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N,N'-DI(AMINO) DIAMIDES OF DICARBOXYLIC ACIDS AS PRINTING ASSISTANTS

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This invention relates to a new type of dyeing and printing assistant, dye compositions containing these assistants and products printed therefrom.

Use of printing-color pastes containing dyes, particularly in printing operations using vat dyes, is sufficiently well-known so that the procedure has become almost standardized. The actual color source may be either a dye paste or a dye powder. In addition to the real color, a dye paste usually contains agents to prevent drying-out, settling and/or freezing. Dye powders, not being subject to these difficulties, do not require these agents but they usually contain agents or are so processed as to promote dispersibility.

In either case, the dye paste or dye powder must be admixed with suitable thickener, usually a gum dispersion, to form a printing-color paste which is suitable for application. In the case of vat dyes, it is also necessary to add a reducing agent and usually an alkali. Because the color yield from printing-color pastes often decreases rapidly as the paste ages after being made up, these printing-color pastes are usually prepared by the fabric finishers just before they are to be used.

The printing-color pastes, however compounded, are then applied to textile, paper or other fabric materials for decorative or protective purposes. The printed pieces are dried, aged in a steam ager, treated with an oxidizing agent, rinsed and finally dried. Usually in processing textiles, the printed fabric also is soaped at or near the boil with about an 0.1% soap solution and again rinsed before the final drying operation.

In making up and applying printing-color pastes it has been found that a material suitable for use as a printing assistant is of advantage in obtaining maximum color yield. The exact way in which these materials act to produce an improved color yield in printing is not entirely understood. It is with these printing aids or assistants that the present invention is particularly concerned.

Although printing aids are desirable in the printing-color pastes, the exact point at which they are added may vary. Dye pastes may contain printing aids as one of their components and printing-color pastes made therefrom will obviously contain the printing assistant. Where a printing assistant is not present in the dye paste, it may be added at the time of making up the printing-color paste.

It is preferable, however, that the printing as-

sistant be incorporated in the actual dye paste. Their addition at the proper point in the manufacture of the paste is not only easier, but in addition they are thus generally more uniformly dispersed throughout a printing-color paste made therefrom. As a result, the printing assistants usually operate more effectively when the printing-color paste is finally applied to the fabric.

It is only relatively recently that dye powders suitable for use in making up printing-color pastes have been available. Most of the printing aids previously used in dye pastes, being either liquid in form or extremely hygroscopic, can not be used with dye powders, the latter being necessarily limited to the use of dry solids. Nevertheless, it is desirable that printing assistants be incorporated in the powders at the time of manufacture for the same reasons which apply in the case of dye pastes.

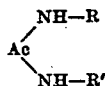
Dye pastes containing various liquid printing assistants have been made. Among the liquid materials used are the alkylol amines, for example, triethanol amine; and/or polyhydric alcohols such as glycerine, glycol, diethylene glycol and the like. Various derivatives therefrom also have been tried. If a printing aid is to be incorporated in a dye powder, a solid printing aid is necessary. Examples of such solids which have been used in the past include the hydrochlorides of alkylol amines; silver salt (sodium anthraquinone beta-sulfonate); anthraquinone and certain metal salts such as those of cobalt and iron.

Unfortunately, most of these printing aids previously used are not satisfactory as may be desired. Many of them will not in all cases produce the intensification of color for which they were intended. Others, such as the polyhydric alcohols, cause deterioration of the printing-color pastes so that marked variations in the strength of prints therefrom are observable even after the printing-color paste has been allowed to stand for only a relatively short time. Many of them are satisfactory with some colors but have an adverse effect on others, even to the extent of visibly altering the shade. None of them are suitable without modification for use both in paste and powder compositions.

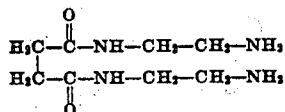
There remains, therefore, a demand for suitable printing assistants which will produce a satisfactory color intensification and will not cause deterioration of the dyeing or printing composition on standing. Preferably also, the assistants should be useful both with dye pastes and dye powders and in addition should be readily available or cheaply and easily prepared. It is,

therefore, the object of the present invention to provide a new type of printing assistant which possesses these desirable properties.

