Patented Nov. 25, 1952 2,619,403

UNITED STATES PATENT OFFICE

2,619,403

EMULSIFIED VOLATILE HYDROCARBON LIQUIDS AS PRINTING PASTE THICKENERS

Leonard Krause, London, and James Arthur Wainwright, Spondon, near Derby, England, assignors to Celanese Corporation of America, a corporation of Delaware

No Drawing. Application March 24, 1949, Serial No. 83,294. In Great Britain April 9, 1948

8 Claims. (Cl. 8—63)

1

This invention relates to improvements in the colouration of textile fabrics, and is more particularly concerned with processes of printing, cover pad printing and padding with aqueous preparations containing dyestuffs which have sufficient affinity for the fabric being coloured to be fixed thereon by ageing or steaming and/or containing discharging agents which operate under the conditions of ageing or steaming.

In the printing of textile fabrics with dyestuffs which can be fixed thereon by ageing or steaming or with discharges, white or coloured, which operate in the ager or steamer, it is customary to make up the printing paste with comparatively large amounts of thickening agents, for example gum tragacanth, starch, methyl cellulose and the like, which give the paste sufficient consistency to be applied, for example to be retained in the cavities of the normal printing roller of a printing machine. Pastes employed in other methods of printing, for example screen printing, block printing and the like, have a similar consistency. Such pastes are applied locally to the fabric, for example as in the direct printing style or the discharging style, or by all-over methods, such as the cover pad printing method, the pin pad method or the padding method, onto a fabric which may or may not carry a resist in a suitable pattern thereon. The colouration or change in colouration is effected by ageing or steaming with or without an intermediate drying, and thereafter the fabric is given a thorough washing and/or soaping treatment to remove the thickener, a process which is necessary to achieve the desired brightness in the colours. Other after-treatments may also be applied, depending on the type of dyestuff employed in the printing paste, for example oxidising treatments in the case of vat dyestuffs applied in the reduced condition. The washing and/or soaping, followed by drying and, of course, stentering to width, constitutes a substantial item in the cost in the printing process as well as being time consuming. We have discovered that dyestuffs and/or discharges which can be fixed on the material by ageing or steaming processes can be applied to the fabrics either locally in a pattern or by an over-all treatment in printing or padding pastes which do not rely upon thickeners or similar film-forming substances for their consistency.

According to the present invention, such dyestuffs and/or discharges are applied in pastes the necessary consistency of which is achieved wholly or substantially by means of aqueous liquid-liquid emulsions, e. g. of the oil-in-water or of the water-in-oil type, but preferably the former. Preferably, whichever type is used, it is so formulated as to be a stable emulsion of the one type, since it is found that borderline emulsions

2

which either consist of or readily turn to compositions containing both oil-in-water and water-in-oil type emulsions are less suitable for the purpose of the present invention than stable emulsions of either the oil-in-water or the water-in-oil type. In making up an oil-in-water emulsion at low concentrations of the oil, for example up to 10%, the viscosity of the emulsion is of the same order as that of the aqueous phase. As the concentration by volume of the oil phase is increased, and particularly above about 20% by volume of oil, the viscosity increases very rapidly, and in this region, by a suitable selection of oil and aqueous phase, can readily achieve the consistency required for printing processes and particularly for printing processes wherein the paste is required to stay in the cavities in the ordinary copper printing rollers of a printing machine. The oil phase may constitute as much as 70 or 80% by volume of the emulsion.

We have found that by employing pastes of this character, i. e. pastes free or substantially free from film-forming solids, subsequent cleaning of the apparatus used, for example a screen in screen printing or the machine in machine printing, and of other utensils and apparatus used in the printing process, is very much facilitated. Using emulsions of the oil-in-water type, the apparatus can be easily and rapidly cleaned by merely rinsing with water. Furthermore, particularly where dyestuffs are employed which have a substantive affinity for the fabric under treatment under ordinary dyeing conditions, all aftertreatments subsequent to the ageing or steaming which fixes the dyestuff or effects the discharge, may be eliminated, thus considerably cheapening the whole process. Such dyestuffs include the substantive cotton dyestuffs for natural and regenerated cellulosic fabrics, for example fabrics of cotton or viscose artificial silk, acid dyestuffs for silk and wool fabrics, and the well-known dispersed water-insoluble dyestuffs for cellulose acetate or other cellulose derivatives, for example the water-insoluble derivatives of the nitrodiarylamine, azo and amino-anthraquinone series. These disperse insoluble dyestuffs have similar properties in relation to fabrics made from nylon or similar polyamides and from polyurethanes, polyacrylonitrile or copolymers of acrylonitrile and other vinyl compounds.

