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COMPOSITION COMPRISING ICE COLOR COUPLING COMPONENTS

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This invention relates to dispersible solubilized compositions containing azo dye intermediates which are devoid of sulfonic acid and carboxylic acid groups, such as the class of which the arylamides of 2:3-hydroxy-naphthoic acid are representative, and to new compositions of matter useful in printing which includes those dispersible solubilized intermediates.

These intermediates are generally known as ice color coupling components and they are extensively used in the making of developed dyeings. One difficulty encountered in the making of developed dyes with these coupling components is that the coupling components are largely insoluble in the ordinary dye bath and they must be first brought into solution in a bath containing an excess of caustic soda. The developed colors have been applied in various ways but they are usually applied by impregnating the entire fabric with one component of the dye, developing by printing onto the fabric in the selected design with a printing paste containing the other component, and then removing the excess of the first intermediate by soaping and washing. The excess of caustic soda in the solution of the coupling component presented an inconvenience. When arylamides, such as an arylamide of 2,3-hydroxy-naphthoic acid were mixed with diazoimino compounds, they had to be wet out with an agent, such as alcohol, "Cellosolve" or some other active solvent before they could be dissolved in caustic soda solution. The wetting out of the coupling component was an operation which was desirable to avoid.

According to the present invention the wetting out of the coupling component in the compounding of a printing paste is avoided. The presence of an undesirable excess of caustic soda in a paste which contains both components of the dye is also avoided. In making a dyeing the printing paste is applied directly to the fabric in the selected design and the dye is developed in the usual way by exposing the printed fabric to a suitable developing agent.

The objects of the invention are attained by thoroughly mixing in an aqueous medium an ice color coupling component of the type represented by the arylamides of 2:3-hydroxy-naphthoic acid, an alkali, dextrin or the sodium salt of Turkey red oil, a dispersing agent such as the condensation product of formaldehyde and naphthalene beta sulfonic acid, subjecting the mixture to milling so as to attain uniformity, drying, and subdividing to selected fineness. It is frequently preferred to dry the compound on an atmospheric drum drier in order to obtain a flaked or granular product and, when this is done, the sodium salt of Turkey red oil is preferred. This composition is readily soluble in aqueous sodium hydroxide solutions. An excess of alkali over that required to form the sodium salt is commonly required in the composition to make the product instantly soluble. It is frequently desirable from the point of view of health to include only enough alkali to produce a turbid suspension. The turbidity of the suspension can then be removed by adding alkali to the bath.

The preferred composition of matter of this invention, consequently, comprises a coupling component of the type described, or the alkali metal salt thereof, alkali, dextrin or the sodium salt of Turkey red oil, and a dispersing agent. The preferred process comprises mixing these components and subjecting them to plastic milling or drying on an atmospheric drum drier.

If a complete composition useful in printing is desired, an alkali stable diazoimino compound is included in the mixture.

Where the free acid form of certain favorable ice color coupling components is used, no alkali is added, and the products wet out and disperse in water rapidly to produce turbid suspensions. Addition of alkali to these suspensions produces clear solutions of the alkali salts of the ice color coupling components. Where the alkali metal salt of the ice color coupling component is used, the products exhibit similar behavior, producing turbid solutions containing both the ice color coupling components in the free state and alkali metal salts if little alkali is added. Clear solutions are produced at once if sufficient alkali is included.

The class of ice color coupling components to which this invention is particularly applicable is the arylamides of 2:3-hydroxy-naphthoic acid, which constitutes a preferred class. The invention is also applicable to the arylamides of other ortho-hydroxy-aryl-carboxylic acids, and to the arylamides of beta-keto-carboxylic acids. In the following examples only the preferred class of arylamides of 2:3-hydroxy-naphthoic acid are used. However, the processes are equally applicable to the preparation of dispersible and/or soluble compositions from all other ice color coupling components, examples of which are the arylamides of 2-hydroxy-carbazole-3-carboxylic-acid, 7-hydroxy-alpha-naphtho-carbazole-6-carboxylic-acid, 2-hydroxy-anthracene-3-carboxylic-acid, and 2-hydroxy-diphenylene-oxide-3-carboxylic-acid, arylamides of acyl-acetic-acids

and tere-phthaloyl-bis-acetic-acids, amino-naphthols, and acylamino-naphthols. Examples of particular coupling components which give products quite as satisfactory as those listed in the examples are:

