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PIGMENTED ORGANIC PLASTICS AND
METHOD FOR PREPARING THE SAME

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This invention relates to pigmented compositions and more particularly relates to the production of pigmented compositions of matter suitable for the coloring of plastics, rubber, resins, waxes, gums or materials of like nature.

The production of plastic masses containing dispersed pigment for incorporation into large batches for coloring purposes is not new. Such dispersions are known to the industry as "color master batches," or, when considering nitrocellulose dispersions as an example, as "lacquer chips." Such master batches are used by many manufacturers of colored plastic, rubber or resinous materials for convenience and economy since, by the use of a master batched color, the need for extensive and costly milling of pigment to incorporate it into the plastic or resinous material is obviated. Further, such color master batches are much easier to handle in the plant, being far less dusting than the uncompounded pigment. The use of properly compounded master batches affords the user a degree of uniformity and quality of pigmentation of the final product which is superior to that obtained by the preparation of these materials from the raw color.

Heretofore, has been necessary, in the production of color master batches, to submit the pigment and plastic along with other materials such as plasticizers, to prolonged and expensive mechanical working to achieve a dispersion of satisfactory quality. Simple ball or pebble milling, for example, could not be used and the pigment was dispersed through the plastic practically by brute force. Equipment commonly used for this purpose includes Banbury mills, Baker-Perkins or Werner-Pfleiderer mills, 2 roll differential speed mills commonly known as "rubber mills," or similar expensive equipment capable of exerting the requisite large shearing stresses required. It has been found that milling times are considerable, the power requirements for such equipment are obviously very high and the constant attendance of skilled labor is required. In addition to the difficulties mentioned, the degree of dispersion obtained by these methods while satisfactory for some applications very often leaves much to be desired when a very fine degree of dispersion is required.

Another major disadvantage in producing the prior color master batches lies in the product itself. The product generally comprises heat-fused lumps of colored plastic or resin of extremely hard character and of relatively difficult solubility due to the unavoidable heating of the

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plastic in the milling operation. In addition, the chromaticity of the pigmented product is low, which is probably also due to the conditions obtained in the drastic milling operations. A still further and more serious objection to prior products is the fact that it almost always contains a large amount of plasticizer or softener necessary for proper mill operation which may be undesirable and actually harmful in the final product to be pigmented.

I have found that color master batches of extremely high quality can be prepared in an efficient manner with simple inexpensive milling of a pigment and a solid plastic by the use of a novel and special type of liquid dispersion and grinding medium which later can be easily removed and even reused, if desired, for new batches. After the removal of the liquid dispersion or grinding medium, the dispersion may then be dried and ground.

As an alternate method of handling, especially in the case of those products which are combustible when dry, such as nitro cellulose, the filter cake resulting from the removal of the grinding medium may be treated by known procedures to displace the water with a non-aqueous liquid such as alcohol. The final product in this case is a wet pigmented composition of matter which can be handled with safety.

The dispersions formed in the above-mentioned procedures are stable, uniform and free from agglomerates and undesired addition products, such as plasticizers. They have a high chromaticity and when used to color plastic masses the full strength of the pigment employed is realized. Coating compositions prepared from these pigmented compositions are uniformly and highly colored. The product is soft and can easily be reduced to a very fine powdery consistency. Yarn and filaments extruded from plastic compositions colored by these materials are not only highly colored and completely uniform but the small particle size or fineness of the dispersion is such that the tensile strength of the yarn or monofilament produced is not affected. The fineness of the dispersion is further attested to by the fact that these master batches can be used in the production of extremely fine monofilaments by spinning from a solution of the plastic or by dry-extrusion without clogging the spinnerets, jets or dies.

One object of the invention is the production of a pigmented composition or master color batch which requires only simple, inexpensive milling in its preparation.

Another object of this invention is the production of pigmented plastic materials containing coloring materials in a state of extremely fine and uniform dispersion, having a high chromaticity.

Still another object of this invention is the production of uniform and fine dispersions of colorants in plastic materials in the form of a dry, free-flowing powder which is easily incorporated into a larger mass of the same or similar plastic material to give a uniformly colored plastic mass, which plastic mass can then be spun, extruded, molded or treated in any of the many ways known to those versed in the art of manipulating such materials for the production of uniformly and strongly colored yarns, filaments, films, lacquers, and similar products.

A further object of this invention is the production of pigmented plastic compositions from which suitable paints, lacquers, enamels, and printing inks can be prepared by simple mixing or stirring of said pigmented material with appropriate solvents.

Other objects of the invention will be apparent from the detailed specifications which follow.

In practicing my invention I placed in a ball, pebble, or colloid mill a mixture consisting of the plastic, resin or other material to be pigmented, the specific pigment desired, and the novel liquid dispersion or grinding medium comprising a solvent for the plastic to be pigmented characterized additionally by its water solubility, and water. The balls or pebbles are added and the mill allowed to grind the mixture until a dispersion of the desired degree is obtained.

