

UNITED STATES PATENT OFFICE

2,383,393

ACYL QUINONE SULPHONAMIDES AS
PRINTING AIDS

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10 Claims. (Cl. 8-70)

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 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 a 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 assistant be incorporated in the actual dye paste. Their addition at the proper point in the manu-

facture 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-sulphonate); anthraquinone and certain metal salts such as those of cobalt and iron.

Unfortunately, most of these printing aids previously used are not as 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.

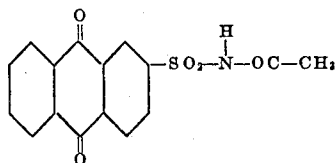
There remains, therefore, a demand for suitable printing assistants which will produce a satisfactory color intensification and will not cause deterioration of the dyeing or printing composition on standing. Preferably also, the assistants should be useful both with dye pastes and dye powders and in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

vide 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 a substituted quinone-sulphonamide having a terminal acyl group. These compounds may be represented by the general formula



in which Q represents the residue of a quinone such as alpha- or beta-anthraquinone and beta-naphthoquinone; R represents the residue of a carboxylic acid amide and x may be one or two. Typical of the sulphonamides of the present invention is the condensation product of beta-anthraquinone-sulphonic acid and acetamide 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.

In preparing the quinone-sulphonamide derivatives used as printing assistants according to the present invention, the quinonyl residue represented by Q in the generic formula may be derived from such compounds as the alpha- and beta-anthraquinones and beta-naphthoquinone, for example. Corresponding derivatives of 1,4-naphthoquinone do not appear to be capable of being isolated, if they form. In the case of beta-naphthoquinone, x in the generic formula is usually one since the disulphonamides of beta-naphthoquinone also are impractical to form.

Acid amides of the quinone-sulphonic acids which are suitable for use as printing assistants in the present invention may be readily prepared by reacting a quinone sulphonyl chloride, such for example as beta-anthraquinone sulphonyl chloride, with an acid amide, such as acetamide. This exemplary reaction will give an excellent printing assistant having the formula set forth above. The invention however is not so limited. Suitable printing assistants may be prepared by condensing the quinone-sulphonic acid with substantially any cyclic or aliphatic acid monoamide.

Of the cyclic acid amides which can be used to form excellent printing assistants according to the present invention phthalimide is perhaps the most commonly available and since it works well is perhaps preferable. Others however may be used. The aliphatic acid amides may be either mono- or dibasic and may be either saturated or unsaturated. Preferably these acids are chosen from the group having from about 2 to 8 carbon atoms since the amide of larger acids tend to cause polymerization. Of the monobasic acid amides, acetamide as noted above is typical. Amides of propionic, butyric acid and the like also give excellent printing assistants. Unsaturated aliphatic acid monoamides of fumaric, maleic, itaconic and the like acids also were found to yield good results. Similarly such saturated aliphatic acids as oxalic, succinic, glutaric, adipic,

sebacic, and the like, for example, were also found to be suitable.

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 set forth in Crossley et al., United States Reissue Patent 21,402, reissued March 19, 1940. By combining the color materials of that patent into printing-paste compositions containing the printing assistants of the present invention, the full advantages of both may be gained with a resultant simplicity in use and excellence of shade and sharpness of color.

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. When 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 powdered 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 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 with continuous stirring until 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 3,100 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. This 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 5,000 parts of water and the mixture heated with continuous stirring until the temperature reached about 185° F. Heating was continued for about 1½ hours after which the source of heat was removed and the gum cooled with stirring to a temperature of approximately 120° F. To this mixture 1,200 parts of potassium carbonate were added which had been previously dissolved in 1,000 parts of water. 1,560 parts of sodium sulphoxylate 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 added and after thorough stirring the whole was bulked to about 12,000 parts. In the succeeding examples this is referred to as thickener C.

Example 4

2.5 parts of a Dark Blue BO dispersed powder (C. I.—1099), prepared according to U. S. Reissue Patent 21,402 and containing about 0.9 part of real color, were blended with 0.25 part of the condensation product of beta-anthraquinone-sulphonic acid with acetamide. This mixture was made into a paste with 97.25 parts of thickener A. A second 5 parts of Dark Blue BO dispersed powder was made into a paste in the same manner except that no printing assistant was added. Each of these pastes were printed on rayon and cotton. The printed pieces were air dried, aged in a steam ager, oxidized, rinsed, soaped at the boil in an 0.1% soap solution for 5 minutes, rinsed again and ironed dry. Prints from the paste containing the printing assistant were much stronger and brighter.

