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PRINTING POLYESTER TEXTILES WITH A DISPERSE DYE PASTE CONTAINING AN ALKYL AMIDE OR ALKYLENE DIAMIDE

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No Drawing. Continuation-in-part of application Ser. No. 255,100, Jan. 30, 1963. This application July 28, 1965, Ser. No. 475,583

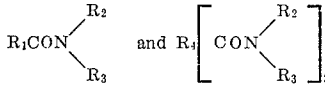
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Int. Cl. D06p 3/54

U.S. Cl. 8—62 5 Claims

ABSTRACT OF THE DISCLOSURE

An improved process for printing organic hydrophobic textiles with an aqueous printing paste comprising a non-polymerizable aqueous paste base and a dyestuff selected from dispersed dyes and vat dyes, improvement relating to the effecting of a deep color with a relatively low fixing temperature and relatively short fixing time by including within the aqueous printing paste from 0.1–20% by weight of a carboxylic acid amide selected from the formulae



wherein R_1 is an aliphatic radical of a monocarboxylic acid, R_2 and R_3 are each selected from the group consisting of hydrogen and lower alkyl radicals and R_4 is an aliphatic radical derived from a dicarboxylic acid, the total number of carbon atoms in the carboxylic acid amide being from 8–22.

This application is a continuation-in-part of Ser. No. 255,100 filed Jan. 30, 1963.

This invention relates to a novel printing paste and more particularly relates to a printing paste usable for printing organic hydrophobic textiles and a process for printing organic hydrophobic textiles.

Conventionally, when organic hydrophobic textiles have been printed by dispersed dyes or vat dyes, a process has been employed which effects dyeing by printing a printing paste on the textile and alternatively, if desired, the printed textile is subjected to a preliminary drying, and thereafter to a dry heating or steaming operation. A fixing method by drying is a continuous and effective method, however, it is generally difficult to advantageously obtain a printed fabric of a deep color by dry heating. To obtain any degree of deep color, it has heretofore been necessary to employ high temperatures for long periods of time. Such high temperatures for long periods of time, however, suffer from the disadvantage of producing textiles that are damaged, deteriorated handling or staining of the non-printed portion of the textile caused by the sublimation of the dyes. Also, the use of a higher temperature and a longer period unfavorably affects textiles consisting of fibers having different heat resistances. Similarly, in a dry heating fixing method, when a printing paste blended with a substance known as a carrier has been used, it has been found impossible to obtain a printed textile of a sufficiently deep color. Also, in a fixing method by steaming used in case of cellulose triacetate textiles or polyester textiles, the steaming is carried out batchwise. Therefore, such process cannot be

employed for large scale production. In a fixing process by steaming, a substance known as a carrier has been blended into a printing paste. The effect by the addition of the carrier, however, has been small and a dyeing of a satisfactorily deep color has not been obtained. Moreover, sometimes the added carrier remains in the printed textile and thus the fastness to light of the product is greatly lowered.

Accordingly, a principal object of this invention is to provide a printing paste for printing organic hydrophobic textiles which makes it possible to obtain dyeing of a sufficiently satisfactory deep color even when a relatively low fixing temperature and/or a relatively short fixing period are(is) employed.

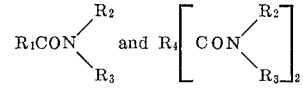
Yet another object of the present invention is to provide a printing paste in which a mono-N dicarboxylic acid amide is advantageously employed to make it possible to obtain dyeing of a sufficiently satisfactory deep color even when a relatively low fixing temperature and/or a relatively short fixing period are(is) employed.

Another object of this invention is to provide a process for printing organic hydrophobic textiles employing a relatively low fixing temperature and/or a relatively short fixing period, nevertheless, allowing dyeing of a sufficiently satisfactorily deep color.

Still another object of this invention is to provide a printing paste capable of being used for the printing of textiles containing fibers of considerably different heat resistance.

Other objects and advantages of this invention will become apparent from the following description.

