Patented Apr. 4, 1944

2,345,879

UNITED STATES PATENT OFFICE

2,345,379

TEXTILE PRINTING PASTE

Malcolm C. Moore, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application July 30, 1940, Serial No. 348,595

5 Claims. (Cl. 260—13)

This invention relates to the art of printing textiles and more particularly relates to an improved textile printing paste containing an inert water-insoluble pigment and to the method of applying the same to a fabric.

Heretofore it has been the practice in the printing of textile fabrics with insoluble coloring agents to print the colors from a paste containing the coloring in a soluble form and thereafter developing the insoluble color on the fabric by suitable after-treatment. As thickeners and carriers for the coloring agents in such printing pastes there have been used such materials as starches and water-soluble gums such as gum tragacanth. After application of the paste to the fabric it has been the practice to develop or fix the color on the fabric and then subject the latter to a washing treatment to remove the starch or gum carrier. The color developing operation is a very delicate one and is subject to considerable variation. Insufficient developing or over-developing are common occurrences in such a process. They result in rejection of the printed goods. Furthermore, in printing of delicate fabrics it is impossible to wash the printed fabric sufficiently to remove the starch or gum carrier, since the fabrics themselves become weakened through the washing treatment.

It is an object of this invention to provide a textile printing paste which overcomes the above disadvantages in textile printing. It is a further object to provide a printing paste containing an inert water-insoluble pigment.

It is another object to provide a method of printing textile fabrics with a printing paste containing an inert water-insoluble pigment which eliminates the developing and washing treatments which have been necessary in using the prior art printing pastes and methods.

Other objects of the invention will appear hereinafter.

The above objects may be accomplished in accordance with this invention by the preparation of printing pastes containing an inert water-insoluble pigment dispersed in an aqueous oil-in-water type emulsion of a solution of a water-insoluble cellulose ether in a volatile organic solvent. The improved printing paste so formed may then be applied to a textile fabric and the fabric dried. Since the pigment is in its fully developed state no after-treatment on the fabric is necessary to develop the color and the only treatment necessary is the drying of the fabric to remove water and volatile solvents from the emulsion. I have found that such an emulsion of a cellulose ether presents many advantages over the starch or gum thickeners used in the prior art printing pastes. I have found that my invention is of particular importance with use of white pigments such as titanium dioxide and that by using such pigments in my emulsions I am able to obtain printed textile fabrics having a purer white color than has been possible heretofore. Furthermore, the pigment is not subject to crocking or washing out.

The water-insoluble cellulose ethers which I have found to be so useful in aqueous oil-in-water type emulsions for textile printing in accordance with this invention are for example, ethyl cellulose, propyl cellulose, butyl cellulose, benzyl cellulose, mixed ethyl benzyl cellulose, mixed ethyl butyl cellulose, etc. Ethyl cellulose is preferred. The ethyl cellulose used will be sufficiently etherified to be insoluble in water and soluble in organic solvents and may have, for example, an ethoxy content within the range of about 41% to about 51%, and preferably from about 44% to about 48%. The viscosity characteristics of the ethyl cellulose used will depend upon the properties desired in the ultimate composition. The high viscosity type is particularly desirable.

A plasticizer for the cellulose ether may be included in the emulsion and as such either a solid or a liquid plasticizer may be used. Suitable plasticizers, for example, are hydrogenated methyl abietate, hydrogenated ethyl abietate, triphenyl phosphate, tributyl phosphate, methylphthalyl methyl glycollate, ethylphthalyl ethyl glycollate, mineral oil, etc.

A synthetic resin which is compatible with the cellulose ether may also be included. Preferably a resin which is resistant to alkalies and which exerts a softening action on the cellulose ether will be used. By softening action I mean the lowering of the melting point of the cellulose ether and not necessarily a plasticizing of the cellulose ether in the strict sense of the term. Resins which I have found to be suitable are rosin modified alkyd resins, such as rosin modified or hydrogenated rosin modified terpene-maleic anhydride resins; rosin modified maleic anhydride resins; drying oil modified terpene-maleic anhydride resins; polymerized hydrocarbon resins, such as polymerized naphthalene or hydrogenated forms thereof; polymerized coumarone-indene resins, or hydrogenated forms thereof; 100% phenolic resins; polyhydric alcohol esters of hydrogenated rosin, as well as other types having the above defined properties.

As emulsifying agents for preparing the cellulose ether emulsions utilized in accordance with the invention, I may employ, for example, the alkali metal salts of the higher aliphatic acid sulfates, as sodium lauryl sulfate, sodium stearyl sulfate, etc.; sulfonated oils, as sulfonated castor oil, sulfonated olive oil, etc.; soaps, as sodium stearate, potassium oleate, sodium oleate, etc.; alkali metal salts of alkyl naphthalene sulfonic acids, as sodium butyl naphthalene sulfonate, sodium isopropyl naphthalene sulfonate, etc.

