Patented Sept. 14, 1954

2,689,162

UNITED STATES PATENT OFFICE

2,689,162

TEXTILE DECORATING COMPOSITION CONTAINING ALDEHYDE-AMINE RESIN AND ZINC SILICOFLUORIDE CURE ACCELERATOR

Samuel Lee and Alfred H. Siepert, Fair Lawn, N. J., assignors to Interchemical Corporation, New York, N. Y., a corporation of Ohio

No Drawing. Application May 26, 1950, Serial No. 164,609

2 Claims. (Cl. 8—69)

1

This invention relates to the printing of textile fabrics, and has particular reference to a method for simultaneously printing and discharging previously dyed fabrics by the use of pigmented water-in-lacquer emulsions having an inner phase comprising an aqueous solution of dye discharge agent, the external phases of which comprise water-immiscible liquids of the film-forming type.

It is known that textile fabrics can be printed by applying water pastes of dyestuffs with water-soluble thickeners to render the compositions printable in consistency. The dyes are applied in solution in water and fixed on the fabric in a variety of ways, following which the fabric is washed to remove thickener, stretched and dried.

When printing on previously dyed cloth, it is conventional practice to remove the color from areas to be printed with a decolorizing agent, commonly known as a discharge agent. Since discharge agents, like printing pastes, were applied in water solution, the discharging of the color did not complicate the printing operation.

In U. S. Patent 2,202,283, issued May 28, 1940, there is disclosed a method of printing textile fabrics in which a solution of a dyestuff in water, generally in the undeveloped state, is emulsified as the inner phase of an emulsion in which the continuous phase is a liquid which is film-forming so as to produce an emulsion, and preferably comprising a lacquer, i. e., a solution of a film-forming solute in a volatile organic solvent—to give a paste of printing consistency, and the resulting paste is then printed onto the fabric. The enveloping of the dyestuff by the lacquer results in a control of deposition of the color, not previously attainable with conventional dye pastes. Similarly, U. S. Patents 2,222,581–2 disclose a method of printing textiles with pigmented water-in-lacquer emulsion.

In U. S. Patent 2,267,620, issued December 23, 1941, there is disclosed the simultaneous printing and discharging of previously colored textiles with printing pastes obtained by emulsifying a discharge agent into the interior phase of an emulsion in which the external film-forming lacquer phase is resistant to the action of the discharge agent. Such emulsions may be pigmented or they may contain a dyestuff or dyestuff component in the aqueous phase. Discharge printing with pigmented emulsions of this type offers several advantages over the use of conventional dyestuffs; shades of color not otherwise obtainable can be produced by using the pigmented emulsions, and brighter colors, sharper prints,

2

and, in many instances, improved permanence, result from discharge printing with pigmented emulsions.

Notwithstanding the many advantages to be derived from printing with pigmented or colored emulsions containing a discharge agent, there are several disadvantages which have prevented the widespread use of such emulsions for this type of printing. Some of these difficulties include: low color value of the print due to failure of the resin to adhere to the fibers of the cloth, breaking of color cuts, gelation of color cuts, and loss of discharge power of cuts on aging.

The present invention is based on the discovery that most of the above difficulties can be substantially completely eliminated by adding a water-soluble metal silicofluoride salt to pigmented emulsions containing discharge agents and thermosetting resin to bind the pigment to the fibers of the cloth. Accordingly, the novel compositions of the present invention comprise a pigmented water-in-lacquer emulsion containing a water-soluble metal silicofluoride salt and a discharge agent, preferably a reducing agent, dissolved in the aqueous phase and a thermosetting resin dissolved in the lacquer phase. The invention also comprehends the novel method of discharge printing using the emulsions of the present invention.

Typical of the water-soluble metal silicofluorides which are operable in the present invention are the zinc, cadmium, mercury, and magnesium salts. Ammonium silicofluoride, although soluble to some extent in water and in many of its reactions behaves as a metal salt, technically is not a true metal salt, and is not operable in the present invention, and hence is not included within the scope of the invention. Of the water-soluble metal silicofluorides, the zinc silicofluoride is especially preferred because, among other reasons, it is readily available at moderate costs, readily soluble in water to give concentrated solutions (as high as 30% solution at room temperature) and exerts a stabilizing influence on the discharge agent.

The water-soluble metal silicofluorides, when used in pigmented printing emulsion containing a thermosetting resin to bind the pigment to the fibers of a cloth and a discharge agent, appear to accelerate the curing or setting of the resin at temperatures conventionally used in the art for processing textile cloth that has been printed with the emulsion. The silicofluoride accelerator is preferably used in concentration of 0.25 to 5.0% by weight of the total emulsion weight.

