	100
Hydrated trisodium phosphate	18
Water	882
	1000

The casein should be added slowly to the grind as needed to secure adequate dispersion. If too large an excess of casein is added at one time, considerable foam may be produced. In no case, however, is the foaming as severe as with the use of a soap-like agent.

When casein is used as a dispersing agent, a preservative should be added to prevent bacterial decomposition. Phenols have been used for this purpose. When preservative materials are added prior to the grinding operation, severe foam of a very permanent nature is produced. If added subsequent to grinding, the dispersion is apt to flocculate and thicken objectionably. I have found that if a phenolic solution of a soap-like product, such as monopole oil, is added near the end of the grind that severe foaming is avoided. Such foam as may be formed is found to break very quickly on standing and is not objectionable. Exceptionally good dispersion is also obtained.

A phenolic solution of Monopole oil is made up according to the following formula:

Phenol	49.5
Sodium hydroxide	8.25
Water	12.25
Monopole oil	30
	100.00

I prefer to use about 1% of this solution based on the weight of the grind. The invention is not limited to these proportions. Other phenols and other types of soap-like materials may be used.

Grinding may be done in any manner capable of reducing an appreciable portion of the ma-

terial to particles below 4 microns in diameter. I have used pebble or ball mills and particularly colloid mills.

Classifications of the particles may be brought about in a centrifuge of the rotating, bowl type, or by gravitation.

If a slurry of an organic material with a density of about 1.3 is ground to 60% below 4 microns in diameter, (at which point further grinding generally becomes inefficient) in a colloid mill, the slurry diluted to 28-30% and centrifuged, it is possible to obtain a slurry with a concentration of 18-20% of solids of which about 95% is fines, i. e. under 4 microns. If the residues from the centrifuging operation are now reground, diluted and centrifuged, it is difficult to obtain a slurry with a concentration above 13-15% of solids. Such dilute slurries are unsuitable for shipment because of the large amount of water which they contain. They also settle badly on storage. However, by the practice of the present invention, the same material may be ground and classified to yield more highly concentrated, stable slurries having a highly uniform particle size, as indicated in the following examples:

Example I.—Grinding and dispersing of ethylene glycol di-beta-naphthyl ether

Eighty pounds of ethylene glycol di-beta-naphthyl ether are ground with 104 pounds of water and 4 pounds of 10% casein solution of the type described above, by recirculation through a colloid mill at the rate of 60 to 250 gallons per hour for a period of 6 hours. Additional casein solution is added as required; generally, 12 pounds are sufficient. Two pounds of a phenolic solution of Monopole oil, prepared as described above, is added to the grind. The grind is then passed into a dilution tank where it is diluted with water to a concentration of 25-30% ether and centrifuged at a rate of about 35 gallons per hour through a 20" horizontal centrifuge rotating at 1200 R. P. M. The slurry of fines so obtained is of about 15% concentration, and while of suitable fineness, is ill adapted for shipment or storage.

The coarse residues from the preceding operation are reslurried with one pound of 10% casein solution prepared as described above, and enough water to yield a 40% suspension. This is ground by recirculation through the colloid mill at a rate of about 100 gallons per hour for a period of 3 hours. Additional casein solution is added as required to secure a good dispersion. Three pounds of additional casein is generally sufficient. A phenolic solution of Monopole oil, prepared as described above, is added in an amount which is approximately 1% of the weight of the slurry, the slurry is passed out through the mill into a dilution tank where it is diluted with water to about 27-30% ether (it may, if desired, be diluted with the fines from the preceding operation). The slurry is passed to a centrifugal separator at a rate of 35 gallons per hour. The slurry of fines is retained, and the coarse material is recrystallized and used over again.

Eighty pounds of ethylene glycol di-beta-naphthyl ether crystals are slurried with 104 pounds of water and 4 pounds of 10% casein solution of the type described above. The slurry is ground for 6 hours by recirculation through a colloid mill and a cooler. Additional casein solution is added as required. Generally 12 pounds more is sufficient. At the end of the grind, 1% by weight (based on the weight of the slurry) of a phenolic

solution of Monopole oil, such as has been described above, is added and the slurry is passed out through the mill into a dilution tub. It is diluted with the fines obtained from a preceding operation. The resulting slurry is passed at a rate of about 35 gallons per hour through a 20-inch horizontal centrifuge, rotating at about 1200 R. P. M. The slurry of fines so obtained generally contains between 25 and 30% of the finely divided ether, 95% or more of which is below 4 microns in diameter. It is suitable for shipment or storage. The residues are removed from the centrifuge and may be reground as described in the preceding paragraph.

Example II.—Using starch acetate and methylene-polynuclear sulfonate

A solution containing 10% starch acetate and 2.5% methylene-polynuclear sulfonate is made up by warming and stirring the following materials:

Starch acetate	100
30% sodium salt of the formaldehyde condensation product of naphthalene-beta-sulfonic acid	83
Water	817
	1000

Eighty pounds of ethylene glycol di-beta-naphthyl ether are ground as described in Example I, using the starch acetate solution described above in place of the casein solution and omitting the addition of the phenolic solution of Monopole oil.

The coarse residues from the grinding and centrifuging of the ether are reslurried with 3.2 lbs. of the solution of starch acetate-sodium salt of the formaldehyde condensation product of naphthalene-beta-sulfonic acid together with enough water to yield a 36-38% suspension. The resulting slurry is ground as previously described in Example I. No preservative need be added in this case. The slurry is then diluted to 32% with water and centrifuged as previously described. The slurry of fines from the previous operation may be used in place of water for the dilution step.