1-(2':3'-hydroxy-naphthoylamino)-4-methylbenzene
1-(2':3'-hydroxy-naphthoylamino)-2:4-dimethyl-benzene
1-(2':3'-hydroxy-naphthoylamino)-2-methoxybenzene
1-(2':3'-hydroxy-naphthoylamino)-4-methoxybenzene
1-(2':3'-hydroxy-naphthoylamino)-2:5-dimethoxy-benzene
1-(2':3'-hydroxy-naphthoylamino)-4-chlorobenzene
1-(2':3'-hydroxy-naphthoylamino)-3-fluorobenzene
1-(2':3'-hydroxy-naphthoylamino)-3-nitro-benzene
1-(2':3'-hydroxy-naphthoylamino)-2-methyl-4-chloro-benzene
1-(2':3'-hydroxy-naphthoylamino)-2-methyl-4-methoxy-benzene
1-(2':3'-hydroxy-naphthoylamino)-2:4-dimethoxy-5-chlorobenzene
Di-4:4'-(2'':3''-hydroxy-naphthoylamino)-3:3'-dimethoxy-diphenyl.

If the composition is to be dried on a drum drier the sodium salt of Turkey red oil should be used, but if other methods of drying are to be used dextrin is preferred. Any of the dextrins can be used. Certain assistants to dextrin, such as sugar, can also be employed.

The dispersing agents used are those customarily employed in the art for the dispersing of dyes. The condensation product of formaldehyde and naphthalene-beta-sulfonic acid is particularly satisfactory, but any such dispersing agent can be used.

The composition must be a uniform mixture such as a mixture producible by plastic milling. By "plastic milling" is meant the subjection of the mass to disintegration by internal work. However, any mixing of the components which produces a uniform composition is satisfactory.

By drying the composition on an atmospheric drum drier flakes may be produced which have the advantage of eliminating dust and all its attending disadvantages from the dye house.

The following examples illustrate the invention but do not limit it. All quantities are stated in parts by weight.

Example I

A mixture of 49 parts of dextrin and 2 parts of the condensation product of naphthalene-beta-sulfonic acid with formaldehyde was placed in a Werner and Pfleiderer mixer and made into a smooth paste by mixing with 30 parts of water. To this paste was added 49 parts of 2-(2':3'-hydroxy-naphthoyl-amino)-naphthalene and the resulting plastic mass was milled for one hour. Additional water (10 parts) was added during the milling to replace part of that lost by evaporation due to the heating up of the plastic mixture. The well-mixed product was removed from the mixer, dried in a vacuum oven, and coarsely ground. The virtually dry product wet out and dispersed readily in water, forming a turbid suspension which dissolved completely when heated in the presence of caustic soda.

Free arylamides of 2:3-hydroxy-naphthoic acid described in the prior art do not wet out and disperse in water. In every case they must first be made into a paste with a wetting out agent, such as an alcohol or a sulfonated castor oil derivative, before an aqueous dispersion can be obtained.

Example II

2':3'-hydroxy-naphthoyl-amino-benzene (40 parts) was stirred to a smooth paste with 20 parts of ethyl alcohol. This paste was diluted with 40 parts of water and transferred from the mixing vessel to a vacuum graining bowl. Dextrin (29 parts), powdered cane sugar (28 parts), and the condensation product from naphthalene-beta-sulfonic acid and formaldehyde (3 parts) were added and the mixture agitated until uniform. Water was removed by warming the mixture under vacuum until a viscous, plastic mass was obtained. This mass was agitated under atmospheric pressure, for one hour, and then dried by warming and applying vacuum. The dried product was removed from the graining bowl and coarsely ground.

The product so obtained wet out and dispersed readily in water and dissolved to a clear solution on addition of caustic soda to the resulting aqueous suspension.

Example III

2-(2':3'-hydroxy-naphthoyl-amino)-naphthalene (34 parts) was stirred to a smooth paste with 20 parts of ethyl alcohol and converted to its sodium salt by addition of 34 parts of 36° Bé. caustic soda solution. This mixture was transferred from the mixing vessel to a vacuum graining bowl. The alcohol was removed by warming slightly and applying vacuum. The residue was diluted with 40 parts of water and then dextrin (27 parts), powdered cane sugar (26 parts), and a dispersing agent (3 parts of the condensation product of formaldehyde and naphthalene-beta-sulfonic acid) were added. This mixture was agitated and the excess water removed by warming under vacuum. The resulting viscous, plastic mass was ground by plastic milling under atmospheric pressure for one hour and then dried by warming and applying vacuum. The dried product was removed from the graining bowl and coarsely ground. When added to water this product rapidly wet out and dispersed. Upon addition of a small amount of alkali complete solution was rapidly obtained.