In general the objects of the present invention are accomplished by using as a printing assistant one or more of the dicarboxylic acid diamides represented by the general formula



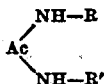
in which Ac represents the residue of a cyclic or aliphatic dicarboxylic acid and R and R' each represent either an aminoalkyl group in which the alkyl radical has from 1 to 8 carbon atoms or an aminoaryl group. Typical of the diamides of the present invention is the N,N'-di(beta-aminoethyl) succinamide which has the probable formula



So far as the present invention is concerned the assistants may be added to the printing-color pastes at any point. They may be incorporated into the thickener; into the dye pastes or powders or may be blended directly into the printing-color paste. However, as pointed out above, it is preferable that they be incorporated in the dye paste or powder during manufacture.

The use of this new class of printing assistants possesses a number of important advantages. These compounds are dry solids, which may be readily powdered and blended in dye powders but are also soluble or dispersible in dye paste suspensions. They have, therefore a general application in both dye pastes and dye powders. They do not cause deterioration of printing-color pastes on standing. They encourage the production of excellent color yields even under hot aging conditions. Their use is simple since they may be employed as powders, as suspensions in water or alcohol, producing excellent color yields whatever the mode of admixture.

The groups represented by R and R' in the general formula



may be quite widely varied. As pointed out, R and R' may represent substantially any aminoalkyl group in which the alkyl radical contains from about 1 to 8 carbon atoms. These alkyl groups may be either saturated or unsaturated. Typical of the amines which may be employed in preparing the compounds to be used as printing assistants according to the present invention are such compounds as ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, dibutylene triamine and the like.

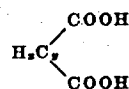
Where the alkylene group includes more than about five or six carbon atoms difficulty is encountered in preparing the diamine due to polymerization and above about eight carbon atoms the difficulty becomes substantially prohibitive in the present purpose. Preferably, the alkyl group is a straight chain compound in order to minimize the tendency toward polymerization, although the branched chain alkylenepolyamines give good results when converted to dicarboxylic acid di-

amides and used as printing assistants in the present invention. As was also pointed out, however, the invention is not limited to the use of alkylenepolyamines. Aryldiamines such as 1,4-aminobenzene, phenylene diamine, the diamino-naphthylenes and the like were found to produce excellent printing assistants when converted to dicarboxylic acid diamides.

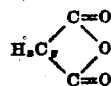
Theoretically the groups represented by R and R' may be different, thus forming a mixed diamide. However, the present application is intended to include only those compounds in which R and R' represent residues of similar alkylene polyamines. Mixed diamides in which R and R' differ in a manner such that one is a quinonyl group are specifically included in the copending application of Keinle and Amick, two of the present inventors, for United States Letters Patent, Serial No. 493,135, filed of even date.

In preparing the compounds to be used as the printing assistants of the present invention the dicarboxylic acid may be quite widely varied. The compounds may be derived from either cyclic or aliphatic dicarboxylic acids. Of the cyclic carboxylic acids, phthalic acid is perhaps the most common and its derivatives have been found to give good results when used according to the present process. The invention however is not meant to be so limited but includes derivatives of such acids as isophthalic, terephthalic, polyhydrophthalic, endoalkylene polyhydrophthalic acids such as endomethylene tetrahydrophthalic, endoethylene hexahydrophthalic and the like, and the naphthalic acids as well as the alkyl-substituted acids derived therefrom.

Where derivatives of aliphatic dicarboxylic acids are used, the original acid or anhydride may be varied over a considerable range. If the original aliphatic acid is considered to have the generic formula



or anhydride



in the case of the anhydride, y may have substantially any value from zero as in the case of oxalic acid to about eight without departing from the scope of the present invention. However, where y is greater than about 6, trouble is encountered in preparing the derivatives. Above about $y=8$, there is a tendency for the compounds to be water-insoluble, preventing satisfactory use. The acids may be either saturated acids such as malonic, succinic, glutaric, adipic, azelic, sebacic and the like or unsaturated such as maleic, fumaric and the like.