The plastic substances which are embodied in the examples of the specification as illustrative of the invention of this application are organic resin plastics of normally solid structure, substantially insoluble in water and at least partially soluble in an organic solvent which is miscible with water. Such a plastic is hereinafter in this specification and in the appended claims termed a "solid organic plastic." Many solid organic plastics, but by no means all such plastics, are enumerated and classified in volume V, chapter 1, on pages 2 to 5, inclusive, of "Protective and Decorative Coatings," edited by Joseph J. Mattiello, Ph. D., and published in 1946 by John Wiley & Sons, Inc., of New York, the solid organic plastics therein listed being incorporated in this specification by reference as including some of the solid organic plastics suitable for the purposes of this invention. Such plastics include natural resins and modified natural resins; alkyd resins, both modified and unmodified types; aldehyde condensation products; vinyl resins; rubber and rubber-like synthetics; hydrocarbon resins; and associated materials such as waxes, etc.

The solid organic plastics incorporated in certain of the species claims appended to this specification are enumerated under the heading "Cellulose resins" on page 3 of Mattiello, hereinbefore identified, and include cellulose acetate, cellulose acetopropionate, cellulose acetobutyrate, cellulose nitrate and ethyl cellulose.

The term "pigment" as hereinafter employed in this specification and in the appended claims comprises any of the solid colorants normally used in the industry for the coloring, opacifying, delustering or otherwise modifying the color of the basic plastic, resin or elastomer. These include the inorganic prime pigments, organic prime pigments, various inert or extender pig-

ments, metallic pigments and the various bone and gas blacks, such as disclosed in Mattiello "Protective and Decorative Coatings," vol. 2, chapter 1, (1942), or the Journal of the Society of Dyers and Colorists, vol. 61 (307), December, 1945. These pigments may be used in the dry form, as pigment pastes, as press cakes wet with water or as aqueous dispersions.

As an essential feature of the invention, the plastic and pigment are mixed with a liquid grinding medium comprising water and a water-miscible solvent for the solid organic plastic employed. It is important that the mixture of water and solvent be substantially a non-solvent for the plastic. By this is meant that, during the time of processing, the mixture of solvent and water must be insufficient to dissolve the plastic or permit it to gell or agglomerate.

To accurately find the point at which the solvent and water composition becomes substantially a non-solvent for the plastic, a series of solutions can be made up comprising the selected solvent with various percentages of water. Such solutions may vary in 5 or 10% increments depending upon the precision desired. Thus, as an example, one may fill nine oil bottles with water-solvent solutions varying from 10% to 90% water by weight. A small amount of the plastic is then added to each bottle, preferably in the physical form in which it is to be used and in an amount of about 1 part of plastic to 4 parts of liquid medium. The mixture is well agitated and the solid organic plastic is then permitted to settle.

One may note that in one or more of the bottles the plastic either goes completely into solution or clumps or conglomerates into a more or less translucent, gell-like mass. It will also be noted that in the remaining bottles, the plastic retains a discrete particle appearance. While these effects can generally be observed almost immediately, it is better to permit about 4 hours of contact before comparisons are made and still more preferably one may allow as much time for contact as is to be given during the actual pigment dispersion operation.

The action of the mixture of water and solvent on the plastic when it is less drastic than that which causes a gelling and conglomeration of the plastic and yet contains sufficient solvent to make the plastic receptive to pigment dispersion can best be termed a "pigment receptive action" on the plastic.

Without wishing to be bound to any theory of operation, it is believed that the liquid grinding medium attacks the plastic so that it is receptive to the entrance of pigment particles which are easily dispersed into the plastic by a simple and uncomplicated milling operation. In some cases it has been noted that a softening effect on the plastic takes place but this is not invariably the case with all plastics.

Those grinding compositions having so much solvent as to cause a solution or a gell-like, fused mass indicate undesirably extensive and drastic solvent action on the plastic. These water-solvent compositions have been found inoperable for the purpose desired since either extremely long milling times are required or the gummy nature of the plastic mass makes it impossible to obtain penetration and dispersion of the pigment therethrough.

The most desirable and optimum water-solvent composition has been found to be the one having that proportion of water just sufficient to pre-

vent the above-mentioned extensive solvent action, and yet have enough solvent present to attack the solid organic plastic and make it receptive to the entrance and dispersion of pigment. It should be clearly understood, however, that for operability there is no precise percentage of solvent in water or precise point where the liquid medium imparts the receptive quality to the plastic but, rather, a range which may vary from about 2 or 3 percent—in the case of particular solvents and particular plastics—to as much as about 30% with other solvents and plastics. The indication that the amount of solvent is "approximately" below that which results in gelling or conglomeration is intended to cover that range where the pigment receptive action on the plastic takes place.

Assuming, for example, that solutions and gellike conditions are observed with mixtures having up to 40% water therein with discrete particles being evident with compositions having from about 50% water and higher, one could select a composition having about 45% water and 55% solvent as the optimum composition but actually one could obtain satisfactory results when operating with a composition having from about 45 to about 60% by weight, or thereabouts, of water as the proper non-solvent mixture depending upon the particular solvent, plastic and pigment involved. Preferably, the liquid composition selected is that having substantially the highest solvent to water ratio in a composition which is still capable of maintaining the plastic in substantially discrete particle form and can therefore be considered substantially a non-solvent for the solid organic plastic.

While the above test may be carried out with any of the plastics to be pigmented, with some plastics and particularly those which are sticky or gummy in their natural state, the following filtration test is frequently useful in determining more precisely the optimum amount of solvent and water to be employed as a liquid grinding medium; and in checking the results obtained with the aforescribed method of test if so desired.

