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#### 3,736,096 PRINTING BY LEVELLING DYES WITH GLYCERINE-ETHYLENE OXIDE-FATTY ACID CONDENSATE

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8 Claims

#### ABSTRACT OF THE DISCLOSURE

Printing process for wool, polyamides, acrylic, polyester or dyeable polypropylene textile materials in which the print paste used incorporates (a) a reaction product of glycerol with, in either order, an alkylene oxide and a carboxylic acid having four or more carbon atoms and (b) a surface-active agent, the amount of (a) being from 0.1% to 0.5% of the total weight of the print paste and the amount of (b) being at least equal to that of (a).

This invention relates to the printing of textile mate- 25 rials, in particular pile fabrics, and more particularly to a process for printing such materials which avoids or minimizes the occurrence in the printed material of the defect known as "frostiness."

It is well known to produce colored prints on pile 30 fabrics, more especially carpets, and a number of different forms of printing machine have been devised for this purpose. Where the pile fabrics are composed of nitrogenous fibers such as polyamides or wool or, to a lesser extent, of acrylic, polyolefin or polyester fibers, the normal practice is to employ acid dyes, basic dyes or disperse dyes in the printing process. A defect which is commonly encountered in such processes is that in the printed pile fabric a proportion of the fibers are found to remain undyed, or to be dyed to a pale shade only, giving rise to the appearance which is generally known as "frostiness." It has been proposed to avoid or minimize this defect by incorporating in the print paste certain auxiliary agents which possess surface-active properties.

A combination of auxiliary agents has now been found 45 which is especially effective in overcoming the occurrence of "frostiness" particularly in printed pile fabrics.

According to the present invention there is provided a process for the printing of textile materials composed of nitrogenous, acrylic, polyester or acid dyeable polypropylene fibers, wherein there is applied to the textile material a print paste which incorporates, in addition to one or more dyestuffs, a mixture of (a) a derivative of glycerol which is an ester of a carboxylic acid having four or more carbon atoms and which also contains one or more oxyalkylene groups and (b) a surface-active agent, the amount of the glycerol derivative (a) being in the range 0.1 to 0.5% of the total weight of the print paste and the amount of the surface active agent (b) being at least equal to that of the glycerol derivative (a).

Glycerol derivatives which are suitable for use in the process of the invention include, for example, the products of reaction of glycerol with an alkylene oxide, such as ethylene oxide or propylene oxide or mixtures thereof, which have thereafter been reacted with a carboxylic acid having four or more carbon atoms, or alternatively partial esters of glycerol with carboxylic acids containing four

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or more carbon atoms the free hydroxyl groups in which have subsequently been reacted with an alkylene oxide. Where a number of moles of alkylene oxide used is in excess of the number of free hydroxyl groups available for reaction therewith, the derivatives may contain chains of two or more oxyalkylene groups in the molecule. Suitable carboxylic acids from which the esters may be derived include, for example, capric acid, lauric acid, stearic acid and commercially available mixtures of fatty acids containing an alkyl chain of more than four carbon atoms. Examples of such glycerol derivatives include the condensates of glycerol monolaurate with 17 moles, 23 moles and 36 moles respectively of ethylene oxide, and the condensate of glycerol mono-oleate with 23 moles of ethylene oxide. A preferred glycerol derivative is the condensate of glycerol monolaurate with 23 moles of ethylene oxide.

Surface-active agents which are suitable for use in the process of the invention include agents of the nonionic, cationic or anionic types, for example condensates of cetyl alcohol with 17 moles, 20 moles and 29 moles respectively of ethylene oxide, the condensates of nonyl phenol with 9 moles of ethylene oxide, the condensate of octadecylamine with 20 moles of ethylene oxide, lauric acid diethanolamide, the sodium salt of sulphated cetyl/oleyl alcohol, sulphonated sperm oil and the ammonium salt of sulphated oxyethylated nonyl phenol. A preferred surface-active agent for use in the process of the invention is lauric acid diethanolamide.

Preferably the amount of the glycerol derivative which is used in the process is in the range 0.1 to 0.3% of the total weight of the print paste. It is further preferred that the amount of the surface-active agent which is employed should be between 1 and 3 times the amount of the glycerol derivative.

A particularly preferred mixture for use in the process comprises 2 parts by weight of lauric acid diethanolamide and 1 part by weight of the condensate of glycerol monolaurate with 23 moles of ethylene oxide.

