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TINTED GRANULES

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ABSTRACT OF THE DISCLOSURE

Water soluble granules of alkali metal bases and salts capable of forming 1% aqueous solutions with a pH greater than 11 are colored by mixing with a coloring agent and a relatively small amount of a water soluble, volatile, polar hydrogen bonding compound, such as an alcohol, and allowing the compound to evaporate. In some cases with hydrated granules of alkali it is preferable to include a non-volatile hydrogen bondable organic compound such as a non-ionic surfactant.

This is a continuation-in-part of U.S. application Ser. No. 748,644 filed July 30, 1968, now U.S. Pat. No. 3,579,299.

BACKGROUND

This invention relates to compositions of alkali metal bases and salts with coloring agents, said composition being capable of forming aqueous solutions with a pH greater than 11.

It has been found desirable in the past to color particles of alkalies, especially such as are used for household detergents. These colored particles are either used as such or mixed with other white particles to provide a pleasing effect, a distinctive product, or to provide a color change with change in pH. Many household laundry compounds have a pH of 10 or below, low enough to be colored with dyes or colorants to give a color that is stable. This has been accomplished for example by mixing a portion of the detergent slurry with the color and then spray drying.

This procedure requires the use of a separate dryer for each color or extensive clean-up either between colors or when changing from colored to white detergent. Whereas the colored spray dried particles have the same density as the white detergent which minimizes segregation, they also have the same particle size distribution, essentially $-10+65$, which is a serious disadvantage because greater contrast occurs when the colored particles are larger. Smaller particles give an overall off-color to the finished detergent. It is obvious then, that a large portion of the spray dried colored particles are either not effective in giving contrast or actually give poorer contrast contributing to an overall dirty appearance. These spray dried particles are also relatively soft and can be broken quite easily reducing contrast and forming colored fines that detract from the product.

Screening of the fine material and reworking it has been practiced, but this is expensive. Spray dried product streams have also been split and a portion screened, colored, and returned to the product. This effectively avoids the initial fines content but gives a product of uneven moisture content and the colored product is not uniform in color. Naturally, this does not change the natural friability of the spray dried particles.

In some cases, for example scouring powders and dry blended detergents, the pH is considerably over 10 and it is difficult to apply the coloring agents without causing severe color changes. A blue, for example, may be entirely

satisfactory on a spray dried laundry detergent of pH 10 but give an uneven red-purple or black color to a detergent of pH 11 or higher. Many times a material with a higher pH may be added not only for its detergent or builder performance but also because it is more resistant to attrition and therefore prevents dusting and preserves contrast.

The alkaline materials are prepared in many ways, for example anhydrous sodium metasilicate can be made by fusion of sodium carbonate and quartz or by drying a concentrated sodium metasilicate liquor. Sodium metasilicate pentahydrate is made by crystallization in a liquor below the melting point of 72° C. Sodium orthophosphate is prepared by neutralization of phosphoric acid with soda ash or caustic and drying. Sodium carbonate is made by drying the bicarbonate in a rotary kiln. Caustic soda is usually prepared from electrolysis of brine.

Taking the sodium metasilicate pentahydrate system, for example, the colorants may be added to the liquor before crystallization to obtain a suitable product. However, this is not economically attractive because of equipment contamination, production of unusable fines, and lower color intensity for a given amount of colorant. The colorants must be alkali stable and be carefully selected so that they will disperse in the high solids, highly alkaline liquor to give a true color. Dispersed phthalocyanine pigment, acid dyes and various other water or oil soluble dyes have been applied in this manner but they either coagulate in the liquor or give a dull or dirty color. We find that the dyes or pigments on a support such as silica or titanium dioxide are likely to give the best color when added to the sodium metasilicate liquor. Colors added to the liquor are strongly held to the surface of the final granules and will not rub off and give a dirty appearance to the detergent.