In carrying out the filtration test, at least three ball mills are used. These are each charged with aliquot amounts of the plastic to be pigmented. Liquid grinding medium having a predetermined amount of water and solvent is added to each mill. To one mill is added the optimum liquid grinding medium having the optimum amount of solvent and water as determined by the bottle test. In the other mills are added liquid grinding compositions which vary a small amount from the optimum concentration, one composition having say 3 to 5% more solvent, the other having 3 to 5% less solvent. The plastic is now ground in all the mills for approximately 48 hours and finally each mill charge is filtered under substantially identical conditions. It has been found that the milled charge which has the highest filtration rate will produce the most desirable final product if one uses substantially the same percentage composition of liquid grinding medium in the actual run.

The amount of liquid grinding medium comprising solvent and water, used in the process, is selected by the operator to be sufficient to permit good grinding action in the particular mill used in the process. A mill with flint pebbles, for example, will generally require more liquid grinding composition than one using steel balls. It is, of course, obvious that one may, if so desired,

use other types of mills for the grinding operation and even the heavy duty, high-power mills heretofore considered necessary in the art. In such cases, one uses only so much liquid grinding medium as is deemed necessary for proper milling operation.

Such water-miscible solvents which will solubilize the solid organic plastics include the alcohols as, for example, methyl, ethyl, iso-propyl alcohol, diacetone alcohol, etc.; dioxane; the glycol ethers as, for example, the Cellosolves and the Carbitols; the esters such as the Cellosolve acetates and methyl or ethyl lactate; the ketones such as acetone, methyl-ethyl ketone; and other solvents or mixture of solvents for the plastics, elastomers, oils and waxes well-known to the art. The term "water-miscible solvent," as used in this specification and in the appended claims, comprises the above enumerated substances. It has been found that the chief characteristic of the solvent is that it must be at least a partial solvent for the solid organic plastic to be pigmented and it also must be at least partially soluble in water.

For a better understanding of the invention, the following examples are given, it being clearly understood that these are merely by way of illustration and not to be considered limitative of the invention. References to the pigments employed utilize the generally accepted trade name. The letter "M" with figure and page number following the name refers to the figures and pages in vol. 5 of J. J. Mattiello's "Protective and Decorative Coatings" which gives the chemical composition. The designation "C. I." refers to the well-known Colour Index published by the Society of Dyes & Colorists.

Unless otherwise noted, all percentages in the following examples are to be considered as being on a weight basis.

Example 1

A 1-gal. porcelain pebble mill is charged with 300 gms. Toluidine Maroon Powder (M; Fig. 83, page 408) and 1300 gms. of a grinding fluid consisting of 15% acetone and 85% water. This is mixed well and to this mixture is added 300 gms. of finely ground Dammar Resin Batavia #1. About 7 lbs. of #00 French flint pebbles are added. After milling for about 70 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 585 gms. of an intensely colored maroon powder which disperses well without grinding in the usual organic lacquer solvents or lacquers such as a clear nitrocellulose lacquer.

In another operation, substantially the same type of product was obtained when isopropyl alcohol was substituted for the acetone.

Example 2

A 1-gal. porcelain pebble mill is charged with 200 gms. Victoria Blue Toner (M; Fig. 22, page 378) and 1200 gms. of a grinding fluid consisting of 10% denatured ethanol and 90% water. This is mixed well and to the mixture is added 200 gms. of finely powdered shellac. About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 390 gms. of a brightly colored blue pow-

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der. When stirred into denatured ethanol a highly colored fluid dispersion is obtained which is suitable for use in the preparation of "aniline" inks.

Example 3

A 1-gal. porcelain pebble mill is charged with 150 gms. Benzidine Yellow Toner (M; Fig. 48, page 391) and 1500 gms. of a grinding fluid consisting of 5% ethanol and 95% water. This is mixed well and to the mixture is added 150 gms. N wood rosin (ground). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. There is obtained 286 gms. of a fine yellow powder which when cut into warm mineral oil produces a well dispersed yellow news ink base.

Example 4

A 1-gal. porcelain pebble mill is charged with 128 gms. Benzidine Yellow Toner (M; Fig. 49, page 391) and 32 gms. of titanium dioxide (printing ink grade) plus 1000 gms. of a grinding fluid consisting of 23% acetone and 77% water. This is mixed well and to the mixture is added 160 gms. of Powder Zitro Resin (a zinc resinate product produced by Newport Industries, Inc.). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried, and pulverized. There is obtained 314 gms. of fine bright yellow powder which is suitable for the preparation of a rotogravure yellow ink without grinding.

Example 5

A 1-gal. porcelain pebble mill is charged with 150 gms. Pyrazolone Red Toner (M; Fig. 71, page 402) and 1100 gms. of a grinding fluid composition comprising 733 gms. of water and 360 gms. of acetone (33.3% solvent). This is well mixed and to the mixture is then added 300 gms. of powdered paraffin. 7 lbs. of French flint pebbles are added and milling is carried out for approximately 45 hours. The mill is then discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is finally washed, dried, and pulverized. One obtains about 435 gms. of a bright red powder paraffin product which is excellently suited for the manufacture of colored candles.

