Patented Aug. 14, 1945 2,381,878

UNITED STATES PATENT OFFICE

2,381,878

TEXTILE PRINTING PASTES AND TEXTILES PRODUCED THEREFROM

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No Drawing. Application July 13, 1939, Serial No. 284,213

4 Claims. (Cl. 260—15)

This invention relates to textiles decorated with coloring matter dispersed in water insoluble binders, and to coloring compositions useful in preparing such textiles. Specifically, this invention relates to textile marking compositions comprising cellulose ethers and urea formaldehyde resins, and to the decorated textiles made therefrom.

The conventional method of coloring textiles is to dye them in the piece, or to print dyes in various designs on the textiles. The dye printing of textiles is an expensive operation, and often open to serious objections due to the failure of many dyes to resist light, washing, dry cleaning and other incidents of normal use. Furthermore, fine designs reproduce poorly, due to the tendency of the dye pastes to spread.

It has been proposed to print textiles by the use of pigmented compositions, formed by dispersing pigment in a variety of binders, applying the compositions in a manner similar to the printing of paper, directly to the untreated fabric. This method of textile decorating has obvious advantages over the dye printing method, since it eliminates the treatment of the fabric before and after printing, necessary in dye printing, permits the use of the cheaper, more light-resistant covering pigments, and gives finer prints. It also permits the use of fabrics which have slight defects, since the pigment tends to hide the defects.

Although the use of pigmented marking compositions possesses very great advantages over the conventional dye printing methods, the method has had but little application, due primarily to other objectionable qualities of the pigmented coating compositions.

A principal objection to these pigmented compositions is the development of what is known in the trade jargon as "hand"—a certain objectionable stiff feel of the cloth in handling, as compared with the smooth feel of the unprinted cloth. This is due only slightly to the thickness of the coating on the individual yarn; it is probably due primarily to the bridging of the film from one yarn of the fabric to the next, whereby agglomerates of yarns are formed which give the impression on handling that the fabric is woven from coarse thread. It is therefore essential that the composition yield a discontinuous film which does not bridge the yarns of the fabric unduly.

A second principal objection is the phenomenon known as "crocking," which is the tendency of the printed fabric to yield color to another fabric, or to the hand, when rubbed against it. While this phenomenon is observable with many dyestuff prints, it is far more serious with pigmented prints, and is one of the principal objections of the trade to pigment-printed fabrics.

A pigmented marking composition must not only meet the requirements of not crocking appreciably, and not giving a noticeable hand to the fabric, but must also meet other requirements. Adhesion to fabric, sufficient strength, flexibility and extensibility to withstand crushing, crumpling and stretching of the fabric, good resistance to washing and dry cleaning agents, and the ability to withstand ironing, are all essential characteristics of a desirable print.

The combination of all of these properties in a single vehicle is obviously difficult of attainment. Extensibility and flexibility are limited by thermoplasticity and a tendency to stick while ironing; a great many desirable film-forming ingredients may not be used because they do not withstand soap or dry cleaning solvents; and most flexible films which are also strong enough to wear well have their usefulness impaired by the "hand" they impart to the fabrics. The problem is further complicated by the fact that film forming binders often act entirely differently in the discontinuous films desirable in textile printing, as compared to the continuous films obtained in the ordinary printing, marking and coating of paper, textiles, wood and non-porous materials.

Attempts have been made to use nitrocellulose as a binder for textile marking compositions, but two serious difficulties have been encountered. First, nitrocellulose undergoes gradual decomposition, particularly under the influence of ultraviolet radiation. In decomposing, it gives off oxides of nitrogen which attack many pigments and ultimately destroy them. Secondly, nitrocellulose by itself is horny and gives the goods a very considerable "hand" because of its horny toughness. When it is treated with plasticizers in sufficient amount to make it flexible, its binding strength is so seriously impaired that the pigment is no longer firmly bound and the prints crock seriously. Cellulose acetate has likewise not proven satisfactory, because its binding strength is not sufficient when plasticized to flexibility.

Cellulose ethers of conventional solubility in organic solvents, such as ethyl cellulose, have likewise been suggested as binders for pigmented textile marking compositions, because of their ex-

cellent properties, when deposited in a discontinuous film on fabric. However, because of their solubility in ordinary dry cleaning fluids such as petroleum hydrocarbons and carbon tetrachloride, it has been found impracticable to use them to any great extent.

I have discovered that small quantities of urea formaldehyde resins may be blended with organic solvent soluble cellulose ether textile printing compositions, and particularly with ethyl cellulose, to form compatible mixtures which yield prints with unusual properties when the resin is converted to the insoluble stage. Notable among these properties are unusual resistance to washing and complete indifference to dry cleaning solvents in which the cellulose ethers are soluble.

Insolubilization of the soluble cellulose ethers may be obtained with as low as 5% of urea resin, based on the cellulose ether present; this insolubilization is accompanied by a noticeable increase in wash resistance and an increase in the plasticity of the film, the urea and cellulose ether being mutual plasticizers. In general, I use between 10 to 100 parts of urea resin to 100 parts of the cellulose ether. Higher percentages may be used, although the essential properties of the ether film may be lost thereby.