Dyes or pigments may also be sprayed onto the particles after crystallization, crushing and screening or the particles can be dipped into a dye or pigment suspension or solution. Unless the dyes or pigments are soluble or dispersible in water or other polar solvents such as methanol, the particles do not color uniformly. Use of such solvents in the amounts necessary to dissolve or disperse the color can lead to structural changes in the particles resulting in higher bulk density or even in the production of finer particles. Spirit-soluble dyes in glycols do not color the particles uniformly and the colors tend to change on aging.

Dry pigments or dyes can be added directly to the surface of these alkalies in varying degrees of uniformity and will adhere sufficiently to color the particles but not strongly enough to prevent a portion of the colorant rubbing off and discoloring the white particles in the detergent.

Thus coloring of these alkalies would require several processes and in some cases coloring would be very difficult during processing, if not impossible. With our method these alkalies can all be colored uniformly and economically with only slight modification of the basic process.

SUMMARY AND DESCRIPTION OF THE INVENTION

We have found that we can color the said alkali products uniformly with a strongly adhering colorant that does not rub off. This invention is by no means an obvious procedure. The surfaces of the alkaline particles must be treated with a water soluble, volatile, organic hydrogen bonding polar solvent or mixture of such solvents as methanol, ethanol, isopropanol, Cellosolve, water, etc. so that all of the surfaces will be receptive to the colorant and coloration will be uniform. In the case of hydrated products we prefer to use, in addition, a non-volatile, organic hydrogen-bondable, water miscible liquid

or mixture of liquids to prevent rub-off of the color onto other ingredients in detergent mixtures:

Nonionic surfactants, such as the alkyl phenoxypolyethoxy ethanols or the alkyl aryl polyether condensation products of higher fatty alcohols with ethylene oxide, e.g. the reaction product of oleyl-alcohol with 10 ethylene oxide units; or

Condensation products of alkylphenols with ethylene oxide, e.g. the reaction product of isooctylphenol with 12 ethylene oxide units; or

Condensation products of higher fatty amides with 5 or more ethylene oxide units; or

Polyethyleneglycol esters of long chain fatty acids, e.g. tetraethylene glycol monopalmitate or hexaethylene glycol monolaurate or nonaethylene monostearate or nonaethylene glycole dioleate, or tridecaethyleneglycol monoarachidate, or tricosaethylene glycol monobehenate, or tricosaethylene glycol dibehenate; or

Ethyleneoxide condensation products of polyhydric alcohol partial higher fatty acid esters and their inner anhydrides (for instance, mannitol-anhydride called Mannitan and Sorbitol-anhydrate called Sorbitan) such as glycerol monopalmitate reacted with 10 molecules of ethylene oxide, or pentaerythritol monooleate reacted with 12 molecules of ethylene oxide, or Sorbitan monostearate reacted with 10 to 15 molecules of ethylene oxide, or Mannitan monopalmitate reacted with 10 to 15 molecules of ethylene oxide; or

Long chain polyglycols in which one hydroxyl group is esterified with a fatty acid and the other hydroxyl group is esterified with a low molecular alcohol, such as methoxy polyethylene glycol 550 monostearate (550 meaning the average molecular weight of the polyglycol ether) are especially effective but other hydrogen-bondable liquids of low volatility such as diethylene glycol, ethylene glycol, glycrine, triethanolamine, etc. may be used. Any combination of these non-volatile spreading agents may be employed. A further advantage of these compounds is an increase in color intensity.

Any order of addition can be used except that preferably the volatile and non-volatile components should not be premixed. However, we prefer to spray on the low-volatile, hydrogen-bondable liquid if required. Dry colors such as phthalocyanine blue or green, ultramarine blue or red, and quinacridone red on a silica support of H–6–3–A and H–6–3–B proprietary colors from Ferro Corporation are suitable. These colors or pigments must be stable to alkali at a pH above about 11. About 0.5–5% pigment is required according to the shade desired. We prefer about 0.5–2% pigment. We prefer about 1–2% of denatured alcohol or isopropanol although 0.1–5% of any suitable polar solvent or mixtures of solvents may be used. We prefer 0.5–2% of a liquid, water miscible nonionic surfactant especially from the group of alkyl aryl polyethers or of any non-volatile hydrogen-bondable liquid but this amount can vary from 0.1–5% depending primarily on the oil absorption characteristics of the base. The higher the oil absorption of the particles, the more of each polar compound is needed, but usually the amount added will be below that which will cause the composition to appear damp.