Dyestuffs which may be employed in the process of the invention include any of those dyestuffs which are conventionally used for printing textile materials, more especially pile fabrics such as carpets, the particular class of dyestuff being dependent upon the nature of the fibers of which the textile material is composed. Thus, for printing of polyamide, acid dyeable (modified) polypropylene and wool pile fabrics, there may be used any of the conventional acid dyestuffs; for the printing of acrylic pile fabrics, any of the conventional basic dyestuffs; and for printing polyester pile fabrics any of the conventional disperse dyestuffs. The particular features of the present invention are, however, as follows. Firstly, it enables uniformly colored prints to be obtained on nitrogenous fibers by the use of dyestuffs which are not normally regarded as suitable for that purpose because of their tendency to give an unacceptable level of frostiness in the print. In many cases such dyestuffs are appreciably cheaper than those which are selected for use in the printing processes of the prior art on the basis of their technical performance. The process of the invention thus may offer a clear economic advantage in the printing of certain pile fabrics where particular shades of color or other dye characteristics are desired. As an instance in which this advantage may be exploited, there may be mentioned the printing of polyamide pile fabrics with some direct dyes or reactive dyes of the halogenotriazine type. Secondly, it enables better visual color yields to be obtained with many

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dyes, even though such dyes may previously have been regarded as giving acceptable results when printed in the presence of surface active agents already well established in the art. In such cases, therefore, it is possible to decrease the concentration of dye employed to achieve a given effect, thereby attaining an economic advantage over previously known printing processes.

The print paste incorporating the dyestuff or dyestuffs together with the glycerol derivative and the surface-active agent according to the invention may also contain other ingredients which are conventional in the textile printing art, such as thickeners and acid-producing or buffering agents. The print paste may be applied to the textile material by any one of the conventional techniques, for example, in the case of pile fabrics, by a design composed 15 of foam rubber segments mounted on a roller, using the Stalwart printing machine, or by screen printing utilizing either high squeegee pressure as in the Zimmer carpet printer or vacuum suction as in the B.D.A. carpet printer. After printing, the textile material may be subjected to 20 the normal processing conditions to effect fixation of the dyestuff, which with pile fabrics in most cases will consist of steaming at 100-115° C. for a period of up to 10 minutes followed by washing-off with water and drying.

It is an essential feature of the invention that the print 25 paste which is employed should contain both the glycerol derivative as hereinbefore defined and the surface-active agent. The omission of either of these ingredients leads to the production of prints which are markedly inferior in respect of frostiness than those which are obtained 30 when both ingredients are used together according to the

process of the invention.

The process of the invention may be used for the printing of any suitable textile material, including in particular carpets, for example those of the loop pile, cut pile 35 or needlefelt types, and also upholstery fabrics and blankets. The textile materials may be composed of nitrogenous fibers, including synthetic fibers of polyamides, such as poly(hexamethylene adipamide) and polycaprolactam, and artificial or natural fibers of regenerated proteins, silk or, more especially, wool, or of blends of such nitrogenous fibers with minor proportions of other fibers such as acetate rayon, polyester or cellulose. The textile material may also be composed of acrylic or modacrylic fibers consisting of polymers of acrylonitrile or copolymers containing a major proportion of acrylonitrile. Yet again, the textile material may be composed wholly of polyester fibers, such as poly(ethylene terephthalate), or of modified (acid dyeable) polypropylene fibers.

The invention is illustrated but not limited by the following examples, in which parts and percentages are by

weight:

#### **EXAMPLE 1**

A printing paste is prepared from:

	Parts
The dyestuff described in the Colour Index as	
C.I. Direct Red 79 C.I. 29065	1
Lauric diethanolamide	0.4
The condensate of glycerol monolaurate with 23	
mol ethylene oxide	0.2
Water	67.65
Locust bean gum ether thickening 4% sol	
Tartaric acid	0.75
Total	100.00

The print paste is applied from an impregnated foam pad to nylon 6.6 loop pile tufted carpet and the carpet is then placed in a steamer at 110° C. for a period of 10 70 min. The carpet is finally rinsed in cold water, hydroextracted and dried. An excellent, tinctorially strong and uniformly colored red print is obtained.

The tinctorial strength and uniformity (i.e. freedom from "frostiness") is much superior to that of a similar 75

print in which either lauric diethanolamide or the condensate of glycerol monolaurate with ethylene oxide is omitted from the printing paste.

A printing paste is prepared as in Example 1, except that the 0.4 part of lauric diethanolamide is replaced with 0.4 part of the condensate of cetyl alcohol with 20 mol ethylene oxide. A very good, tinctorially strong and uniformly colored print is obtained, almost equal to the print obtained by the procedure of Example 1.

The tinctorial strength and uniformity are superior to those of a print made in a similar manner, in which the cetyl alcohol/ethylene oxide condensate, or, alternatively, the condensate of glycerol monolaurate with ethylene oxide is omitted from the printing paste.