Example 6

In Example 2 involving the use of shellac, it has been found that the keeping qualities can be greatly improved by the addition of a synthetic resin, such as Amberol 820. Consequently the same procedure is carried out as is disclosed in Example 2 except that one uses 160 gms. of finely powdered shellac and 40 gms. of Amberol 820 instead of the 200 gms. of shellac. The product is essentially the same, being a blue powder of high color intensity but with greatly improved storage qualities.

Example 7

A 1-gal. porcelain pebble mill is charged with 100 gms. Phthalocyanine Green (M; Fig. 144, page 439) and 1200 gms. of a grinding fluid consisting of 33 1/3% dioxane and 66 2/3% water. This is mixed well and to the mixture is added 200 gms. of ethyl cellulose powder 10C. About 7 lbs. of

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#00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 291 gms. of a fine soft-textured bright green powder which disperses very easily into lacquer solvent to make a standard ethyl cellulose lacquer.

When dioxane was replaced with isopropyl alcohol in the same ratio, a substantially similar product was obtained.

Example 8

A 1-gal. porcelain pebble mill is charged with 200 gms. Phthalocyanine Green (M; Fig. 144, page 439) and 1000 gms. of a grinding fluid consisting of 66 2/3% acetone and 33 1/3% water. This is mixed well and to the mixture is added 100 gms. of ethyl cellulose powder 10C. About 20 lbs. of steel balls, averaging 1/2" in diameter, are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 304 gms. of a 66 2/3% pigment and 33 1/3% ethyl cellulose composition. This powder disperses very easily in lacquer solvents to form a dispersed system suitable for automotive nitro-cellulose lacquers.

Example 9

A 1-gal. porcelain pebble mill is charged with 200 gms. Indo Maroon Pigment (M; Fig. 118, page 426) and 1460 gms. of a grinding fluid consisting of 50% acetone and 50% water. This is mixed well and to the mixture is added 200 gms. of ethyl cellulose powder N10. About 20 lbs. of steel balls, averaging 1/2" in diameter, are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 394 gms. of vivid maroon powder which yields a beautiful dispersion characterized by high lustre when cut into a nitro cellulose lacquer containing a resin compatible with ethyl and nitro cellulose.

In another operation using 60° acetone and 40° water and with a different pigment—namely, Fanchon Maroon (M; Fig. 105, page 419)—a bright, fine, soft-textured powder is obtained which when cut into a suitable plasticized, nitro-cellulose lacquer forms a clear high luster dispersion. In both operations, the filtrate is led to a recovery still where the solvent is recovered for reuse.

Example 10

A 1-gal. porcelain pebble mill is charged with 159 gms. Tungstated Green Toner (M; Fig. 33, page 383) and 1322 gms. of a grinding fluid consisting of 10% acetone and 90° water. This is mixed well and to the mixture is added 318 gms. Amberol 820 (a rosin modified maleic resin produced by The Resinous Products & Chemical Co.). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 459 gms. of a fine bright soft-textured green powder which disperses readily into alcohol to form a highly dispersed system useful for aniline inks.

Example 11

A 1-gal. porcelain pebble mill is charged with 572 gms. Benzidine Yellow Toner Presscake of 17.5% dry content (M; Fig. 49, page 391) and 518 gms. additional water and 110 gms. acetone. The grinding liquid, therefore, exclusive of pigment now consists of 10% acetone and 90% water. The mill is run for 15 minutes to pre-mix the presscake, water and acetone. It is then opened and there is added 200 gms. Amberol #820 Powder (a rosin modified maleic resin produced by The Resinous Products & Chemical Co.). About 7 lbs. #00 French flint pebbles are added. After milling for about 20 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. There is obtained 286 gms. of a fine soft-textured bright yellow toner suitable for the manufacture of spirit and rotogravure inks.

Example 12

A 1-gal. porcelain pebble mill is charged with 200 gms. Cadmium Red, Light (lithoponic type of cadmium sulfoselenide) and 1600 gms. of a grinding fluid consisting of 50% acetone and 50% water. This is mixed well and to the mixture is added 200 gms. cellulose acetate powder. About 7 lbs. of #00 French flint pebbles are added. After milling for about 70 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filtrate is treated to recover the solvent for reuse and the filter cake is washed, dried and pulverized. One obtains 383 gms. of a fine, soft-textured red powder.

In another operation wherein the same amount of titanium dioxide, anatase type replaces the above pigment, 380 gms. of a soft-textured white powder is obtained.

Both of these products are dissolved in acetone and are used for pigmenting cellulose acetate spinning solutions.

Example 13

A 1-gal. porcelain pebble mill is charged with 980 gms. of 10.2% Lithosol Fast Blue BCS Paste containing 100 gms. of dry pigment (C. I. 1114), 20 gms. of water and 900 gms. of acetone to make 1800 gms. of a grinding fluid consisting of 50% acetone and 50% water. This is mixed well and to the mixture is added 200 gms. of cellulose acetate powder. About 7 lbs. French flint pebbles are added. After milling for about 70 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 286 gms. of a fine, soft-textured blue powder which is used for coloring a cellulose acetate spinning solution.