The fabrics printed according to the present invention have, as can be seen from the nature of the process, substantially uniform flexibility over their entire surface, a desirable property which is not achieved in the lacquer print method of applying colours, in which the colour is printed in a paste containing nitrocellulose cellulose acetate or synthetic resins or resin-forming reagents. Such film-forming substances are not removable by washing and remain on the fabric with con-

sequent change in its flexibility in the printed areas.

To achieve the maximum advantage from the present invention, the printing pastes should have a low content in total solids; for example, the solids should represent below 15% by weight of the total printing paste and preferably less than 10% or 7½%. Furthermore, as already indicated, of these total solids, the film-forming solids should form a very low proportion of the total printing paste, and particularly less than 3% by weight. Preferably the proportion of film-forming solids is below 1.5% by weight, and particularly below 0.75% by weight, and to achieve the maximum advantage the content of film-forming solids may be brought down to nil. Preferably, any film-forming solids present are such as will yield water-soluble films on the materials and not water-insoluble films. Of the total constituents of the printing paste, preferably more than 80% consist of liquids which are volatile under the ageing or steaming conditions. The proportion of volatiles may amount to 90% or 95% or more of the total printing paste.

As already indicated the emulsions used according to the present invention may be either of the oil-in-water or of the water-in-oil type. Whichever type of emulsion is used, it is preferable that the continuous phase has a comparatively high-surface tension. This is of particular importance in direct printing styles or other styles in which the printing paste is applied locally, as it helps to prevent spreading of the paste beyond the confines of the pattern either during application or in the subsequent ageing or steaming. For this reason it is preferable that the continuous phase should be aqueous and that any dispersing or emulsifying agents used for the purpose of making or stabilising the emulsion should not lower the surface tension of the aqueous phase to values which cause that phase to run over the surface of the fabric. In particular, we prefer to employ a continuous phase in which the surface tension as measured on that phase apart from the emulsion is not less than about half the surface tension of water at ordinary temperatures. Additions of glycerol or glycols, and particularly polyglycols, to water do not substantially lower the surface tension of the water. On the other hand, the anionic and cationic soaps, if used in suitable proportions, can lower the surface tension of the aqueous phase very substantially, and hence we prefer not to employ such substances as emulsifying agents. Other emulsifying agents are available which do not have such a profound effect upon the surface tension, for example sodium lignin sulphonate, lecithin and solid emulsifying agents of the type of bentonite, as well as the recognised non-ionic dispersing agents which are usually glycols, glycerine, polyglycols or other polyhydric alcohols partially esterified with lauric acid, palmitic acid, stearic acid, naphthenic acid or other soap-forming acids. Examples of these non-ionic dispersing agents are glycol mono-laurate, glycol mono-naphthenate and oxyalkylated derivatives thereof such as nona-ethylene glycol mono-laurate. This type of dispersing agent is sold under the trade name of Span, Tween, and Dispersol VL. In some cases, satisfactory results may be achieved by using as dispersing or emulsifying agent a mixture of a non-ionic dispersing agent and an anionic soap, and particularly an anionic soap formed from a soap-forming acid and an organic base such as triethanolamine or asymmetric diethyl ethylene diamine. The use of an aqueous phase as the continuous phase is especially important in machine printing from the point of view of adequately wetting the colour printing rollers.

In some cases, any tendency to spread on steaming may be reduced or eliminated by including small quantities of a film-forming substance, for example methyl cellulose or hydroxy-ethyl cellulose in the external or continuous phase, or a substance of the character of that sold under the trade name of Syton, which is a dispersion of colloidal silica in glycerol, water etc. Such additions of solids should, however, represent only a small proportion of the total printing paste, as already indicated. Very satisfactory prints can be obtained using a composition consisting substantially of an emulsion of water-immiscible liquid (e. g. hydrocarbon) in an aqueous solution of methyl cellulose, the content of the latter being for example 0.25 to 0.75%. For instance, the emulsion may contain (together with the requisite colouring matter) 45 to 75 parts of hydrocarbon, and 0.25 to 0.75% methyl cellulose, the balance being water with or without minor proportions, e. g. up to 10%, of water-miscible liquids such as methyl, ethyl or propyl alcohol, ethyl lactate, or diacetone alcohol.

The methyl cellulose may be a product having a methoxy content of 22 to 30%, e. g. 22 to 26% and a viscosity, measured in 2% aqueous solution at 25° C., of 300 to 1000 centipoises or more.