In the making of a composition for application to and development on a fabric, a diazoimino compound, such as the compound made by reacting piperidine-alpha-carboxylic acid with 4-chloro-2-amino-toluene, is added to the mixture after it has been well mixed with alkali and the plastic milling is continued. The resulting dried product is made into a paste in the usual way with starch tragacanth thickener, applied to a roll and by a roll to the fabric. The printed fabric is subjected to hot acetic acid vapors which overcome the alkalinity of the composition and permit coupling on the fiber. Material prepared by this procedure wets out and dissolves completely in hot dilute caustic soda solution.

2':3'-hydroxy-naphthoyl-amino-benzene processed by the above procedure yields a product which dissolves completely in water without the addition of more caustic soda solution.

The presence of dextrin in these mixtures of alkali metal salts of arylamides of 2:3-hydroxy-naphthoic acid protects them from decomposition over reasonable periods of time and the mix-

tures wet out and disperse rapidly in water. Products of the prior art neither exhibit the ease of solubility shown by these products nor involve the use of a protective agent.

Example IV

1-(2':3' - hydroxy - naphthoyl - amino) -naphthalene (34 parts) was stirred to a smooth paste with 20 parts of ethyl alcohol and converted to a sodium salt by addition of 34 parts of 36° Bé, caustic soda solution. This mixture was dissolved in 125 parts of a 30% solution of an assistant, such as the condensation product of beta-naphthalene-sulfonic acid with formaldehyde. This solution was further diluted by the addition of a solution of 15 parts of dextrin and 8 parts of powdered cane sugar in 60 parts of water. The solution was thoroughly mixed and then dried on a rotary drum drier. The dried product, in the form of flakes, wet out and dissolved completely in warm water.

Example V

1-(2':3'-hydroxy-naphthoyl-amino)-2-ethoxybenzene (40 parts) was stirred to a smooth paste with 25 parts of ethyl alcohol and the paste was diluted by the addition of 135 parts of a 30% solution of an assistant, such as the condensation product of beta-naphthalene-sulfonic acid with formaldehyde. This suspension was further diluted by the addition of a solution of 15 parts of dextrin and 8 parts of powdered cane sugar in 50 parts of water. The suspension was thoroughly mixed and then dried on a rotary drum drier. The product wet out rapidly in water and dissolved to a clear solution in dilute, aqueous caustic soda solution.

Example VI

A water-soluble composition of matter suitable for the production of dyes on the fiber was prepared by mixing a dispersible ice color coupling component of this invention with a water-soluble diazoimino or diazoamino compound in approximately equimolecular proportions. Such a composition consising of 100 parts of the dispersible sodium salt of 1-(2':3'-hydroxy-naphthoyl-amino)-2-methyl-benzene of 40% strength and 40 parts of a diazoimino compound, obtained by reacting the diazo compound from 4-chloro-2-amino-toluene with piperidine-alpha-carboxylic acid was completely soluble in hot water. An aqueous solution of the above mixture was added to neutral starch gum tragacanth thickener and printed on cotton cloth. The printed material was dried and then subjected to steam and acetic acid fumes for a short period. A red printed pattern of good brilliance and fastness was obtained.

Example VII

A mixture consisting of 100 parts of the dispersible sodium salt of 1-(2':3'-hydroxy-naphthoyl-amino)-2-ethoxy benzene prepared according to this invention and 40 parts of diazoimino compound obtained by condensing the diazo compound from 4-chloro-2-amino-toluene with piperidine-alpha-carboxylic acid was completely soluble in hot water. An aqueous solution of the above mixture was added to neutral starch gum tragacanth thickener and printed on cotton fabric. The printed material was dried and then subjected to steam and acetic acid fumes. A bright scarlet pattern of good fastness was obtained.