While the dye and printing paste compositions of the present invention are not limited to the use of any particular dyes or dye forms, they are especially suitable for use with vat-dyes in either paste or powder form. Particularly good results may be obtained using the vat dye powders of high autodispersibility as set forth in Crossley et al., United States Reissue Patent No. 21,402, reissued March 19, 1940. By combining the color materials of that patent into printing paste compositions containing the assistants of the present invention, the full advantages of both may be

gained with a resultant simplicity in use, excellence of shade and sharpness of color.

Printing pastes made in this way have the particular advantage that the dyes remain in a highly dispersed state as individual particles rather than as dispersions of particle aggregates. In the present specification and claims, where highly-dispersed dyes are referred to, reference to pastes in which the dye particles are so dispersed is intended.

The invention will be more fully set forth in connection with the following examples which are intended to be illustrative and not by way of limitation. All parts are by weight unless otherwise noted.

In the succeeding examples, test prints were made on two different fabrics. Where rayon is referred to, a titanium-dioxide-pigmented, all-viscose-rayon flat-crepe was used. The cotton fabric referred to is an 80 x 80 bleached, unmercerized, cotton print-cloth. Ageing of the prints was carried out in a steam ager which was constructed in such a manner that controlled temperatures could be used. The temperature range normally used was 100°-105° C. Those ageings referred to as plant or hot ageings were carried out in the temperature range of about 106°-110° C. In the case of the cotton prints, ageing periods of 3 minutes, 5 minutes or both were used. On rayon ageing periods of 5 and 10 minutes or both were used. The shortest period which gives a satisfactory ageing is preferable.

Example 1

A paste was prepared by slurring 2,000 parts of 177 British gum (Stein Hall) in 5,000 parts of water and the mixture was heated with continuous stirring until the temperature reached about 185° F. Heating was continued for about 1½ hours after which 450 parts of powder potassium carbonate and 450 parts of powdered sodium carbonate were added and the mixture stirred until the carbonates dissolved. Heating was discontinued but stirring was continued until the temperature reached approximately 150° F. at which time 700 parts of sodium sulfoxylate were dissolved therein, 600 parts of glycerine were added and the paste bulked to about 10,000 parts. Stirring was continued until the paste cooled to room temperature. In the succeeding examples this paste is referred to as thickener A.

Example 2

2,100 parts of B-2 British gum, 200 parts of tapioca flour and 500 parts of cornstarch were added to 2,500 parts of water and heated over a steam bath for approximately 1½ hours after the temperature reached about 185° F. The source of heat was then removed but stirring was continued until the temperature decreased to 130° F. at which time 2,100 parts of potassium carbonate which had been previously dissolved in hot water was added to the cooked gum. 1,100 parts of sodium sulfoxylate formaldehyde were added to the common mixture at a temperature of about 150° F. Subsequently, 1,400 parts of glycerine were added and after thorough stirring the whole was bulked to about 10,000 parts. The mixture was cooled and stirred continuously until the mass reached room temperature. In the succeeding examples this mixture is referred to as thickener B.

Example 3

720 parts of B-2 British gum and 720 parts of KAC-4 gum (Stein Hall) were added to 5,600

parts of water and heated over a steam bath for approximately 1½ hours after the temperature reached 185°-190° F. The source of heat was then removed but stirring was continued until the temperature decreased to 120° F. at which time 1,200 parts of potassium carbonate which had been previously dissolved in 1,000 parts of water was added to the cooked gum. 1,560 parts of sodium sulfoxylate formaldehyde were dissolved in 1,500 parts of water at a temperature of about 140° F. and added to the common mixture with stirring until the whole was thoroughly mixed. 360 parts of glycerine were then added and after thorough stirring the whole was bulked to 12,000 parts. In the succeeding examples this mixture is referred to as thickener C.