Example 14

A 1-gal. porcelain pebble mill is charged with 300 gms. Para Toner (Light)—(M; Fig. 66, page 400) and 1500 gms. of a grinding fluid consisting of 23% acetone and 77% water. This is mixed well and to the mixture is added 4½ gms. borax, 4½ gms. boric acid, and 225 gms. Teglac Z-152 (dibasic acid modified alkyd resin—American Cyanamid Co.). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then

washed, dried and pulverized. One obtains 513 gms. of a fine, soft-textured bright red powder consisting substantially only of pigment and plastic which disperses readily into an oil modified alkyd resin to produce a high lustre smooth pigmented enamel. In this example the boric acid and borax mixture was included to maintain neutrality, acting to neutralize the acidity of the Teglac resin which would otherwise possibly cause a modification of the quality of the pigment. Being water-soluble, these neutralization agents are removed in the final washing step.

Example 15

A 1-gal. porcelain pebble mill is charged with 200 gms. Para Red Toner (M; Fig. 66, page 400) and 1200 gms. of a grinding fluid consisting of 5% ethyl acetate and 95% water. This is mixed well and to the mixture is added 200 gms. of Teglac Z-152 (dibasic acid modified alkyd resin—American Cyanamid Co.). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 395 gms. of a red powder suitable for dissolving into a solvent for the preparation of a pigmented enamel.

The substitution of the same amount of butanol for the ethyl acetate does not materially change the operation or the product obtained.

Example 16

A 1-gal. porcelain pebble mill is charged with 300 gms. Toluidine Maroon Powder (M; Fig. 83, page 408) and 1200 gms. of a grinding fluid consisting of 4% acetone and 96% water. This is mixed well and to the mixture is added 300 gms. of pure glyceryl phthalate powder. About 7 lbs. of #00 French flint pebbles are added. After milling for about 70 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 556 gms. of a dark maroon powder which disperses easily when cut into acetone.

Example 17

A 1-gal. porcelain pebble mill is charged with 160 gms. Lithol Red Barium Toner (M; Fig. 93, page 413) and 1000 gms. of a grinding fluid consisting of 35% acetone and 65% water. This is mixed well and to the mixture is added 160 gms. Krumbahr 707 (hard modified phenolic resin manufactured by Krumbahr Chemicals). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 312 gms. of a soft-textured bright red powder which, when mixed with a bodied varnish and passed through a loosely set roller mill, produces a well-dispersed homogeneous red printing ink.

Example 18

A 1-gal. porcelain pebble mill is charged with 30 gms. Lithosol Red 2B Calcium Toner (M; Fig. 91, page 412) and 1000 gms. of a grinding fluid consisting of 50% acetone and 50% water. This is mixed well and to the mixture is added 270 gms. Beetle Molding Powder produced by the American Cyanamid Co. (urea formaldehyde

alpha cellulose filled resin). About 7 lbs. #00 French flint pebbles are added. After milling for about 45 hours, the grinding mixture consists of a heavy slurry which is removed from the ball mill, placed in pans and dried. One obtains a bright red powder suitable for the molding of colored plastic articles.

In another operation using 100 gms. of the above-mentioned pigment and 200 gms. of Melmac (melamine-formaldehyde molding powder also produced by the American Cyanamid Co.) in place of the Beetle resin, a bright red powder is obtained which is also suitable for molding in the usual manner to yield colored molded articles.

Example 19

A 1-gal. porcelain pebble mill is charged with 200 gms. Indanthrene Blue (C. I. 1113) and 1200 gms. of a grinding fluid consisting of 50% acetone and 50% water. To this was also added 40 gms. of Turkey red oil. This is mixed well and to the mixture is added 400 gms. Vinylite VYHH Powder (co-polymer of vinyl chloride and vinyl acetate produced by the Carbide & Carbon Chemicals Corp.). About 7 lbs. of #00 French flint pebbles are added. After milling for about 70 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 608 gms. of a soft-textured blue powder which dissolves easily into methyl iso-butyl ketone to produce an excellent dispersion.

Example 20

A 1-gal. porcelain pebble mill is charged with 100 gms. Lithosol Red 2B Manganese Toner (M; Fig. 90, page 412) and 1200 gms. of a grinding fluid consisting of 75% acetone and 25% water. To this was also added 20 gms. Turkey red oil. This is mixed well and to the mixture is added 200 gms. Vinylite VYHH Powder (co-polymer of vinyl chloride and vinyl acetate produced by the Carbide & Carbon Chemicals Corp.). About 7 lbs. of #00 French flint pebbles are added. After milling for about 70 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 310 gms. of a soft fine bright red powder which dissolves into methyl iso-butyl ketone solvent to produce an excellent dispersion of color in vinyl resin.

In this example, the Turkey red oil was added to facilitate the filtration and produce a softer color.

Example 21

A 1-gal. porcelain pebble mill is charged with 160 gms. Pyrazolone Red Toner (M; Fig. 71, page 402) and 880 gms. of a grinding fluid consisting of 80% dioxane and 20% water. To this is added 32 gms. of Turkey red oil. This is mixed well and to the mixture is added 240 gms. Geon Resin #101 Powder (polymerized vinyl chloride resin powder produced by the B. F. Goodrich Co.). About 20 lbs. steel balls, averaging $\frac{1}{2}$ " in diameter, are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 414 gms. of a bright, soft-textured red powder which is a good dispersion as judged by the fineness of its solution in straight dioxane.