The oil phase in the emulsions used according to the present invention is preferably wholly or substantially wholly volatile, and for reasons of economy may consist of cheap oils of the character of kerosene or other fractions of petroleum or aromatic or naphthenic hydrocarbons, for example toluene, the xylenes and the like. Mixtures of aromatic and/or naphthenic hydrocarbons with each other or with petroleum hydrocarbons may be used.

If desired, swelling agents for the material of the fabric which are compatible with the emulsion and do not render it unstable may be included in the printing pastes. They may be so chosen that they are soluble in the aqueous phase or soluble in the oil phase. Such additions are particularly advantageous in the case of fabrics made of or containing cellulose acetate or other cellulose ester or ether or of nylon or similar hydrophobe polymers. Glacial acetic acid is particularly suitable in the case of screen printing of cellulose acetate, though not, of course, suitable for use on a copper roller printing machine, and diacetone alcohol is also of value in the aqueous phase of emulsions for screen or machine printing of cellulose acetate fabrics. Dimethyl phthalate and similar relatively volatile solvents for the cellulose acetate or other hydrophobe polymeric material may be included in the paste so as to dissolve in the oil phase, and may indeed partly replace the kerosene or other oil forming the bulk of the oil phase.

Such swelling agents are not necessary when printing dyestuffs or discharges which have affinity for the material of the fabric under ordinary dyeing conditions, though they may be included in such pastes. They find their greatest advantage in the application of those dyestuffs which have little or no affinity under ordinary dyeing conditions but which can be fixed on the fabric under ageing or steaming conditions. Such dyestuffs include, for example, the acid colours applied to cellulose acetate and the vat colours,

particularly when applied in the form of the leuco compounds. The best results are as a rule obtained when the dye employed is not soluble in the oil phase. Some commercial dyestuffs contain salts which break or tend to render unstable the emulsions. In such cases the salt constituents of the dyestuffs should be removed before incorporation of the dyes in the emulsions, for example by extraction with alcohol or other suitable organic solvent.

The following are examples of emulsions which may be applied for the screen printing of cellulose acetate fabrics. In all cases the parts are by weight.

(1)	Kerosene	64
	Water	26
	Sodium lignin sulphonate	5
	Glycerol	2.5
	Glacial acetic acid	2.5
	2.4 - dinitro-4'-hydroxy-diphenylamine	0.01
(2)	Kerosene	62.5
	Water	25
	Sodium lignin sulphonate	5
	Glacial acetic acid	2.5
	Syton 20G (a 20% dispersion of silica in glycerol)	5
	2.4-dinitro-4'-hydroxy - diphenylamine	0.01
(3)	Kerosene	66
	Water	26.5
	Sulphite lye	5
	Glacial acetic acid	2.5
	Methyl cellulose	0.05
	1.4-diamino-anthraquinone	0.01

Such pastes may be applied to the fabric by ordinary screen printing methods, the fabric then dried and the dyestuff fixed by a short steaming.

The following examples are of suitable printing pastes to be applied by a printing machine to cellulose acetate fabric, the parts again being by weight.

(4)	Kerosene	76
	Water	18.8
	Sodium lignin sulphonate	4.6
	Span 20 (sorbitan monolaurate)	0.3
	Tween 20 (polyoxyethylated sorbitan monolaurate)	0.3
	1.4-diamino-anthraquinone	0.01
(5)	Kerosene	23
	Water	50
	Stearic acid	5
	Triethanolamine	1
	Cetyl alcohol	1
	Diacetone alcohol	20
	1.4-diamino-anthraquinone	0.01
(6)	Kerosene	23
	Water	50
	Stearic acid	4.75
	Triethanolamine	1
	Cetyl alcohol	1
	Diacetone alcohol	20
	Methyl cellulose	0.25
	Solway Ultra Blue BS (desalted)	0.01
(7)	Kerosene	60.4
	Water	39.0
	Methyl cellulose	0.6
	Cellulose acetate dye—As required	
(8)	Kerosene	60.4
	Water	34.0
	Methyl cellulose	0.6
	Methylated spirit	5.0
	Cellulose acetate dye—As required	

The dye in emulsions Nos. 7 and 8 may be for example 1-hydroxy - ethylamino-anthraquinone, 1-amino - 4 - phenylamino - anthraquinone-2-carboxylic - hydroxyethylamide, or 2:4-dinitro-4'-amino-diphenylamine. Again the fabric is printed with the paste, dried and given a short steaming. With emulsion No. 6, a light soaping, say with ½% soap solution at 40° C., is desirable to remove any unfixed colour, while with emulsions 7 and 8 the material may be given a wash in cold or warm water, the colour being thus rendered somewhat brighter.