Example 5

Example 4 was duplicated except that the reaction product obtained from alpha-anthraquinone-sulphonic acid and acetamide was used in place of the printing assistant of the preceding example. Again the prints obtained from the paste containing the printing assistant was stronger and brighter than those obtained from the paste containing color only.

Example 6

Example 4 was duplicated except that 2.5 parts of Golden Orange G powder (C. I.—1096) containing about 0.5 part of real color was substituted from the Dark Blue BO of Example 4. Prints obtained from the paste containing the printing assistant were definitely stronger, brighter and more even than those obtained from the paste in which no printing assistant was present.

Example 7

Example 6 was duplicated using the printing assistant of Example 5. Satisfactory results essentially the same as those of Example 6 were obtained.

Example 8

A sample of wet presscake of Vat Orange R (C. I.—1217) was dispersed with a sodium salt of disulpho-dinaphthylmethane and adjusted with water to contain 12% of real dye. Ten parts of this mixture were mixed with 0.5 part of the con-

densation product of anthraquinone-beta-sulphonic acid and maleyl-amide. In this case thickener C was used. Each of these pastes were printed on rayon and cotton. The results obtained from the paste containing the printing assistant were much stronger and brighter than those obtained from the paste in which no printing assistant was present.

Example 9

The procedure of Example 8 was duplicated except that the reaction product of alpha-anthraquinone-sulphonic acid and maleyl amide was used in place of the printing assistant described in Example 8. Each of the pastes were printed on samples of rayon and cotton. Test prints obtained from the paste in which the printing assistant was used were stronger and brighter than those obtained in which no printing assistant was present.

Example 10

The procedure of Example 8 was duplicated except that the condensation product of beta-anthraquinone-sulphonic acid with succinyl amide was used. Prints obtained from the paste in which the printing assistant was present again proved to be stronger and brighter than those obtained from the paste in which only printing thickener is used. This was particularly true when aged under commercial ageing conditions.

Example 11

Example 8 was repeated using the condensation product of beta-anthraquinone-sulphonic acid and fumaric acid as the printing assistant. This product gave excellent strength and brightness when compared with prints obtained from pastes in which no printing assistant was used.

Example 12

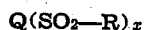
The procedure of Example 8 was duplicated except that the condensation product of beta-anthraquinone-sulphonic acid and phthalimide was used as the printing assistant. Again the prints obtained from the pastes in which the assistant was used were much stronger and brighter than the prints obtained in which no printing assistant was used.

Example 13

Example 4 was duplicated except that Vat Brown RR dispersed powder containing about 0.8 part of real color was used in the place of the Dark Blue BO. Prints obtained from the paste in which the printing assistant was used were very much stronger than the prints obtained from the pastes containing no printing assistant. This assistant produced the maximum color value of the Vat Brown RR in a much shorter ageing time than was possible and gave better color yields than when no printing assistant was used. This is of definite commercial advantage.

We claim:

1. A color composition comprising a vat dye and a quinone-sulphonamide derivative having the general formula



in which Q represents a quinonyl radical selected from the group consisting of beta-naphthoquinonyl and the anthraquinonyl radicals, R represents the residue of an amide selected from the group consisting of the aliphatic monocarboxylic acid amides and the monoamides of the aliphatic dicarboxylic acids having from 2 to 8

carbon atoms, phthalimide, and the monoamides of cyclic-dicarboxylic acids and x is a small whole number selected from the group consisting of 1 and 2.

2. A dye powder composition comprising a vat dye and a powdered quinonyl sulphonamide derivative having the general formula



in which Q represents a quinonyl radical selected from the group consisting of beta-naphthoquinonyl and the anthraquinonyl radicals, R represents the residue of an amide selected from the group consisting of the aliphatic monocarboxylic acid amides and the monoamides of the aliphatic dicarboxylic acids having from 2 to 8 carbon atoms, phthalimide, and the monoamides of cyclic-dicarboxylic acids and x is a small whole number selected from the group consisting of 1 and 2.