We can use any suitable equipment to apply the color and liquids. We prefer to spray the liquids onto the agitated material, but a reasonably satisfactory product can be prepared by dripping the liquids on the solid in a mixer. A screw conveyor, ribbon blender, simple rotating drum, or any apparatus which will give an intimate mixture and even distribution are suitable mixing devices.

In the coloring procedure, the alkaline particles, the color and the polar volatile compound are tumbled together until they become uniformly damp and deep colored; the rotating unit or tumbling unit is then opened and the tumbling continued until the polar volatile compound has disappeared. This polar volatile additive serves to spread and intensify the color on the particle surfaces,

to attach the color more strongly to minimize later rub-off, and then to evaporate readily after having done its part.

The inorganic alkalies used in this invention are the well known alkalies useful as detergents and as detergent builders for use in washing fabrics, as in a laundry, for use in washing dishes, and for use in cleaning metal. The inorganic alkalies included are those which will provide a pH of 10 or greater in a solution containing 0.02% of Na_2O. This group includes caustic soda, soda ash, sodium orthophosphate, sodium orthosilicate, sodium sesquisiliate, sodium metasilicate and sodium disilicate, as examples. These may be anhydrous or hydrated. The particles may be either expanded or dense but must be sufficiently alkaline to form a 1% solution having a pH greater than 11; preferably they will have a pH greater than 12 and the process and product are even more particularly applicable to alkali granules forming such solutions with a pH of 13 and above.

The volatile polar hydrogen bonding water soluble organic compounds are low molecular weight alcohols and polyalcohols, amines, ketones, aldehydes and the like. The nonvolatile hydrogen bondable organic compounds are non-ionic surface active agents, polymeric glycols, high molecular weight alcohols, amines and aldehyde and ketones in general.

The colors which are useful in this application are pigments or dyes which are stable under alkaline conditions. They may be organic or inorganic. For most purposes we prefer water insoluble colors. Alkali-resistant inert mineral pigments usually exclude lead colors or those with reactive calcium or magnesium and reactive heavy metals. There are many which are useful such as chromium oxide and derivatives, lime-free iron oxides, alkali resistant ultramarines, ochre, umber, manganese dioxide, grease-free graphite, cobalt silicate and combinations of such pigments. Organic lakes are usually satisfactory and many alkali-resistant direct dyes are well known such as phthalocyanines, monastrals and cyanogreens, and also the colors described by R. W. Kumler in TAPPI 41 (3), 173A (1958). Water soluble dyes such as phenol and thynolphthalein and methyl red are also applicable. In general the dyes and pigments known to be useful as soap dyes, casein colors, and for roofing granules may be employed. It is only necessary to check a small portion with the alkali detergent particles to determine their compatibility.

EXAMPLES

In these examples the following alkali-stable colors were used:

Ultramarine Blue (59–4977) from United Ultramarine & Chemical Co. Inc.

Green (Dry Color 37–1471) from Ferro Corp.

Imperial A 2989CP Toluidine Toner from Hercules Chemical Co. (red)

Jet Milled Synthetic Red Oxide J–3103 from Mineral Pigments Corp.

Hercules A–4329 Para Toner Extra Light from Hercules Chemical Co. (red)

United Ultramarine Red RU 2001 (lavender) from United Ultramarine & Chemical Co. Inc.

Chili Red Pigment (molybdate orange toner) from Imperial Chemicals Co.—50% Quinacridone red extended with 50% of hydrated finely divided silica (fuschia red).

Ferro H–6–3–B (blue) from Ferro Corporation.

Ferro H–6–3–A (green) from Ferro Corporation.

The alcohol was denatured ethanol formula SD–30 or 40–7.