Example 22

A 1-gal. porcelain pebble mill is charged with 75 gms. Carbethoxy Pyrazolone Red Toner (M; Fig. 81, page 407), 600 gms. of dioxane and 600 grams of water resulting in a grinding fluid consisting of 50% dioxane and 50% water. This is mixed well and to the mixture is added 675 gms. Saran Polymer B115 (vinylidene chloride polymer produced by the Dow Chemical Co.). About 7 lbs. of #00 French flint pebbles are added. After milling for about 70 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 740 gms. of a fine soft dry powder characterized by extreme intensity of color indicating a uniform high degree of dispersion of the pigment onto the resin. The substitution of Heliogen Blue Press Cake (type of copper phthalocyanine) containing 13.8% dry pigment for the above-mentioned pigment resulted in a soft, dry blue powder of striking intensity of color.

Example 23

A 1-gal. porcelain pebble mill is charged with 1400 gms. of a grinding fluid consisting of 50% dioxane and 50% water. To this mixture is added 200 gms. polystyrene (emulsion polymerized, produced by Bakelite Corp.) and 200 gms. of Indo Red RV-20 (chemically: methyl amino anthraquinone). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 398 gms. of a fine bright red sandy powder of a good dispersion of this coloring matter in polystyrene resin.

Example 24

A 1-gal. porcelain pebble mill is charged with 100 gms. Carbethoxy Pyrazolone Red Toner (M; Fig. 81, page 407) and 1400 gms. of a grinding fluid consisting of 7.1% ethyl acetate and 92.9% water. This is mixed well and to the mixture is added 200 gms. polystyrene (emulsion polymerized, produced by Bakelite Corp.). About 7 lbs. #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 293 gms. of a fine soft-textured red powder.

Example 25

A 1-gal. porcelain pebble mill is charged with 100 gms. Standardized Toluidine Toner (M; Fig. 64, page 399) and 1200 gms. of a grinding fluid consisting of 7% ethyl acetate and 93% water. To this is added 2 gms. borax. This is mixed well and to the mixture is added 100 gms. Parlon 20 C (chlorinated rubber, produced by Hercules Powder Company). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. Before filtration the pH of this mixture is 6.9. One obtains 175 gms. of a fine bright red powder which disperses readily in coal-tar hydrocarbons.

Example 26

A 1-gal. porcelain pebble mill is charged with

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100 gms. Titanium Dioxide Anatase Type and 1500 gms. of a grinding fluid consisting of 32% acetone and 68% water. This is mixed well and to the mixture is added 200 gms. Plexiglas A-100 (polymethyl methacrylate molding powder produced by Rohm & Haas). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 303 gms. of a white granular mass which can be pulverized for molding purposes.

Example 27

A 1-gal. porcelain pebble mill is charged with 100 gms. Carbethoxy Pyrazolone Red Toner (M; Fig. 81, page 407) and 1600 gms. of a grinding fluid consisting of 20% acetone and 80% water. This is mixed well and to the mixture is added 200 gms. Cumar MH $2\frac{1}{2}$ (para cumarone indene resin, produced by the Barrett Division of the Allied Chemical & Dye Corp.). About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. One obtains 300 gms. of a fine soft bright red powder easily dispersible into rubber.

Example 28

A 1-gal. porcelain pebble mill is charged with 100 gms. Dianisidine Blue Toner (M; Fig. 43, page 388) and 1600 gms. of a grinding fluid consisting of 50% denatured ethanol and 50% water. This is mixed well and to the mixture is added 200 gms. stearic acid triple pressed pearls. About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. After filtration and washing, the cake is dried at 120° F., which is below the melting point of stearic acid and the dried product is then pulverized. One obtains 294 gms. of deep blue lumps which may be comminuted and screened to any desired size, thus forming a non-dusting particle which disperses readily into rubber.

In another operation, Fanchon Maroon Toner (M; Fig. 105, page 419) is substituted as the pigment. The resulting product comprises deep maroon lumps easily comminuted to form granules of a non-dusting color base suitable for melting into appropriate lipstick base to form a good dispersion possessing great tinctorial power.

Example 29

A 1-gal. porcelain pebble mill is charged with 150 gms. Rhodamine B Benzoated Lake (M; Fig. 34, page 384 but the aluminum benzoate lake instead of the phosphotungstic acid lake) and 1600 gms. of a grinding fluid consisting of 30% denatured ethanol and 70% water. This is mixed well and to the mixture is added 150 gms. cetyl alcohol fine shavings. About 7 lbs. of #00 French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product is collected, filtered, washed and dried at 120° F., after which it is pulverized to produce fine non-dusting granules used for the coloring of lipstick base. The filtrate was recovered and used as the grinding medium for another batch of a similar product.

Example 30

A 1-gal. porcelain pebble mill is charged with

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200 gms. Toluidine Maroon Powder (M; Fig. 83, page 408) and 1200 gms. of a grinding fluid consisting of 30% denatured ethanol and 70% water. This is mixed well and to the mixture is added 200 gms. powdered dicyclohexyl phthalate (also sold under the trade-name of "Elastex DCHP" produced by the Barrett Division of the Allied Chemical & Dye Corp.). About 20 lbs. of steel balls, averaging $\frac{1}{2}$ ", are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product is collected, filtered, washed and dried at 120° F., after which it is pulverized. One obtains 393 gms. of a bright maroon non-dusting powder which disperses easily into nitrocellulose lacquers.