The printing paste of this invention comprises a paste base, dyes having affinity to the textiles to be printed and in an amount of 0.1–20% by weight based on the weight of the entire paste of a carboxylic acid amide of the general formulae



wherein R_1 is an aliphatic radical of a monocarboxylic acid; R_2 and R_3 are each selected from the group consisting of hydrogen and lower alkyl radicals; and R_4 is an aliphatic radical derived from a dicarboxylic acid, the total number of carbon atoms in the carboxylic acid amide being preferable from 8–22.

These materials are hereinafter referred to as "thermosol carriers." The preferred thermosol carriers are those in which R_2 and R_3 are hydrogen. Examples of such materials include octyllamide, laurylamide, myristylamide, palmitylamide, stearylamide, adipic amide, azelaic amide, sebacic amide, suberic amide, dodecandioic acid amide and octadecanedioic amide. Examples of the N-substituted acid amides are N,N-diethyl pentylamide, N-butyllaurylamide, N,N-dibutylacetamide, N,N - dibutyllaurylamide, N,N-diethylstearylamide, N,N,N',N' tetraethyl adipic amide, N,N' dibutyl sebacic amide, etc. The preferred thermosol carriers wherein R_2 and R are hydrogen are normally solid and have relatively high boiling point, whereas the N-substituted acid amides are in general normally liquid and have lower boiling point. The former gives rise to less bleeding and sharper printing than the latter, and also exhibits excellent carrier effects.

In accordance with this invention it has unexpectedly been found that the amount of thermosol carrier employed, i.e., from 0.1–20% by weight on the total weight of the paste is critical. If amounts less or greater than this amount are employed the necessary paste will not be formed, and the unusual and unexpected color fastness and deep color associated with low fixing temperature and relatively short fixing period capable of being

employed by the use of the formulations of the present invention will not be observed.

As mentioned previously, the printing paste of this invention comprises a paste base, dyes having affinity to the textiles to be printed and a thermosol carrier in an amount of 0.1–20% by weight based on the weight of the entire paste. Paste bases unstable in this invention are known. The paste base is a non-polymerizable base, i.e., does not polymerize upon heating. As a paste base, for instance, an aqueous paste of sodium alginate (solid content: about 6%), sodium salt of carboxymethylcellulose (solid content: about 4%), Nafka crystal gum (solid content: about 33%), starch (solid content: about 12%), locust bean gum (solid content: about 25%) and tragacanth gum (solid content: about 6%) may be used. A "Yuzen paste" consisting of 20 parts of glutinous rice powder, 20 parts of nonglutinous rice powder, 5 parts of sodium chloride and 75 parts of water is a preferable base usable in this invention. An aqueous paste of polyvinyl alcohol may also be employed. Also, an emulsion thickenings are usable.

The printing paste of this invention can be used particularly advantageously for printing organic hydrophobic textiles. The textiles to be printed can be in the forms of woven or knitted fabrics, nonwoven fabrics, tow or yarn. These organic hydrophobic textiles can be manufactured from semi-synthetic fibers such as cellulose acetate and cellulose triacetate fibers or from synthetic fibers such as polyesters, polyvinyl chloride, polyamides, polyacrylonitrile and polypropylene fibers. Also, these textiles can be mixed spun or mixed woven products of more than one of these organic hydrophobic textiles or mixed products of these fibers and other natural or man-made fibers. For example, textiles obtained by mix spinning polyethylene terephthalate staple fiber and cotton (or rayon staple fiber) and textiles obtained by mix spinning polyethylene terephthalate staple fiber, polyvinyl chloride staple fiber and rayon staple fiber can be advantageously printed by the printing paste of this invention.