Anhydrous sodium metasilicate was Metso Beads 2048 from the Philadelphia Quartz Co. This is anhydrous sodium metasilicate having a principal particle size range from 20 to 48 mesh (Tyler Screen Size).

Trisodium phosphate-12 hydrate was the technical crystalline product sold by J. T. Baker Co.

Washington soda ($Na_2CO_3.1H_2O$) was the Arm & Hammer concentrate sold by Church & Dwight Co.

Triton X–100 is a non-ionic surface active agent, octyl phenoxy polyethoxy ethanol, sold by Rohm & Haas Co.

Triton CF 10 is a non-ionic alkyl aryl polyether surfactant with low foaming properties and a freezing point of 61–63° C. sold by Rohm & Haas Co.

Triton N–101 is a non-ionic nonylphenoxy polyethoxy ethanol sold by Rohm & Haas Co.

Color stability was examined by exposing the color granules of alkali to sunlight. Glass jars containing the colored product were closed to prevent entrance of moisture. No change in appearance was found over a period of two months.

Color rub-off was determined by rotating a jar containing the colored granules and fragments of unglazed porcelain for about one minute. Colored alkaline particles to which the color had not been bonded with the volatile hydrogen bonding agent showed considerable loss of color to the unglazed porcelain fragments. Color bound by the evaporation of the volatile hydrogen bonding component showed very little discoloration of the unglazed poreclain with anhydrous materials. Most hydrated alkaline particles required a non-volatile hydrogen bonding agent in addition to the volatile one.

The added color had practically no effect on the performance of the alkali granules. The insoluble content, of course, was increased slightly. This was compared by agitating a solution of 5% of colored granules in water at room temperature for 5 minutes and then filtering and drying the filter papers. The uncolored granules had a residue of 0.02% and the colored granules had residues from 0.3 to 0.9%. The dissolving rate was checked by making up dispersions of 5% in water at 49° C. Within a minute the alkali had totally dissolved, whether colored or not.

The colored granules were used in the detergent in a standard automatic dishwasher on new and old white plastic surfaces and on a white enamel. The effect was tested by measuring the reflectance with a Hunter reflectometer.

EXAMPLE 1

In an enclosed glass cylinder, 250 parts by weight of anhydrous sodium metasilicate particles in the Tyler Screen Size range of 20–48 mesh and from 0.25% to 1% of a colored pigment based on the weight of the sodium metasilicate were tumbled at room temperature until an even dispersion was obtained. Then 2.5 parts by weight of denatured ethanol was scattered on the aggregates (as by spraying) and the cylinder further tumbled and rotated until the contents were uniformly damp. The cover was then removed and the cylinder rotated until no odor of alcohol remained and the cylinder had lost approximately the weight of the alcohol added. The pigments used in this test were Ultramarine Blue 59–4977; Green (Dry Color 37–1471); Jet Milled Synthetic Red Oxide J3103; Imperial A2989CP Toluidine Toner; Hercules A4329 Para Toner Extra Light; Ultramarine Red RU 2001; Chili Red Pigment (Molybdate Orange Toner), and 50% Quinacridone Red spray dried on 50% of hydrated finely divided silica. Colored particles of alkali were tested for color adherence. When a control portion of 250 parts by weight of the anhydrous sodium metasilicate particles and 2.5 parts by weight of the color, e.g. ultramarine blue, were dry blended to uniformity and then rotated for one minute with a fragment of white porcelain, the porcelain developed a bluish tint.

When, however, the color was bound to the anhydrous metasilicate by the above drying procedure with alcohol, only a faint tint developed on the porcelain even with 1% of the color. Colors varied somewhat in their resistance to rubbing but none gave more than a faint tint to the porcelain fragments.

Comparative tests were run in a Kitchen-Aid dishwasher to determine deposition of color on plastic dishes and enameled objects. Twelve complete cycles were run on each of the following materials:

(1) A commercial dishwashing detergent.

(2) A commercial dishwashing detergent with 10% of green colored anhydrous particles, and

(3) A commercial dishwashing detergent with 10% of blue colored anhydrous particles.