Additional plasticizer should be added for best results on many fabrics, particularly the synthetics. The normal plasticizers used with the cellulose ethers may be used successfully. Solvent plasticizers such as tricresyl phosphate and dibutyl phthalate are useful; and alkyd resins make very acceptable plasticizers for most purposes.

The following are typical examples of my invention:

Example 1

	Parts by weight
Indanthrene Blue GCDS (Schultz No. 1234) 16.5% water pulp	10.00
Low viscosity ethyl cellulose	3.75
Urea resin solution (50% in 30 butanol—20 xylol)	2.50
Pine oil	15.00
Xylol	6.25
Solvesso #3 (hydrogenated petroleum naphtha, boiling range 175–210° C.)	42.50
Water	20.00

The ethyl cellulose is dissolved in the solvents, and blended with the urea resin solution; the pulp is then stirred in, and then the water, and the resultant water-in-lacquer emulsion is ready for use as a printing paste. It makes an exceptionally good printing medium for cottons, and the prints are unusually resistant to both washing and dry cleaning, provided the urea resin is insolubilized by heating the fabric after printing.

Example 2

	Parts by weight
Lithosol Blue GLR (20% water pulp) (Du Pont)	10.0
Benzyl cellulose (high viscosity)	4.0
Ethanol	3.2
Toluol	12.8
Beetle 227—8 sol. (50% urea formaldehyde resin in 20 xylol—30 butanol)	5.0
White pine oil	15.0
Solvesso #2 (hydrogenated petroleum naphtha, boiling range 135–177° C.)	30.0
Water	20.0

Made like Example 1, and similarly useful.

Example 3

	Parts by weight
Monastral Blue (copper phthalocyanine) 20% water pulp	10.0
Ethyl cellulose (500 c./p. viscosity)	3.1
White pine oil	6.2
Solvesso #2	52.7
Butanol	3.0
Urea formaldehyde resin (50% solids—30 butanol—20 xylol)	5.0
Water	20.0

Made like Example 1.

Cellulose esters may be mixed with the ethers, provided the cellulose ether remains the major portion of the cellulose derivative, without greatly affecting the film properties. A typical example of such a composition is the following:

Example 4

	Parts by weight
Watchung Red (Krebs Color & Pigment Corp.) dispersion in ½'' nitrocellulose solution	12.1
Ethyl cellulose—low viscosity	4.4
15'' RS nitrocellulose solution	10.7
Tricresyl phosphate	8.0
Paraplex RG2—60% solution (Resinous Products Corp.), (a complex glycerol-sebacic acid ester)	6.0
Butyl acetate	18.0
Butanol	20.0
Toluol	18.8
Urea formaldehyde solution of Example 1	2.0

Ultimate constitution:

	Parts by weight
Pigment	2.4
½'' RS nitrocellulose	1.5
Ethyl cellulose	4.4
15'' nitrocellulose	2.1
Tricresyl phosphate	8.5
Paraplex	3.6
Butyl acetate	25.0
Butanol	21.5
Toluol	30.0
Urea resin	1.0

This example is particularly useful for printing on synthetic yarns. The compositions of the first three examples, plasticized with alkyd resins modified with 50 to 60% of oil fatty acids, also make very desirable printing pastes for synthetic yarns.

The urea formaldehyde resin used can be replaced by other similar resins made from urea, its homologues and derivatives, and from compounds yielding urea. Of the cellulose ethers, those of conventional solubility in organic solvents may be used. Water soluble ethers, such as methyl cellulose, must be avoided, since the resultant prints are affected by washing.

Other examples of the invention can be multiplied without departing from the scope of the invention, which is defined in the claims.

I claim:

1. A textile printing paste comprising a dispersion of color in a vehicle comprising a water-insoluble cellulose ether soluble in carbon tetrachloride, and a solvent-soluble urea-formaldehyde resin, in mutual solution in organic solvents, the ratio of urea resin to cellulose ether being between 1 to 20 and 1 to 1, the paste being characterized by the complete indifference to carbon tetrachloride and the resistance to laundering of discontinuous films of the compositions after

application to fabric and conversion of the resin to its insoluble form.

2. A textile printing paste comprising a dispersion of color in a vehicle comprising a water-insoluble ethyl cellulose soluble in carbon tetrachloride, and a solvent-soluble urea-formaldehyde resin, in mutual solution in organic solvents, the ratio of urea resin to ethyl cellulose being between 1 to 20 and 1 to 1, the paste being characterized by the complete indifference to carbon tetrachloride and the resistance to laundering of discontinuous films of the compositions after application to fabric and conversion of the resin to its insoluble form.

3. An emulsion for textile printing comprising a composition as defined in claim 2 having water dispersed therein to form a water-in-lacquer emulsion.

4. In the combination of a textile fabric with markings comprising discontinuous films of binder holding pigment onto the fabric in simulation of conventional dye markings, the improvement which consists in using as the pigment binder a wash-resistant carbon-tetrachloride indifferent combination of ethyl cellulose in itself normally soluble in carbon tetrachloride, and insolubilized urea-formaldehyde resin, both deposited from a mutual solution in organic solvents, the ratio of resin to ethyl cellulose being between 1 to 20 and 1 to 1.

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