Eighty pounds of crystals of ethylene glycol-di-beta-naphthyl ether are slurried with 1650 pounds of the solution of starch acetate-sodium salt of the formaldehyde condensation product of naphthalene-beta-sulfonic acid together with 104 pounds of water. This is ground as described above, without the addition of a preservative agent. This slurry is then diluted with a slurry of fines obtained from a preceding operation, and is centrifuged as described in Example I. The resulting slurry of fines contains 20-30% solids and 90% or more below 4 microns in diameter, and it is suitable for shipment or storage. The residues may then be again reground as described in the preceding paragraph.

The present invention is particularly applicable to the preparation of finely divided organic pigments adapted for use in the delustering of artificial thread such as rayon. The delusterant is introduced into the cellulosic solution prior to extrusion through the spinneret, for example, in the delustering of rayon of the regenerated cellulose type prepared from viscose, the delusterant is introduced into the viscose, the solution then being extruded through the spinneret, coagulated, regenerated, and subsequently processed in the usual fashion. It is essential that the ma-

dial used for delustering be finely divided; that be uniform in size and have all but a few per cent of the particles under 4 microns; and that it be capable of uniform dispersion throughout the iluolose solution. These conditions are necessary in order that the thread be uniformly de-stered, that the treatment be uniformly distributed throughout the thread so as to produce read of uniform strength and in order that the articles of delusterant pass through the spinneret without difficulty and in order that the de-sterant will not seriously abrade the different ements of the spinning machine.

Among the organic delusterants to which the invention may be applied with great benefit are:

1. Organic ethers, their —S—, —Se—, —Te—, and —NH— analogues, such as ethylene glycol [—b-naphthyl ether, di-benzthiazyl-mercaptothane and N-di-b-naphthyl diphenylene di-

mine;

2. Chlorinated ring hydrocarbons such as octachloro naphthalene and the other solid highly chlorinated naphthalenes, chlorinated diphenyl and the other chlorinated diphenyls, as well as the other solid halogenated ring hydrocarbons;

3. Organic heterocyclic compounds such as nethyl-dinaphtho-xanthene and thianthrene.

In addition to those classes of organic delusterants specifically mentioned, other organic delusterants may be similarly ground in accordance with the practice of the invention as described.

Any variation or modification which conforms to the spirit of the invention is intended to be included within the scope of the claims.

I claim:

1. The process of producing slurries of materials having a substantially uniform particle size which comprises grinding said materials, diluting the grind, and classifying whereby to remove the fine particles from the coarse particles, characterized in that the ground materials prior to classification are diluted with the fine particle slurry removed during a previous operation.

2. The process of producing slurries of water-insoluble, substantially colorless, polynuclear, aromatic organic materials, having a substantially uniform particle size which comprises grinding said materials, diluting the grind, and classifying whereby to remove the fine particles from the coarse particles, characterized in that the ground materials prior to classification are diluted with the fine particle slurry removed during a previous operation.

3. The process of producing slurries of materials in water containing a dispersing agent, having a substantially uniform particle size which comprises grinding said materials, diluting the grind, and classifying whereby to remove the fine particles from the coarse particles, characterized in that the ground materials prior to classification are diluted with the fine particle slurry removed during a previous operation.

4. The process of producing slurries of materials in water containing a dispersing agent having a molecular weight above four hundred and having a plurality of hydrophylic groups, having a substantially uniform particle size,

which comprises grinding said materials, diluting the grind, and classifying whereby to remove the fine particles from the coarse particles, characterized in that the ground materials prior to classification are diluted with the fine particle slurry removed during a previous operation.

5. The process of producing slurries of materials in water containing a dispersing agent having a molecular weight above four hundred and having a plurality of hydrophylic groups substantially symmetrically arranged within the molecule, having a substantially uniform particle size, which comprises grinding said materials, diluting the grind, and classifying whereby to remove the fine particles from the coarse particles, characterized in that the ground materials prior to classification are diluted with the fine particle slurry removed during a previous operation.

6. The process of producing slurries of materials in water containing a dispersing agent having a molecular weight above four hundred and having a plurality of hydrophylic groups substantially symmetrically arranged within the molecule, having a substantially uniform particle size, which comprises grinding said materials, diluting the grind, and classifying whereby to remove the fine particles from the coarse particles, characterized in that the ground materials prior to classification are diluted with the fine particle slurry removed during a previous operation, said process being further characterized in that a preservative for said dispersing agent is added.

7. The process of claim 5 characterized in that the dispersing agent is peptized casein.

8. The process of claim 6 characterized in that the dispersing agent is peptized casein, and the preservative is a phenol.

9. The process of claim 6 characterized in that the dispersing agent is peptized casein, and the preservative is an aqueous phenolic solution of a water-soluble sulfonate.

10. The process of producing a slurry of ethylene glycol-di-beta naphthyl ether having a substantially uniform particle size which comprises grinding said ether with a dispersing agent, diluting the grind with the fine slurry obtained from a previous grinding operation, and classifying whereby to remove the fine particles from the coarse particles.

11. The process of producing a slurry of octachloro naphthalene having a substantially uniform particle size which comprises grinding said octachloro naphthalene with a dispersing agent, diluting the grind with the fine slurry obtained from a previous grinding operation, and classifying whereby to remove the fine particles from the coarse particles.

12. The process of producing a slurry of dibenzthiazyl-mercapto ethane having a substantially uniform particle size which comprises grinding said dibenzthiazyl-mercapto ethane with a dispersing agent, diluting the grind with the fine slurry obtained from a previous grinding operation, and classifying whereby to remove the fine particles from the coarse particles.

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