Washing temperatures were 140/160° F. There was no noticeable change in any of the objects. When measured with a Hunter Reflectometer, no significant changes were detected. For example, a new white plastic saucer showed 1% less whiteness after washing with a standard dishwasher compound. When tested with the detergent containing blue particles, the change was —1.5%. With the old saucer the standard material gave a change of —3.8% while the colored beads gave —0.2 and —1.5, respectively. In the case of the enameled pan, the standard material gave a change of —1.3 of whiteness while the two colored beads tested showed —.1 and —3.1, respectively.

EXAMPLE 2

To 100 lbs. of anhydrous sodium metasilicate granules having a particle size in the range of 20 to 48 mesh (Tyler Screen Size) was added 0.2% by weight of an alkali-resistant insoluble color, Ultramarine Blue (59–4977). These were mixed in a drum until the color was well distributed and then 1 part by weight of denatured ethanol was sprayed onto the mixture with mixing continued until the mass was uniformly damp and even in color. Evaporation was prevented. At this point the cover was removed and the mixing continued until the alcohol evaporated. The product was discharged when the odor of the alcohol had disappeared. The resulting granules were uniformly colored and did not rub off when mixed in a detergent or when tested with the porous porcelain plate.

EXAMPLE 3

To form a colored additive, 2% blue pigment (Ferro H–6–3–B) was added to —10+28 mesh expanded pentahydrate sodium metasilicate in a jar and then rolled in the jar on a roller mill until thoroughly dispersed. Then 10% of this colored material was added to a white detergent. Contrast was excellent but when the mixture was vigorously shaken by hand, blue color came off the pentahydrate sodium metasilicate and discoloured the whole detergent. Heat treatment and treatment of the blue pigment with acetone increased the color but did not prevent the rub-off when mixed in the detergent.

Uncolored product was then treated with 2 to 4% Triton X–100 surfactant and 2% of the blue pigment (Ferro H–6–3–B). When mixed with white detergent, these products gave little or no rub-off.

In further tests with this product treated with from 2 to 10% of Triton X–100 and 2% of either the blue or green Ferro pigment, a non-uniform coloring was noticed with some particles or particle faces white and others colored. Change in the order of addition did not give any improvement.

When the product, expanded pentahydrate sodium metasilicate, was treated with 1% ethanol, or 1% isopropanol, or 1% acetone, either before or after color addition, and treated with Triton X–100, the final product was uniform and did not rub off in the white detergent. It was found that 2% of the dry color gave uniform results when added with the alcohol and Triton treatments. The alcohol was followed to evaporate before tests were made.

A total of 252 kilos of the expanded pentahydrate sodium metasilicate product having an apparent density of 36 lbs./ft.^{3} and —10+48 mesh was loaded into a rotary

concrete mixer. One percent by weight of denatured alcohol was run in on the tumbling bed of low density pentahydrate sodium metasilicate through a distributor pipe from the tank mounted on top of the mixer normally used for water addition. Next, 1.5% (3.75 kilos) of blue pigment (Ferro H–6–3–B) was added while the mixer was turning. Another 1% of denatured alcohol was then added giving a uniform color. Mixing was continued and about 5 minutes later 1% (2.5 kilos) of a non-ionic detergent oil, Triton X–100, was sprayed into the tumbling bed with a Devilbiss Spray Gun at 70 p.s.i.g. After approximately 5 more minutes, the mixer was discharged into fiber drums and the remaining alcohol was allowed to evaporate. The resulting product was uniformly colored and the color did not rub off when mixed with a white detergent. Because of improved mixing, the color was as intense as the 2% of pigment used in laboratory preparations.

EXAMPLE 5

$Na_3PO_4 \cdot 12H_2O$ was screened to 20–48 mesh (Tyler). 120 parts by weight of the screened material was tumbled as in Example 1 with 0.6 parts by weight of Ultramarine Blue 59–4977. 20.2 parts were removed and the remainder treated with 1% denatured alcohol formula 40–7 while tumbling. When the color and texture were uniform, the alcohol was allowed to evaporate. Both materials gave some rub-off of color in the porcelain plate test.