Dyes usable in the printing paste of this invention are known per se. So long as they have affinity to the textiles to be printed, and contain no solubilizing sulfonic acid groups, any vat or dispersed dyes can be employed. Examples of such dyes are Dispersol Fast Yellow G, (CI 11855 CI Disperse Yellow 3), Dispersol Fast Scarlet B (CI 11110 CI Disperse Red 1), Fenacet Fast Blue FFN (CI 61505 CI Disperse Blue 3); vat dyes such as Mikethren Gold Yellow GK (CI 59100 CI Vat Yellow 4), Indanthren Brilliant Orange GR (CI 71105 CI Vat Orange 7), suprafix paste, Mikethren Brilliant Pink R (CI 73360 CI Vat Red 1), Mikethren Red Violet RH (CI 73385 CI Vat Violet 2), Mikethren Blue GCD (CI 69810 CI Vat Blue 14), Mikethren Brilliant Green FFB (CI 59825 CI Vat Green), and Mikethren Printing Black B (CI 73830 CI Vat Black 2). Acid dyes and basic dyes may also be used. The dyes may be applied to polyester textiles, polyvinyl chloride textiles, polyamide textiles, polyacrylonitrile textiles and polypropylene textiles. Ordinarily, these dyes are blended in an amount of about 0.1–8% by weight based on the weight of the entire paste, but it is possible to blend these dyes in an amount of up to 30% by weight as occasion demands.

There is no special restriction on the process of mixing the paste base, dyes and the thermosol carrier of this invention. It is possible to merely add the thermosol carrier to the paste base, but it is preferable to make an emulsion or a dispersion of the thermosol carrier by using a proper emulsifier or a dispersing agent and then adding the emulsion or dispersion to the paste base.

When the printing paste of this invention is printed on textiles and after a preliminary drying when a fixing by dry heating or steaming is carried out, the thermosol carrier in the printing paste has a function of promoting diffusion of the dyes in the paste layer. Ordinarily, a preliminary drying may be carried out at a temperature of 50–100° C. for a period ranging from several minutes to several hours. Even during this period, the dyes move onto the surface of textiles in the paste layer. During the process of fixing by dry heating or steaming, dyes rapidly diffuse in the paste layer, simultaneously or subsequently being dyed to the textiles. The conditions of dry heating and steaming vary depending on the kind and the form of textiles to be printed; however, ordinarily a dry heating at a temperature of 100–220 C. for a period ranging from several seconds to several minutes and a steaming under atmospheric pressure to 1.8 kg./cm.^{2} gauge pressure for a period ranging from several minutes to one hour are proper. Also the higher the temperature of the heat treatment, the shorter the treating period.

In a printing process using the printing paste of this invention, because of the diffusion promoting function of the thermosol carrier in the printing paste, greater dyeing is promoted than in conventional processes and a print of a deeper color is obtained. Also, in the present process, even when a lower temperature of a heat treatment in conventional processes and/or a shorter period than that of conventional processes are(is) employed, a printing effect equal or greater than the printing effect in the conventional processes is attained.

In a preferable mode of this invention, it is possible to add a so-called dip dyeing carrier as a dyeing accelerator for the purpose of increasing the velocity of diffusion of dyes into textile.

As these carriers, there are, for example, benzoic acid, its derivatives such as methyl ethyl, propyl, butyl, amyl, phenyl, benzyl, and naphthyl benzoates and m-nitrobenzoic acid; salicylic acid and its derivatives such as methyl ethyl, butyl, phenyl and benzyl salicylates and phenyl p-bromosalicylate; benzenedicarboxylic acid and their derivatives such as dimethyl diethyl, dibutyl, dioctyl, diphenyl, and dibenzyl benzenedicarboxylates; cinnamic acid and its derivatives such as methyl, ethyl, butyl, phenyl and benzyl cinnamates; ketones such as acetophenone propiophenone, benzophenone and 2,4-dihydroxy-acetophenone; phenols such as p-nitrophenol, p-chlorophenol, o-chlorophenol, p-bromophenol, 2,4,6-trichlorophenol, 2,4,6-tribromophenol and m-cresol; ethers such as anisol, p-bromophenyl methyl ether and methyl β-naphthyl ether; halogenated aroamtic hydrocarbons such as 1, 2, 5-trichlorobenzene, α-bromonaphthalene and α-chloronaphthalene; phenylmethane derivatives such as diphenyldichloromethane, triphenylchloromethane and triphenyl carbinol; diphenyl and its derivatives such as o-phenylphenol, p-phenylphenol, 4,4′-dihydroxydiphenyl and 4,4′-diaminodiphenyl; and naphthalene and its derivatives such as α-naphthoic acid, β-naphthoic acid, methyl and ethyl naphthoates, β-methyl naphthalene and 1,2,3,4-tetrahydronaphthalene.