#### EXAMPLE 3

A printing paste is prepared as described in Example 1, except that the 0.4 part of lauric diethanolamide is replaced with 0.4 part of the condensate of nonyl phenol with 9 mols ethylene oxide, and is applied to a nylon tufted carpet in the manner therein described. A good tinctorially strong and uniformly colored print is obtained, almost equal in appearance to the print obtained by the procedure of Example 1.

### **EXAMPLE 4**

The procedure described in Example 3 is repeated, except that the 0.4 part of lauric diethanolamide is replaced by 0.4 part of cetyl/oleyl sodium sulphate. A similar result to that of Example 1 is obtained.

#### EXAMPLE 5

The procedure described in Example 1 is repeated, except that the 0.4 part of lauric diethanolamide is replaced by 0.4 part of an aq. emulsion of sulphonated sperm oil and pine oil. A similar result to that of Example 1 is obtained.

#### **EXAMPLE 6**

The procedure described in Example 1 is repeated, except that the 0.4 part of lauric diethanolamide is replaced by 0.4 part of the condensate of actadecylamine with 20 mols of ethylene oxide. A similar result to that of Example 1 is obtained.

## **EXAMPLE 7**

The procedure described in Example 1 is repeated, except that the 0.2 part of the condensate of glycol monolaurate with 23 mols of ethylene oxide is replaced by 0.2 part of a condensate of glycerol monolaurate with 17 mols of ethylene oxide. A good, tinctorially strong print is ob-

#### EXAMPLE 8

The procedure described in Example 1 is repeated, except that the 0.2 part of the condensate of glycerol monolaurate and 23 mols of ethylene oxide is replaced by 0.2 part of condensate of glycerol monolaurate and 36 mols of ethylene oxide. A similar result to that of Example 1 60 is obtained.

# EXAMPLE 9

The procedure described in Example 1 is repeated, except that the 0.2 part of the condensate of glycerol mono-65 laurate and 23 mols of ethylene oxide is replaced by 0.2 part of a condensate of glycerol monooleate and 23 mols of ethylene oxide. A good tinctorialy strong print is obtained, equal to the print obtained in Example 1.

In each of Examples 7, 8 and 9 above the tinctorial strength and uniformity (i.e. freedom from frostiness), of the print obtained is much superior to that of a similar print obtained by a procedure in which either a surface active agent or a condensate of glycerol monolaurate (or oleate) with ethylene oxide is omitted from the printing paste.

#### 5 EXAMPLE 10

A printing recipe is prepared from:	Parts
The dyestuff described in the Colour Index as CI	
Acid Green 27 C.I. 61580	1
Lauric diethanolamide	0.4
The condensate of glycerol monolaurate with 23	
mols ethylene oxide	0.2
Water	67.65
Locust bean gum ether thickening, 4% solution	30
Tartaric acid	0.75
Total	100.00

The print paste is applied by means of a typical carpet printing screen to nylon 6.6 loop pile tufted carpet and the carpet is then placed in a steamer at 110° C. for a period of 10 min. The carpet is finally rinsed in cold water, hydroextracted and dried. An excellent, tinctorially strong and uniformly colored green print is obtained.

The strength and uniformity (i.e. freedom from "frostiness") is much superior to that of a similar print in which either lauric diethanolamide or the condensate of glycerol monolaurate with ethylene oxide is omitted from the printing pasts.

#### **EXAMPLE 11**

The procedure of Example 10 is repeated except that the dyestuff used therein is replaced by a similar amount of the dyestuff described in the Colour Index as Direct Orange 34. C.I. 40215. The strength and uniformity of the print obtained is much superior to that of a print obtained by a similar procedure in which either lauric diethanolamide or the condensate of glycerol monolaurate with ethylene oxide is omitted from the printing paste.

#### **EXAMPLE 12**

The procedure of Example 10 is repeated except that the dyestuff used therein is replaced by a similar amount of the dyestuff described in the Colour Index as CI Reactive Orange 35. Again a strong uniformly coloured orange print is obtained.

#### EXAMPLE 13

The procedure of Example 10 is repeated except that 45 the dyestuff used therein is replaced by a similar amount of the dyestuff described in the Colour Index as CI Reactive Brown 12. An excellent tinctorialy strong and uniformly colored brown print is produced.

#### **EXAMPLE 14**

# A printing paste is prepared from:

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	Parts	
The dyestuff described in the Colour Index as CI		
Acid Black 48 C.I. 64005	1.5	55
Lauric diethanolamide	0.4	
The condensate of glycerol monolaurate with 23	٠,,	
mol ethylene oxide	0.2	
Water	67.8	
Locust bean gum ether thickening, 4% solution	30	60
Acetic acid (80%)	0.1	
	1000	

The print paste is applied from an impregnated foam 65 pad to a cut pile wool tufted carpet and the carpet is then placed in a steamer at 110° C. for 10 min. The carpet is finally rinsed in cold water, hydroextracted and dried. An excellent, tinctorially strong, uniformly colored grey print is obtained.