In a similar way, other fabrics may be printed with similar emulsions; for example emulsion No. 6 may be used for printing a silk fabric, in which case the diacetone alcohol may be omitted from the recipe.

The invention also includes applying discharges, which may be white or coloured, in emulsions of the type referred to above. The discharging agents may be of the oxidising type, for example chlorate discharges, or of the reducing type, for example hydrosulphite discharges. For a reducing discharge soluble in the aqueous phase, sodium or other alkali metal formaldehyde sulphoxylate may be used, while for discharges soluble in the oil phase heavy metal formaldehyde sulphoxylates, for example zinc formaldehyde sulphoxylate (Decrolin), may be employed.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for the production of patterned effects on textile materials, which comprises steaming the material after printing with a printing composition consisting of a substance capable of effecting a color change in a paste of printing consistency, said paste consisting substantially of water and a volatile hydrocarbon liquid selected from the group consisting of kerosene, toluene and xylene emulsified together with 0.25–0.75% of a water-soluble methyl cellulose, based on the weight of the paste.

2. Process for the production of patterned effects on textile materials, which comprises steaming the material after printing with a printing composition consisting of a substance capable of effecting a color change in a paste of printing consistency, said paste consisting substantially of water and kerosene, emulsified together with 0.25–0.75% of a water-soluble methyl cellulose, based on the weight of the paste.

3. Process for the production of patterned effects on textile materials, which comprises steaming the material after printing with a printing composition consisting of a dye in a paste of printing consistency, said paste consisting substantially of kerosene and water, emulsified with water-soluble methyl cellulose, the kerosene representing 45–75% and the methyl cellulose representing 0.25–0.75% of the weight of the paste.

4. Process for the production of patterned effects on textile materials of cellulose acetate, which comprises steaming the material after printing with a printing composition consisting of a dye in a paste of printing consistency, said paste consisting substantially of kerosene and water, emulsified with water-soluble methyl cellulose, the kerosene representing 45–75% and the methyl cellulose representing 0.25–0.75% of the weight of the paste.

5. Process for the production of patterned effects on cellulose acetate textile material, which comprises printing the material with a composition consisting of a water-insoluble cellulose acetate dye in a paste of printing consistency, said paste consisting substantially of kerosene

and water, emulsified with water-soluble methyl cellulose, the kerosene representing 45–75% and the methyl cellulose representing 0.25–0.75% of the weight of the paste and then steaming the material.

6. Process for the production of patterned effects on cellulose acetate textile material, which comprises printing the material with a composition consisting of a water-insoluble cellulose acetate dye in a paste of printing consistency, said paste consisting of kerosene, water, water-miscible swelling agent for cellulose acetate, and water-soluble methyl cellulose, the kerosene constituting 45–75%, the water-miscible swelling agent constituting up to 10%, and the methyl cellulose, constituting 0.25–0.75% by weight of the paste, and the balance being water and then steaming the material.

7. Process for the production of patterned effects on cellulose acetate textile material, which comprises printing the material with a composition consisting of a water-insoluble cellulose acetate dye in a paste of printing consistency, said paste consisting of kerosene, water, ethyl alcohol, and water-soluble methyl cellulose, the kerosene constituting 45–75%, the ethyl alcohol constituting up to 10%, and the methyl cellulose constituting 0.25–0.75% by weight of the paste, and the balance being water.

8. Process for the production of patterned effects on cellulose acetate textile material, which comprises printing the material with a composition consisting of a water-insoluble cellulose acetate dye in a paste of printing consistency, said paste consisting of kerosene, water, ethyl alcohol, and water-soluble methyl cellulose of viscosity 300–1000 centipoises as measured in 2% aqueous solution at 25° C., the kerosene constituting 45–75%, the ethyl alcohol constituting up to 10%, and the methyl cellulose constituting 0.25–0.75% by weight of the paste, and the balance being water.

LEONARD KRAUSE.
JAMES ARTHUR WAINWRIGHT.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,792,152	Ellis	Feb. 10, 1931
1,929,573	Whitehead	Oct. 10, 1933
2,133,470	Olpin	Oct. 18, 1938

FOREIGN PATENTS

Number	Country	Date
550,637	Germany	May 14, 1932

OTHER REFERENCES

"Melliand Textilberichte" for 1938, volume 19, pages 804 to 807 inclusive.