Example 31

A 1-gal. porcelain pebble mill is charged with 85 gms. Carbon Black (Neo-Spectra Mark II, produced by Binney & Smith) and 1700 gms. of a grinding fluid consisting of 53% acetone and 47% water. This is mixed well and to the mixture is added 170 gms. of cellulose acetate powder. Twenty pounds of steel balls (average diameter $\frac{1}{2}$ ") are added. After milling for about 20 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. There is obtained 246 gms. of a fine soft-textured black powder which disperses with simple stirring into acetone to yield a master dispersion suitable for the pigmentation of cellulose acetate spinning "dopes."

In another operation 62.5 gms. of a Binney & Smith Superba Carbon Black is used together with 125 gms. of cellulose acetate powder. In this case the grinding fluid replaces acetone with dioxane. The same type of product is obtained by this procedure.

Example 32

A 1-gal. porcelain pebble mill is charged with 150 gms. of cellulose acetate powder and 840 gms. of acetone. To this mixture is then added approximately 7 lbs. of French flint pebbles and the mill is run for about 2 hours to dissolve the cellulose acetate. One then adds 760 gms. of water to precipitate the cellulose acetate out of solution. The addition of the stated amount of water yields 1600 gms. of a grinding fluid containing approximately 52.5% acetone. To the mixture is now added 150 gms. Carbon Black (Excelsior Grade, Binney & Smith). After milling for about 20 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. Approximately 283 gms. of a soft-textured black powder is obtained suitable for the pigmentation of cellulose acetate spinning liquid.

Example 33

A 1-gal. porcelain pebble mill is charged with 150 gms. Carbon Black (Excelsior Grade, Binney & Smith) and 1600 gms. of a grinding fluid consisting of 40% acetone and 60% water. This is mixed well and to the mixture is added 150 gms. of cellulose acetate powder. Seven lbs. of French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. There is thus obtained about 295 gms. of a fine soft-textured black powder.

Example 34

A 1-gal. porcelain pebble mill is charged with 150 gms. Carbon Black (Excelsior Grade, Binney & Smith) and 1600 gms. of a grinding fluid consisting of 65% acetone and 35% water. This is mixed well and to the mixture is added 150 gms. of cellulose acetate powder. Seven lbs. of French flint pebbles are added. After milling for about 45 hours, the mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed, dried and pulverized. There is thus obtained about 296 gms. of a fine soft-textured black powder.

Example 35

With some types of gummy or sticky resins it is at times necessary to treat the resin and pigment in a preliminary step prior to grinding in accordance with the teachings of the invention.

In such a case one proceeds as follows: A resin emulsion is first prepared by mixing 5 grams of a wetting agent (such as Duponol ME, produced by the E. I. du Pont de Nemours & Company), 5 gms. of cyclohexanol, and 10 gms. of water. This mixture is added slowly and with good agitation to 154 gms. of a 65% solution of a melamine-formaldehyde resin dissolved in xylene. The specific resin used is Resamine 882 produced by the Monsanto Chemical Company. To the resin solution 400 gms. of cold water is added gradually, producing a thick, creamy emulsion. This emulsion is added to a smooth slurry of 100 gms. of Amberine Maroon produced by coupling of diazotized 5-nitro-2-amino-anisole with naphthol AS-D in 3000 gms. of cold water. This is stirred for about 5 minutes, by which time the emulsion is broken. The resin and pigment precipitate out of solution at this point. The slurry is then filtered, washed with slightly alkaline water and dried for about 45 hours at 135° F. and then pulverized. It is necessary to dry the presscake to remove the water-immiscible solvents present in the melamine-formaldehyde resin solution.

About 200 gms. of the dry, pulverized, pigmented resin powder produced as aforesaid is placed in a ball mill to which is added 600 gms. of a grinding fluid consisting of 10% ethyl alcohol and 90% water and run for 48 hours, using approximately 7 lbs. French flint pebbles. The mill is discharged and rinsed out with water. The product and wash liquid are collected and filtered. The filter cake is then washed with slightly alkaline water, dried, and pulverized. The yield is approximately 197 gms. of a deep maroon powder. The final product comprising approximately 50% pigment is then formulated by ball mill grinding into a finished alkyd-melamine automotive enamel and compared with a similar enamel prepared in the conventional manner from dry pigment and the various resin solutions. The enamel made by the process of the invention shows a vastly improved richness in shade, higher gloss, and improved transparency.

It will be noted from the above examples that with regard to the percentage of water employed in the liquid grinding medium, one may use from as little as approximately 10% to as much as about 95% by weight, depending upon the solvent selected and the particular plastic to be pigmented. Thus, a more readily soluble plastic, as, for example, Amberol 820, requires a larger percentage of water in the grinding fluid than does a more difficultly soluble solid organic plastic such

as Vinylite VYHH. As stated hereinbefore, the ratio of water to solvent necessary for the selected plastic to be pigmented is determined by the test procedure described earlier. By this test one selects the proper ratio of water to solvent where the liquid composition is a non-solvent for the solid organic plastic.