Example VIII

2':3' - hydroxynaphthoylamino - benzene (50 parts) was mixed with ethyl alcohol (25 parts) and water (50 parts) to form a smooth paste. To this paste was added Turkey red oil (10 parts) and isopropylated naphthalene-beta-sulfonic acid (1.5 parts). This mixture was agitated and caustic soda solution (70 parts, 36° Bé.) was added. The resulting paste of the 2':3'-hydroxy-naphthoylamino-benzene-sodium-salt was diluted with water (50 parts), thoroughly mixed, and then dried on a rotary drum drier. The dried product was collected in the form of dense flakes which were virtually non-dusting, and which wet out and dissolved completely in cold water.

Example IX

2':3'-hydroxybenzoylamino-benzene (10 parts) was mixed with Turkey red oil (2.5 parts) and an aqueous solution of isopropylated beta-naphthalene-sulfonic-acid (0.8 part in 10 parts of water). This mixture was stirred to a smooth paste and caustic soda solution (17 parts, 36° Bé.) was added to convert the 2':3'-hydroxynaphthoyl-amino-benzene to its sodium salt. The resulting thick paste was thoroughly mixed and then diluted with an aqueous solution of sodium carbonate (1.8 parts in 10 parts of water). The resulting mixture was further diluted with water (4 parts), agitated until uniform, and then dried on a rotary drum drier. The product was collected as non-dusting flakes which showed excellent wettability and solubility in cold water.

The usual diazoimino compounds can be employed, examples of which are the reaction products of diazo compounds from primary arylamines with sarcosine, proline, and methyl-glucamine. The diazo components are preferably free from sulfonic and carboxylic acid groups. Examples of these primary arylamines are

Aniline
m-Chloro-aniline
2:5-dichloro-aniline
5-chloro-2-amino-toluene
4-chloro-2-amino-anisole
2:5-dimethoxy-aniline
4-nitro-2-amino-toluene
5-nitro-2-amino-toluene
4-nitro-2-amino-anisole
5-nitro-2-amino-anisole
Dianisidine
4-benzoylamino-2:5-diethoxy-aniline
4-carbomethoxy-amino-2:5-diethoxy-aniline

The composition of the new compositions other than the ice color coupling components may vary widely. Dextrin may be supplemented by cane sugar or similar water-soluble carbohydrate material. The ratio of protective colloid and diluent to ice color coupling component also may vary widely, but the preferred products contain from 20% to 70% of the ice color coupling component. As wetting out and dispersing agents, numerous materials may be used. The wetting out of the coupling components may be effected during the preparation of the new compositions merely by the addition of a water miscible solvent such as alcohol, acetone, ethylene glycol or its ethyl ether. If these agents are used for the original wetting out, they are removed during the drying process. On the other hand wetting agents such as sulfates of higher alcohols, alkylated naphthalene sulfonic acids, and sulfonated castor oil may be used. In these in-

stances, the wetting out agents remain in the finished dry compositions.

The wet compositions may be converted to virtually dry products by evaporation in graining bowls containing heavy duty agitators. During the drying process, the materials are subjected to plastic milling in such equipment. Alternatively the mixtures may be dried on rotary drum driers, on vacuum tray driers, or in other suitable equipment. The compositions are uniformly constituted and no lack of uniformity is noticeable in the subdivided products. In order to obtain the best wetting out characteristics in the finished products, the dry materials should contain a small amount of residual moisture, usually less than 2%. The products are virtually dry, somewhat porous and friable. They are easily subdivided to a suitable degree of fineness and uniformity, as by grinding. The subdivided material is granular. There is no advantage in extremely fine grinding. The grain sizes in the preferred products range from approximately 10 to 200 mesh but larger or smaller grain sizes can be used.

The new compositions of the present invention are especially useful for the preparation of baths for padding textile fibers with the ice color coupling components, such fibers subsequently to be dyed or printed with diazo salts. The dry compositions also may be mixed with dry water-soluble diazoimino compounds, with dry nitrosamines (antidiazotates) prepared from arylamines, or with dry diazo sulfonates, to produce mixtures suitable for dyeing and printing. Such mixtures show advantages in wetting out and dispersing properties over similar mixtures containing the ice color coupling components in the form of their free acids.

The products of the present invention are superior to those of the prior art in ease of preparation of dye baths, and printing pastes. It is well known that the alkali metal salts of the arylamides of 2:3-hydroxy-naphthoic acid are quite unstable to storage. However, the compositions containing such alkali metal salts described in the present application are stable.