Those skilled in the art can properly and easily select the carrier for dip dyeing to be used according to the kinds of textiles to be printed.

These carriers are added ordinarily in an amount of about 10–400% by weight based on the weight of the thermosol carrier. When a thermosol carrier of this invention and a dip dyeing carrier are used jointly, printing can be carried out even more effectively.

The following examples are for the explanation of this invention.

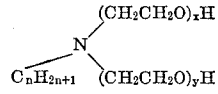
EXAMPLE 1

A printing paste of the following composition was printed on a fabric of polyethylene terephthalate.

	G.
Fenacet Fast Blue	50
Laurylamide	50
Sodium alginate (6% aqueous solution)	600
Water	300
	1000

In preparing the above composition, 50 g. of Fenacet Fast Blue FFN and 300 g. of water mixed. Thereto 50 g. of laurylamide and 600 g. of sodium alginate (6% aqueous solution) were added and mixed.

Thereafter, the fabric was preliminarily dried, and fixed by dry heating at 190° C. for 60 seconds. Thereafter, the fabric was subjected to a reduction clearing at 80° C. for 20 minutes with an aqueous solution containing 0.2% each of NaOH, hydrosulfite and Amirajin. Amirajin is a non-ionic surfactant having the following structural formula:



n, *x* and *y* are positive integers. A printed fabric having good color fastness and of deep dark blue was obtained.

EXAMPLE 2

A printing paste of the following composition was printed on a fabric of polyamide synthetic fiber (nylon 66).

	G.
Dispersed Fast Scarlet B	50
Laurylamide	50
Sodium lauryl sulfate	25
Water	25
Yuzen paste, Nafka paste[1] (1:1)	600
Water	250
	1000

[1] Nafka paste is prepared by reacting natural rubbers with hydrochloric acid under pressure and thereafter solubilizing the resultant product.

In preparing the above composition, 50 g. of laurylamide were mixed with 25 g. of sodium lauryl sulfate. The mixture was heated to 100° C. Thereafter, 25 g. of water were gradually added thereto and the laurylamide was dispersed. Next, a printing paste was prepared according to the conventional method. Thereafter, the fabric was preliminarily dried, fixed by dry heating at 150° C. for 4 minutes, and rinsed soaped. A printed fabric having good color fastness and a deep scalet color was obtained.

EXAMPLE 3

A printing paste of the folowing composition prepared by method as shown in Example 2 was printed on a knitted fabric of polyacrylonitrile.

	G.
Dispersol Fast Yellow G	60
Stearylamide	40
Triethyleneglycol-mono-laurylether	5
Yuzen paste, Nafka paste (1:1)	600
Water	295
	1000

Thereafter, the knitted fabric was dried and fixed by dry heating at 140° C. for 7 minutes, followed by rinsing and soaping. A printed knitte fabric having good color fastness and a deep yellow color was obtained.

EXAMPLE 4

A printing paste of the following composition prepared by method shown in Example 2 was printed on a fabric consisting of 65% of polyester synthetic fiber and 35% of cotton.