As was indicated hereinbefore, the amount of liquid grinding medium employed in the process is selected to provide a consistency suitable for optimum milling operation. For example, in using a ball mill employing steel balls, a heavier consistency is utilized than the consistency necessary when employing flint pebbles in the same mill. As can be seen, wide variation in the amount of liquid used is possible depending upon the amount of solids to be milled, the type of milling desired and the types of plastic and pigment to be mixed. Thus, with regard to the milling of pigments with cellulose derivatives, for example, the weight ratio of solids to liquid will involve 1 part of solids to about 3 to 10 parts of liquid grinding medium.

The amount of pigment used in the process, and therefore being present in the final composition, may vary from as little as about 1% to as high as approximately 95% by weight, depending on the end use. For most purposes, however, a range of approximately 30-70% pigment is preferred. For example, in the pigmentation of cellulose acetate spinning dopes where a final pigment concentration of less than 5% by weight is desired, a pigmented cellulose acetate color master batch containing 10-30% pigment would be supplied. On the other hand, in pigmenting plastics to be used in paints, for example, Teglac Z-152, a pigment content of 50% or greater is desirable to allow full freedom in formulation of the paint.

It may be pointed out that one may disperse either a single pigment or a mixture of pigments in a plastic in order to obtain shades not obtainable with a single color.

As will also be noted from the examples given above, it is occasionally advantageous to use additional materials in the milling operation. For example, many solid organic plastics are highly acid and this acidity might adversely affect the final quality of the pigment or might seriously corrode the milling equipment. To overcome this difficulty, one employs suitable buffering or neutralizing agents, preferably water-soluble, and thus capable of being easily removed in the washing operation. Similarly, it is possible to add wetting agents and other materials to improve and modify the color of the final product just as is done in the manufacture of dry color. Thus, one may add Turkey red oil, metallic soaps or other pigment modifying agents to the mixture during the grinding operation to obtain the effect desired.

For the evaluation of the quality of the final product, namely, the dispersion of pigment in plastic, it is frequently convenient to employ a filtration test somewhat similar to that described in the Childs patent, No. 2,059,088, dated October 27, 1936, making necessary modifications for the type of plastic and pigment employed and the nature of the end-use contemplated for the product. These modifications may include operating at pressures higher than that disclosed in this patent or varying the filtering medium employed so that proper comparisons can be made.

The terms color "value," "chromaticity" or "chroma" as used hereinabove or in the claims

are terms well-known in the art and are employed substantially as described and discussed in "Handbook of Colorimetry" by A. C. Hardy, published by the Technology Press.

Having described my invention, what I claim is:

1. A process of manufacturing a dispersion of pigment in solid organic plastic which comprises milling the pigment and plastic for a substantial period of time in a liquid grinding medium consisting essentially of water and a liquid organic water-miscible solvent in which the plastic is at least partially soluble, the water and the solvent being present throughout the milling operation in such proportions that the liquid grinding medium does not dissolve a substantial amount of the plastic and does not cause substantial agglomeration of the plastic, the liquid grinding medium being present at all times in such amounts as to give a fluidity to the mixture which permits effective milling action, continuing the milling operation until a dispersion of pigment in plastic is obtained, and thereafter separating the solid portion from the liquid portion of the milled mixture.

2. A composition of matter produced by the process of claim 1 which consists essentially of pigment dispersed in solid organic plastic in the form of dry, free-flowing particles possessing a chromaticity substantially not less than the pigment portion thereof.

3. A master color batch produced by the process of claim 1 wherein the amount of pigment is within a range of approximately 30-70% of the color batch by weight.

4. The process of claim 1 wherein the solid organic plastic is a cellulose compound.

5. The process of claim 1 wherein the solid organic plastic is selected from a class consisting of cellulose acetate, cellulose acetopropionate, cellulose acetobutyrate, nitro cellulose and ethyl cellulose.

6. A process of dispersing pigment in cellulose acetate which comprises milling the pigment and cellulose acetate in a liquid grinding medium consisting essentially of water and a liquid organic water-miscible solvent in which the cellulose acetate is at least partially soluble, the water and solvent being present throughout the milling operation in such proportions that the liquid grinding medium does not dissolve a substantial amount of the cellulose acetate and does not cause substantial agglomeration of the cellulose acetate, the liquid grinding medium being present at all times in such amounts as to give a fluidity to the mixture which permits effective milling action, continuing the milling action until a dis-

persion of pigment in cellulose acetate is obtained, and thereafter separating the solid portion from the liquid portion of the milled mixture.

7. The process of claim 6 wherein pigment and cellulose acetate are each added to the liquid grinding medium in particulate form, and wherein the cellulose acetate particles are caused to become pigment-receptive by action of the liquid grinding medium thereon, and wherein the milling action produces impinging contact of pigment particles with pigment-receptive cellulose acetate particles.

8. A composition of matter produced by the process of claim 6 comprising pigment dispersed in cellulose acetate in the form of dry, free-flowing particles possessing a chromaticity approaching, or higher than, that of the pigment.

9. A master color batch produced by the process of claim 6 comprising pigment dispersed in cellulose acetate and possessing the property of dispersing readily in a solvent for the plastic portion thereof to yield a colloidal dispersion of pigment in a solution of plastic.

10. A master color batch produced by the process of claim 6, wherein the proportions of pigment to cellulose acetate range approximately from 50-100 to 100 parts by weight.

11. The process of claim 6 wherein the liquid organic water-miscible solvent is acetone.

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