Example 4

A 20% aqueous slurry of N,N'-di(beta-aminoethyl) maleic acid diamide was prepared by grinding the solid and water in a ball mill until a uniform suspension was obtained. Six parts of a dispersible Orange R powder (C. I.—1217), prepared according to U. S. Reissue Patent 21,402 and containing 2.4 parts of real dye were pasted with 3 parts of the aqueous diamide suspension and then blended with 91 parts of thickener A to produce a homogeneous printing paste. To a second 6 parts of the same Orange R powder, 3 parts of water were added and then 91 parts of thickener A. This was the control sample. Each of these pastes were printed on cotton and rayon. After drying in a hot air dryer, the prints were aged in a steam ager, oxidized, rinsed and soaped in a 1% soap solution for 5 minutes at the boil, again rinsed and ironed dry. The prints made from the pastes containing the reaction product of ethylene diamine and maleic anhydride gave better color yields than those made from the pastes containing water only.

Example 5

The procedure of Example 4 was followed exactly except that N,N'-di(gamma-aminopropyl) maleic acid diamide was used as the printing assistant in place of N,N'-di(aminoethyl) maleic acid diamide. The prints obtained from the paste containing the printing assistant gave much stronger and superior results than those prints made from the pastes containing water only.

Example 6

The procedure of Example 4 was again followed except using N,N'-di(para-aminophenyl) maleic acid diamide as the printing assistant. Both the control sample and the one containing the printing assistant were printed on cotton and rayon. The prints obtained from the paste containing the printing assistant gave better color yields than those made from the pastes containing water only.

Example 7

The procedure of Example 4 was repeated using N,N'-di(beta-aminoethyl) succinamide. The prints obtained from the pastes containing the reaction product of ethylene diamine and succinic anhydride gave very markedly stronger and superior results than those prints made from the control paste.

Example 8

20 parts of Vat Yellow GC powder (C. I.—1118, prepared according to U. S. Reissue Patent 21,402, and containing about 2 parts of real color was first slurried with 3 parts of

the aqueous diamide suspension of Example 4 and then blended with 77 parts of thickener B. A control sample was prepared without the printing assistant. Both samples of the paste were printed on rayon. After the finishing operations, the color of the prints obtained from the paste containing the assistant was very definitely superior to that obtained from the control sample.

Example 9

The procedure of Example 8 was duplicated except that thickener A was used in place of thickener B. Again the prints made from the paste containing the reaction product of ethylene diamine and maleic anhydride were very decidedly superior to those obtained from the control sample.

Example 10

A sample of wet presscake of Orange R (C. I.—1217) was dispersed with the sodium salt of disulfo-dinaphthyl methane and adjusted with water to contain about 12% real dye. Then 10 parts of this color were mixed with 0.3 part of N,N' di(beta-aminoethyl) succinamide and stirred until the mixture was homogeneous and thoroughly wet, after which 90 parts of thickener A were added. A control sample was also prepared but no printing assistant was added. Each of these pastes were printed on rayon and cotton. The printed pieces were then dried in a hot air dryer, aged, oxidized, soaped, and rinsed. After drying, the color value of the prints made from the pastes containing the printing assistant were 10-20% stronger than those obtained from the control sample.

Example 11

The procedure of Example 10 was duplicated except that the N,N' di(beta-aminoethyl) adipic acid diamide was used as the printing assistant. Prints made from the paste containing the N,N' di(beta-aminoethyl) adipic acid diamide were much stronger in color yield than those obtained from the paste containing water only.

Example 12

The procedure of Example 10 was also repeated except that N,N' di(beta-aminoethyl) phthalic acid was used as the printing assistant. A control sample was also prepared from the Orange R presscake but no printing assistant was added. Each of these pastes were printed on rayon and cotton. Prints obtained from the paste containing the printing assistant were superior to those obtained from the control sample.

Example 13

Another set of comparative pastes was prepared according to the procedure of Example 10 using N,N' di(beta-aminoethyl) fumaramide in one paste as the printing assistant. Prints obtained from the paste containing the fumaramide had much better color value than those obtained from the control sample.