	G.
Fenacet Fast Blue FFN	40
Mikethren Blue GCD	40
Strearylamide	25
Sodium stearyl sulfate	25
Water	50
Sodium alginate (6% aqueous solution)	600
Water	200
	1000

After the fabric was printed, it was dried and then heat treated at 190° C. for 1 minute. Immediately thereafter, a chemical paste consisting of 8 g. of hydrosulfite, 7 g. of NaOH, 3 g. of Betagum J (trademark of a paste produced by Meisei Kagaku Kogyo Co.) and 82 g. of water was printed on the fabric by blotch roller and fixed at 100° C. for 40 seconds by steaming. Thereafter, the fabric was rinsed, treated at 40° C. for 30 seconds by a 2% aqueous solution of acetic acid, rinsed, treated at 40° C. for 30 seconds by a 0.7% aqueous solution of hydrogen peroxide, rinsed, soaped and dried.

Thus, the fabric printed with a printing paste added with stearylamide displayed a deeper blue color than that of the fabric printed with a printing paste not added with stearylamide.

EXAMPLE 5

When the stearylamide of Example 4 is replaced with sebacic amide, the fabric printed with the printing paste added with sebacic amide displays a deeper blue color than that of the fabric with a printing paste not added with sebacic amide.

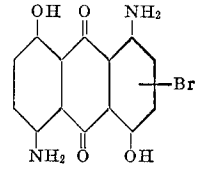
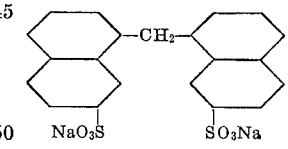
EXAMPLE 6

When the stearylamide of Example 4 is replaced with N,N-diethylstearylamide a deeper blue color is also observed.

It will be understood, of course, that the printing pastes of the present invention can contain other dyeing assistants such as surface active agents, wetting agents, and solvents for the dyes.

EXAMPLE 7

Printing pastes of the following compositions were printed on a fabric of polyethylene terephthalate.

	Paste A (g.)	Paste B (g.)
 (Dyestuff)	20	20
	20	20
 (Dispersing agent)	30	30
Stearylamide	0	50
N-methylformamide	50	0
Sodium alginate (6% aqueous solution)	600	600
Water	350	350
	1,000	1,000

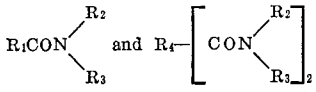
The fabric was preliminarily dried, and heated at 190° C. for 60 seconds. Thereafter, the fabric was subjected to a reduction clearing at 80° C. for 20 minutes with an aqueous solution containing 0.2% each of NaOH, hydrosulfite and Amirajin.

The color difference of the printed fabric was measured by a color difference meter and the color difference ΔE (NBS unit) was calculated using a fabric printed with the corresponding paste without a thermosol carrier as a standard. The fabric printed with paste A showed ΔE of 17.37 whereas the fabric printed with paste B showed ΔE of 2.86. Further, the bleeding of the latter was greater than that of the former by about 0.5 mm.

We claim:

1. In a process for the printing of linear polyester textiles with an aqueous printing paste consisting essentially of a non-polymerizable aqueous paste base and a dyestuff selected from the group consisting of dispersed

dyes and vat dyes, said dyes having an affinity for the textile, with subsequent fixing and washing of the textile, the improvement which comprises dyeing the textile a deep color with a relatively low fixing temperature and relatively short fixing time by including with said aqueous printing paste from 0.1–20% by weight of a carboxylic acid amide selected from the group consisting of amides of the formula



wherein R_1 is an alkyl radical of a fatty monocarboxylic acid, R_2 and R_3 are each selected from the group consisting of hydrogen and lower alkyl radicals and R_4 is an alkylene radical of a dicarboxylic acid, the total number of carbon atoms in the carboxylic acid amide being from 8–22.

2. The process of claim 1 wherein the carboxylic acid amide is lauryl amide.

3. The process of claim 1 wherein the carboxylic acid amide is stearyl amide.

4. The process of claim 1 wherein the carboxylic acid amide is N,N-diethylstearylamide.

5. The process of claim 1 wherein the carboxylic acid amide is sebacic amide.

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DONALD LEVY, Primary Examiner

U.S. Cl. X.R.

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