0.25% of a non-ionic (Triton N–101) was added to the alcohol treated blue material and tumbling continued until uniform, after which the alcohol was evaporated. Rub-off of color was very faint when compared to the samples without the non-volatile hydrogen bonding agent.

EXAMPLE 6

120 parts by weight of concentrated washing soda ($Na_2CO_3 \cdot H_2O$) of 20–48 mesh was treated as in Example 1 with 1% Ultramarine Blue, 8% alcohol, because of its high absorptivity, and 0.25% Triton N–101. The alcohol was then evacuated. The resulting product was brighter and had very faint rub-off compared with a sample omitting the alcohol and Triton N–101 entirely.

More or less specific claims will be presented hereinafter and even though such claims are rather specific in nature, those skilled in the art to which this invention pertains will recognize that there are obvious equivalents for the specific materials recited therein. Some of these obvious equivalents are disclosed herein and other obvious equivalents will immediately occur to one skilled in the art and still other obvious equivalents could be readily ascertained upon rather simple routine noninventive experimentation. Certainly no invention would be involved in substituting one or more of such obvious equivalents for the materials specifically recited in the claims. We intend that all such obvious equivalents be encompassed within the scope of this invention and patent grant in accordance with the well known doctrine of equivalents as well as changed proportions of the ingredients which do not render the composition unsuitable for the disclosed purposes.

What we claim is:

1. The process for forming colored granules which consists essentially of:

(A) agitating together in a suitable mixing zone:

(a) water-soluble alkaline granules capable of forming a 1% aqueous solution having a pH of at least 11, said granules consisting of alkali metal bases and salts that are useful for detergents and detergent builders,

(b) 0.5 to 2% by weight of alkali-stable water-insoluble pigments and dyes,

(c) 0.1 to 5% by weight of a polar, volatile, hydrogen-bondable, water-soluble, organic solvent,

(B) continuing said agitation until the granules are uniformly damp and deep colored,

(C) evaporating said polar, volatile, hydrogen-bondable, water-soluble, organic solvent from said admixture, and

(D) recovering the alkaline granules having an alkali-resistant color uniformly distributed and securely bound to their surfaces.

2. The process of claim 1 wherein said alkali metal bases and salts are selected from the group consisting of caustic soda, soda ash, sodium orthophosphate, sodium orthosilicate, sodium sesquisilicate, sodium metasilicate and sodium disilicate.

3. The process of claim 2 wherein said polar, volatile, hydrogen-bondable, water-soluble low molecular weight organic solvent is selected from the group consisting of low molecular weight alkanols, lower alkyl ethers of ethylene glycol, and low molecular weight ketones.

4. The process of claim 1 wherein there is also introduced into the mixing zone 0.1 to 5% by weight of a non-volatile, hydrogen-bondable, organic water-miscible non-ionic surface active agent capable of wetting both the water-soluble alkaline granules and the alkali-stable water-insoluble pigments and dyes.

5. The process of claim 4 wherein said water-soluble alkaline granules are hydrated.

6. The process according to claim 3 wherein there is introduced into the mixing zone a non-volatile, hydrogen-bondable, organic, water-miscible, non-ionic surface active agent selected from the group consisting of (a) the alkyl aryl polyether condensation products of higher fatty alcohols with ethylene oxide, (b) condensation products of alkylphenols with ethylene oxide, (c) condensation products of higher fatty amides with five or more ethylene oxide units, (d) polyethyleneglycol esters of long chain fatty acids, (e) ethylene oxide condensation products of polyhydric alcohol partial higher fatty acid esters and their anhydrides, (f) long chain polyglycols in which one hydroxyl group is esterified with a fatty acid and the other hydroxyl group is esterified with a low molecular weight alcohol, (g) diethylene glycol, (h) ethylene glycol, (i) glycerine, and (j) triethanolamine.

7. A colored water-soluble alkaline granule produced in accordance with the process of claim 1.

8. A colored water-soluble alkaline granule produced in accordance with claim 4.

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