Example 14

900 parts of Vat Pink FF (6,6' dichloro 4,4' dimethyl 2,2' bis-thio-naphthene indigo) presscake were deflocculated with the sodium salt of disulfo-dinaphthyl methane, then passed through a Mikro colloid mill to give a smooth uniform suspension. This product was called Vat Pink FF deflocculated presscake. After determining the dye content of this material, a

weighed quantity was entered in a ball mill. Enough water was added to this mass to reduce the dye content to approximately 15%, and the mix was ground for 24 hours. This 15% Pink FF water paste was called the blank. Another portion of Vat Pink FF deflocculated presscake containing approximately 30 parts of dye was ground in a ball mill with 6 parts of printing assistant of Example 4 (N,N' di(beta-aminoethyl) maleic acid amide). The dye content of this mixture was reduced by adding water and the mix was ground for approximately 24 hours. Both samples were then analyzed for extracted solids. The efficiency factor was determined by print-testing against the blank and comparing the color value of the prints. Comparison on a recording spectrophotometer indicated an efficiency factor of 1.28.

Example 15

The procedure of Example 14 was duplicated using N,N' di(beta-aminoethyl) succinamide. In this case the efficiency factor was 1.2.

Example 16

10 parts of Dark Blue BO dispersed powder (C. I.—1099), prepared according to United States Reissue Patent 21,402 and containing about 3.7 parts of real dye were blended with 0.3 part of the printing assistant of Example 14 and 90 parts of thickener C. After intimate mixing, prints were made of this paste and also of the control sample prepared in the same way except that no printing assistant was added. Prints on both cotton and rayon obtained from the paste containing the maleic acid diamide were stronger than those obtained from the blank. This was true especially when the samples were aged under plant ageing condition at 106-110° F.

We claim:

1. A color composition comprising a vat dye and at least one substance represented by the formula



in which Ac represents the residue of a dicarboxylic acid selected from the group consisting of the phthalic acids, naphthalic acids and the saturated and unsaturated aliphatic dicarboxylic acids of from 2 to 10 carbon atoms and R represents a radical selected from the group consisting of the aminoalkyl radicals of from 1 to 8 carbon atoms and the aminoaryl radicals.

2. A composition according to claim 1 in which the dye is a thio-indigo vat dye.

3. A dye powder composition comprising a vat dye and at least one solid, powderable substance represented by the formula



in which Ac represents the residue of a dicarboxylic acid selected from the group consisting of the phthalic acids, naphthalic acids and the saturated and unsaturated aliphatic dicarboxylic acids of from 2 to 10 carbon atoms and R represents a radical selected from the group consisting of the aminoalkyl radicals of from 1 to 8 carbon atoms and the aminoaryl radicals.

4. A dye composition comprising a vat dye powder of high autodispersibility and at least one powdered substance represented by the general formula



in which Ac represents the residue of a dicarboxylic acid selected from the group consisting

of the phthalic acids, naphthalic acids and the saturated and unsaturated aliphatic dicarboxylic acids of from 2 to 10 carbon atoms and R represents a radical selected from the group consisting of the aminoalkyl radicals of from 1 to 8 carbon atoms and the aminoaryl radicals.

5. A printing paste composition comprising a vat dye, a thickener and at least one substance represented by the general formula



in which Ac represents the residue of a dicarboxylic acid selected from the group consisting of the phthalic acids, naphthalic acids and the saturated and unsaturated aliphatic dicarboxylic acids of from 2 to 10 carbon atoms and R represents a radical selected from the group consisting of the aminoalkyl radicals of from 1 to 8 carbon atoms and the aminoaryl radicals.

6. A printing paste composition comprising a

highly-dispersed vat dye, a thickener and a printing assistant comprising at least one substance represented by the general formula



in which Ac represents the residue of a dicarboxylic acid selected from the group consisting of the phthalic acids, naphthalic acids and the saturated and unsaturated aliphatic dicarboxylic acids of from 2 to 10 carbon atoms and R represents a radical selected from the group consisting of the aminoalkyl radicals of from 1 to 8 carbon atoms and the aminoaryl radicals obtainable by compounding a colloided vat dye powder of high autodispersibility and the printing assistant with the thickener.

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