In preparing a printing paste in accordance with the invention, an aqueous solution of a discharge agent such as sodium hydrosulfite, zinc hydrosulfite, sodium sulfoxylate, zinc sulfoxylate, or basic zinc sulfoxylate, and a water-soluble metal silicofluoride is emulsified into a water-immiscible phase comprising pigment dispersed in a volatile, water-immiscible organic solvent solution of binder resin, including a thermosetting resin. If concentrated solutions are used, the emulsion concentrate which results can be diluted with additional amounts of volatile water-immiscible solvent and additional amounts of water emulsified therein to give an emulsion paste of the desired concentration and printing consistency. After cutting with solvent and water the printing paste should preferably contain from 0.5 to 10% of binder resin (up to 5% of which may be thermosetting resin), 5 to 30% of discharge agent, 0.25 to 5.0% of water-soluble metal silicofluoride, and as a practical matter will contain at least about 40% and not more than about 80% of aqueous phase.

Printing pastes having this composition can be arrived at by methods conventional to the art. For instance, the textile printer may be supplied with a concentrated color dispersion consisting of pigment dispersed in a concentrated lacquer, i. e. a concentrated solution of a binder resin dissolved in a volatile water-insoluble organic solvent. After dilution to the desired concentration, an aqueous solution of a discharge agent may be emulsified into the pigment lacquer and, finally, an aqueous solution of the water-soluble metal silicofluoride is emulsified into the lacquer.

The following examples in which the parts are by weight are given to further illustrate the invention.

Example 1

	Parts
Titanium dioxide	15.0
70% oil modified glyceryl phthalate (e. g. Beckasol P 296)	7.5
Urea-formaldehyde resin (e. g. Beetle 227–8)	2.5
in	
Xylol	33.5
Butanol	1.5
20% aqueous solution of basic zinc sulfoxylate	35.0
and	
30% aqueous solution of zinc silicofluoride	5.0

A printing emulsion is prepared from the above ingredients by dispersing the titanium dioxide pigment in a solution of the glyceryl phthalate and urea-formaldehyde resins in a mixture of the xylol and butanol and then emulsifying the aqueous solution of basic zinc sulfoxylate and zinc silicofluorides therein to obtain a water-in-lacquer emulsion. The resulting emulsion printing paste simultaneously prints white and discharges colored fabrics dyed with a direct dye, such as an azo dye.

Example 2

	Parts
Ethyl cellulose lacquer (10% solution of standard ethoxy type, 50–100 cp. ethyl cellulose in a solvent consisting of 80 parts xylol and 20 parts pine oil)	12.
Mineral spirits	20.
30% aqueous solution of sodium sulfoxylate	63.
30% aqueous solution of zinc silicofluoride	5.

A clear emulsion was prepared by diluting the ethyl cellulose lacquer with the mineral spirits and then emulsifying the sodium sulfoxylate and zinc silicofluoride solutions therein. Then a color dispersion, prepared by dispersing 10 parts phthalocyanine blue pigment in 20 parts of a 50% melamine-formaldehyde resin solution in equal parts of xylol and butanol (e. g. Melmac 245–8) and diluting the dispersion with 70 parts of turpentine, was added to the clear emulsion in the amount required to produce the desired effect. For instance, 10 parts of the color to 100 parts of the clear emulsion produces a discharge printing paste that will print a pastel blue shade on a dischargeable background.

Example 3

	Parts
70% drying oil modified glycerol phthalate resin, 50% solution in xylol (e. g. Beckasol P 27	5.
15% solution of natural rubber, smoked sheet, in xylol	20.
Pine oil	5.
Mineral spirits	15.
30% aqueous solution of sodium hydrosulfate	50.
15% aqueous solution of magnesium silicofluoride	5.
Phthalocyanine green dispersion, consisting of 15 parts phthalocyanine green dispersed in 30 parts of Melmac 245–8 (50% solution of melamine-formaldehyde resin in equal parts xylol and butanol) and 55 parts of turpentine	5.

The clear water-in-oil emulsion was prepared by emulsifying the aqueous solutions of sodium hydrosulfite and magnesium silicofluoride into the mixed solutions of glyceryl phthalate resin and rubber, diluted with the pine oil and mineral spirits. The color dispersion was then added to give a water-in-oil discharge printing paste that prints a light green on a dischargeable dark background, such as navy blue.

We claim:

1. A discharge printing paste for textiles comprising a pigmented water-in-lacquer emulsion, the outer phase of which comprises a pigmented water-immiscible solution of a thermosetting resin of the group consisting of urea-formaldehyde resin and melamine-formaldehyde resin in a volatile organic solvent, and the inner phase of which is an aqueous solution of a textile dye discharge agent of the group consisting of water-soluble metal hydrosulfites and sulfoxylates and 0.25 to 5% of zinc silicofluoride.

2. A discharge printing paste for textiles comprising a pigmented water-in-lacquer emulsion, the outer phase of which comprises a water-immiscible solution of a thermosetting resin of the group consisting of urea-formaldehyde resin and melamine-formaldehyde resin in a volatile organic solvent, and the inner phase of which is an aqueous solution of a textile dye discharge agent of the group consisting of water-soluble metal hydrosulfites and sulfoxylates and 0.25 to 5% of zinc silicofluoride, wherein the aqueous phase constitutes at least 40% of the emulsion.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,267,620	Cassel	Dec. 23, 1941
2,361,277	Enderlin et al.	Oct. 24, 1944
2,413,624	Harris	Dec. 31, 1946
2,555,277	Boyer	May 29, 1951