The dyeing value of the products of the present invention in every case is equal to that of the coupling components of the prior art per unit of active ingredient, and in some instances improvement in the tinctorial value and brilliance of the dyeings is observed with the new compositions. This perhaps may be attributed to the other constituents of the compositions contributing to fixation of the coupling components and the color produced therefrom. In addition to reducing the labor required in preparing baths and printing pastes containing ice color coupling components, the new products also solve another problem of the prior art. Dry mixtures of the components are dusty and cause a definite health hazard in textile plants. The new compositions are friable and they subdivide into grains without producing dusty products.

From the foregoing disclosure it will be recognized that the invention is susceptible of modification without departing from the spirit and scope thereof and it is to be understood that the invention is not restricted to the specific illustrations thereof herein set forth.

We claim:

1. A virtually dry granular article of a uniform porous friable composition which comprises a subdivided compound of a group consisting of the alkali metal salts of the ice color coupling components, said coupling components being from the group consisting of arylamides of ortho-hydroxy-aryl-carboxylic acids and beta keto-carboxylic acids which are devoid of sulfonic acid and carboxyl groups; at least a sufficient amount of a dispersing agent and Turkey red oil alkali metal salt to make a dispersion when the composition is added to water; and an excess of an alkali metal hydroxide over that necessary to form an alkali metal salt of the coupling component; said composition being characterized by its property to wet-out rapidly with water, by being rapidly soluble in water, by being non-dusting and by stability upon storage.

2. A virtually dry flaked non-dusting article of a uniform porous friable composition which comprises a subdivided compound of a group consisting of the alkali metal salts of the ice color coupling components, said coupling components being from the group consisting of arylamides of orthohydroxy - aryl - carboxylic acids and beta keto-carboxylic acids which are devoid of sulfonic acid and carboxyl groups; at least a sufficient amount of dispersing agent and Turkey red oil alkali metal salt to make a dispersion when the composition is added to water; and at least a sufficient excess of an alkali metal hydroxide over that necessary to form an alkali metal salt of the coupling component to make the composition soluble in water; said composition being characterized by being non-dusting, by its property to wet-out rapidly with water, by being readily soluble in water and by stability upon storage.

3. A virtually dry flaked article of a uniform porous friable composition which comprises a subdivided alkali metal salt of an arylamide of an ortho - hydroxy - aryl - carboxylic acid which is devoid of sulfonic acid and carboxyl groups; sufficient dispersing agent and Turkey red oil alkali metal salt to make a dispersion when the composition is added to water; and at least a sufficient excess of an alkali metal hydroxide over that necessary to form an alkali metal salt of the coupling component to make the composition soluble in water; said composition being characterized by being non-dusting, by its property to wet-out rapidly with water, by being readily soluble in water and by stability upon storage.

4. A virtually dry flaked article of a uniform porous composition which comprises a subdivided sodium salt of a 2,3-hydroxy-naphthoyl-arylamide of the benzene series which is devoid of sulfonic acid and carboxyl groups; sufficient of a dispersing agent and the sodium salt of Turkey red oil to make a dispersion when the composition is added to water, said dispersion agent being the condensation product of naphthalene-beta-sulfonic acid with formaldehyde; and at least a sufficient excess of sodium hydroxide over that necessary to form the sodium salt of the coupling component to make the composition soluble in water; said composition being characterized by being non-dusting, by its property to wet-out rapidly with water and by stability upon storage.

5. The process which comprises intermixing water; an arylamide of an acid from the group consisting of ortho - hydroxy - aryl - carboxylic acids and beta-keto-carboxylic acids which are devoid of sulfonic acid and carboxyl groups; at least sufficient of an alkali metal hydroxide to

form an alkali metal salt of said coupling component, at least a sufficient amount of a dispersing agent and the alkali metal salt of Turkey red oil to make a dispersion when the virtually dried composition is added to water; subjecting the mixture to plastic milling until a uniform composition is produced; and removing volatile liquid constituents until the composition is virtually dry and porous and subdividing the virtually dry porous composition.

6. The process which comprises intermixing water; a volatile liquid organic wetting agent; an arylamide of an ortho-hydroxy-naphthalene-carboxylic acid which is devoid of sulfonic acid and carboxyl groups; an excess of sodium hydroxide over that necessary to form the sodium salt of said arylamide; at least a sufficient amount of a dispersing agent and the alkali metal salt of Turkey red oil to make a dispersion when the virtually dried composition is added to water; subjecting the mixture to plastic milling until a uniform composition is produced; and removing volatile liquid constituents until the composition is virtually dry and subdividing the virtually dry composition.

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