3. A dye powder composition comprising a vat dye powder of high autodispersibility, and a powdered quinonyl sulphonamide derivative having the general formula



in which Q represents a quinonyl radical selected from the group consisting of beta-naphthoquinonyl and the anthraquinonyl radicals, R represents the residue of an amide selected from the group consisting of the aliphatic monocarboxylic acid amides and the monoamides of the aliphatic dicarboxylic acids having from 2 to 8 carbon atoms, phthalimide, and the monoamides of cyclic-dicarboxylic acids and x is a small whole number selected from the group consisting of 1 and 2.

4. A color composition according to claim 1 in which Q represents the beta-naphthoquinonyl group.

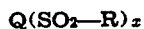
5. A color composition according to claim 1 in which Q represents an anthraquinonyl group.

6. A printing paste composition comprising a vat dye, a thickener, and a quinone-sulphonamide derivative having the general formula



in which Q represents a quinonyl radical selected from the group consisting of beta-naphthoquinonyl radicals, R represents the residue of an amide selected from the group consisting of the aliphatic monocarboxylic acid amides and the monoamides of the aliphatic dicarboxylic acids having from 2 to 8 carbon atoms, phthalimide, and the monoamides of cyclic-dicarboxylic acids and x is a small whole number selected from the group consisting of 1 and 2.

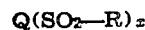
7. A vast dye composition comprising a dye, a thickener and a quinone-sulphonamide derivative having the general formula



in which Q represents a quinonyl radical selected

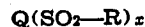
from the group consisting of beta-naphthoquinonyl and anthraquinonyl radicals, R represents the residue of an amide selected from the group consisting of the aliphatic monocarboxylic acid amides and the monoamides of the aliphatic dicarboxylic acids having from 2 to 8 carbon atoms, phthalimide, and the monoamides of cyclic-dicarboxylic acids and x is a small whole number selected from the group consisting of 1 and 2.

8. A printing paste composition comprising a highly-dispersed vat dye, a thickener and a quinone-sulphonamide derivative having the general formula



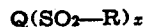
in which Q represents a quinonyl radical selected from the group consisting of beta-naphthoquinonyl and anthraquinonyl radicals, R represents the residue of an amide selected from the group consisting of the aliphatic monocarboxylic acid amides and the monoamides of the aliphatic dicarboxylic acids having from 2 to 8 carbon atoms, phthalimide, and the monoamides of cyclic-dicarboxylic acids and x is a small whole number selected from the group consisting of 1 and 2 obtainable by compounding a colloidized vat dye powder of high autodispersibility and the quinone-sulphonamide derivative with the thickener.

9. A method of printing with vat color which comprises printing a fabric with a printing paste composition comprising a vat dye, a thickener and a quinone-sulphonamide derivative having the general formula



in which Q represents a quinonyl radical selected from the group consisting of beta-naphthoquinonyl and anthraquinonyl radicals, R represents the residue of an amide selected from the group consisting of the aliphatic monocarboxylic acid amides and the monoamides of the aliphatic dicarboxylic acids having from 2 to 8 carbon atoms, phthalimide, and the monoamides of cyclic-dicarboxylic acids and x is a small whole number selected from the group consisting of 1 and 2.

10. An article of manufacture comprising a fabric printed with a composition comprising a vat dye and a quinone-sulphonamide derivative having the general formula



in which Q represents a quinonyl radical selected from the group consisting of beta-naphthoquinonyl and anthraquinonyl radicals, R represents the residue of an amide selected from the group consisting of the aliphatic monocarboxylic acid amides, the monoamides of the aliphatic dicarboxylic acids having from 2 to 8 carbon atoms, phthalimide and the monoamides of cyclic-dicarboxylic acids and x is a small whole number selected from the group consisting of 1 and 2.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 50, claim 6, after "onyl" insert --and anthraquinonyl--; line 58, claim 7, for the word "vast" read --vat--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of February, A. D. 1946.

(Seal)

Leslie Frazer
First Assistant Commissioner of Patents.