The tinctorial strength and uniformity are much superior to those of a print prepared by a similar method in which either the lauric diethanolamide or the glycerol monolaurate/ethylene oxide is omitted from the print paste.

### **6** EXAMPLE 15

#### A printing paste is prepared from: Parts 1 8 1 The dyestuff described in the Colour Index as CI 0.6 Basic Red 18 \_\_ 0.4 Lauric diethanolamide \_\_\_\_ The condensate of glycerol monolaurate with 23 0.2 mol ethylene oxide \_\_\_\_\_ 63.8 Water 10 Locust bean gum ether thickening, 4% solution \_\_ 30 4 Propylene carbonate \_\_\_\_\_\_ Acetic acid (glacial) 100.0

The print paste is applied from an impregnated foam pad to a cut pile acrylic tufted carpet and the carpet is then placed in a steamer at 110° C. for 10 min. The carpet is finally rinsed in cold water, hydroextracted and dried. An excellent, tinctorially strong, uniformly colored red print is obtained. The tinctorial strength and uniformity are superior to those of a print prepared by a similar method in which no surface active agents have been added.

#### **EXAMPLE 16**

# A printing paste is prepared from:

	TA FAMILIA DE FATE DE FATE DE LA COMPANION DEL COMPANION DE LA	Parts
•	The dyestuff described in the Colour Index as CI Acid Red 37 C.I. 17045	1
U	Lauric diethanolamide	0.4
	The condensate of glycerol monolaurate with 23 mol ethylene oxide	0.2
	Water	64.4
5	Locust bean gum ether thickening, 4% solution	30
•	Formic acid	4
		100.0
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The print paste is applied from an impregnated foam pad to a cut pile acid dyeable polypropylene tufted carpet and the carpet is then placed in a steamer at 110° C. for 10 min. The carpet is finally rinsed in cold water, hydroextracted and dried. An excellent, tinctorially strong, uniformly colored red print is obtained.

The tinctorial strength and uniformity are superior to those of a print prepared by a similar method in which either the lauric diethanolamide or the glycerol monolaurate/ethylene oxide is omitted from the print paste.

# EXAMPLE 17

## A printing paste is prepared from:

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5	The dyestuff described in the Colour Index as CI Disperse Blue 56 Lauric diethanolamide The condensate of glycerol monolaurate with 23 mol ethylene oxide Sodium meta nitro sulphonate Para phenyl phenol Water Locust bean gum ether thickening, 4% solution Acetic acid	65.5 30
5	Acetic acid	100.0

The print paste is applied from an impregnated foam pad to a polyester needlefelt material. After printing the polyester needlefelt is placed in a steamer for 20 min. at 120° C. The material is finally rinsed in cold water, hydroextracted and dried. An excellent, tinctorially strong print is obtained.

The uniformity is superior to that of a print prepared by a similar method in which no surface active agent has been added. We claim:

1. A process for the printing of textile materials composed of fibers selected from polyamide, acrylic and polyester fibers, wherein there is applied to the textile material a print paste which incorporates, in addition to at least one dyestuff, a mixture of (a) a reaction product of glycerol with alkylene oxide and a carboxylic acid having at least four carbon atoms and (b) a surfaceactive agent other than the reaction product (a), the amount of the reaction product (a) being in the range 10 of 0.1 to 0.5% of the total weight of the print paste and the amount of the surface active agent (b) being at least equal to that of the reaction product (a).

2. A process as claimed in claim 1, wherein the reaction product (a) is the condensate of glycerol mono- 15

laurate with 23 moles of ethylene oxide.

3. A process as claimed in claim 1, wherein the surface-active agent is lauric acid diethanolamide.

4. A process as claimed in claim 1, wherein the amount of the reaction product (a) is in the range 0.1 to 0.3% 20 of the total weight of the printed paste.

5. A process as claimed in claim 1, wherein the amount of the surface-active agent (b) is between 1 and 3 times

the amount of the reaction product (a).

6. A process as claimed in claim 1, wherein the print paste incorporates a mixture of 2 parts by weight of lauric acid diethanolamide and 1 part by weight of the condensate of glycerol monolaurate with 23 moles of ethylene oxide.

7. A process as claimed in claim 1, wherein the textile

material is a pile fabric.

8. A process as claimed in claim 7, wherein the pile fabric is composed of polyamide fibers.

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DONALD LEVY, Primary Examiner

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