In preparing the cellulose ether emulsions, the cellulose ether together with the plasticizer and the resin, if either or both are employed, will preferably be dissolved in a suitable water-immiscible solvent or solvent mixture before emulsification and the solvent solution emulsified in water by means of the emulsifying agent. Suitable solvents or solvent mixtures may include for example, light aromatic hydrocarbons, as for example, toluol, xylol, Hi-Flash naphtha, etc.; petroleum hydrocarbons as, for example, Stoddard solvent, Solvesso No. 2, Solvesso No. 3, etc.; butanol, pine oil, etc. By Stoddard solvent, Solvesso No. 2 and Solvesso No. 3, I mean the petroleum hydrocarbon solvents known in the industry by those names. They may be generally characterized as follows:

	Boiling range	Specific gravity
Stoddard solvent	152-195	.767
Solvesso No. 2	135-177	.858
Solvesso No. 3	175-210	.884

The inert, water-insoluble pigments which I incorporate in my improved textile printing paste described in accordance with this invention may be either the inorganic or the organic materials of this type which are commonly used in printing pastes. The organic pigments are those which consist either wholly or in part of dyestuffs which have been rendered insoluble in water and oil. These include those organic pigments which are made by precipitation on a suitable base. I particularly prefer to use white pigments in the emulsion since I have found that particularly desirable results are obtainable with use of white pigments such as, for example, titanium dioxide. Textile printing pastes which will print white and which will provide a water-insoluble white print of a high degree of whiteness are, therefore, possible in accordance with my invention. Some of the more common inert, water-insoluble pigments which I may use in addition to titanium dioxide are the following: Monastral Fast Green GSF, Monastral Fast Blue BNSF, Chrome Yellow, Ponsol Blue BCL Double Paste, zinc oxide, etc.

Starch may be included in the printing paste produced in accordance with this invention if desired. It is desirable to include an excess of emulsifying agent such as potassium oleate in the printing paste formulation over the amount required to emulsify the ethyl cellulose composition, since the stability of the emulsion is aided thereby.

The textile printing paste described in accordance with this invention may be prepared by addition of the inert water-insoluble pigment in suitable form to the aqueous oil-in-water type emulsion of the water-insoluble cellulose ether. The pigments may be mixed into a paste with water or with the emulsifying agent such as potassium cleate before addition to the cellulose ether emulsion. The body and thickness of the printing paste may be varied as desired by varying the ingredients of the cellulose ether emulsion as well as by inclusion of other thickening materials such as, for example, starch. The body may also be varied by varying the amount of dissolved solids in the oil-in-water type emulsion as well as by the amount of pigments employed.

The solids content of the aqueous oil-in-water type emulsion of a solution of a cellulose ether in a volatile organic solvent utilized in the printing paste will usually not be in excess of about 40% by weight and preferably will be within the range of about 2% to about 20%. The amount of inert, water-insoluble pigment included in the printing paste may be adjusted to provide the shade and quality of print desired and will depend to a large extent on the particular pigment employed. Generally speaking, the total solids content of the printing paste will not exceed about 60% by weight and preferably will be within the range of about 2% to about 45% by weight.

The improved printing paste described in accordance with this invention may be applied to a textile fabric by means of printing rollers or screens such as are used in screen printing, followed by drying of the printed fabric in any suitable manner. The temperature of drying, for example, may be within the range of about 180° to about 320° F. and preferably may be within the range of about 220° to about 300° F. Developing of the color on the fabric or washing and soaping of the printed fabric are not necessary since development of the color is not required and removal of the solids deposited from the cellulose ether emulsion is not necessary and is not possible by washing and soaping. The drying to which the printed fabric is subjected merely removes the water and other volatile solvents contained in the emulsion.

The printed fabric produced by printing a textile fabric with the printing paste described in accordance with this invention will be characterized as carrying in its printed portion an inert, water-insoluble pigment bonded to the fabric by means of the cellulose ether composition. Such cellulose ether composition may be a water-insoluble cellulose ether alone or mixed with either a plasticizer or a suitable synthetic resin or both. The printed fabric is substantially resistant to crocking and is also resistant to laundering. In the case of the printed fabrics obtained with use of white pigments the printed portion will have a purer white color than is obtainable by the use of the prior art methods. The printed fabrics will be further characterized by uniformity of shade in the printed areas and by a depth of shade which may be varied by the amount of color incorporated into the printing paste. The following examples serve to illustrate the preparation and application of the improved printing pastes.

EXAMPLE 1

A solution of an ethyl cellulose composition was prepared containing the following ingredients:

	Parts by weight
Ethyl cellulose (high viscosity)	32
Triphenyl phosphate	16
Glycerol ester of hydrogenated rosin	10
Xylol	106
Hi-flash naphtha	20
Butanol	16

The above solution was then emulsified with 100

parts by weight of water containing 1.5 parts by weight of potassium oleate. The oil-in-water type emulsion obtained was passed through a suitable homogenizer in order to reduce the particle size of the emulsion. This emulsion was then used to prepare a printing paste containing the following ingredients:

	Parts by weight
Ethyl cellulose emulsion	1,000
Potassium oleate	16
Water	243
Pine oil	10
Corn starch 10% solution	800
Titanium dioxide (Ti-pure FF Krebs)	200

The printing paste was prepared by stirring the titanium dioxide and the potassium oleate together with 85 parts of the water to form a smooth paste. The pine oil was then added together with approximately 80 parts by weight of water and stirred until a smooth mix was formed. This mixture was then added slowly to the starch solution with stirring and the remaining portions of the water added. To this paste the oil-in-water ethyl cellulose emulsion was added and stirring continued until a smooth paste resulted. The printing paste so formed had a total solids content of 21% and a pigment content of 9% by weight. An 80 x 80 print cloth was printed with the paste, after which the printed cloth was subjected to a drying treatment over heated rolls at a temperature of about 240° F. The printed fabric obtained was resistant to washing and crocking and the printed portion exhibited a high degree of whiteness.

EXAMPLE 2

A solution of an ethyl cellulose composition was prepared containing the following ingredients:

	Parts by weight
Ethyl cellulose (high viscosity)	32
Triethylene glycol ester of hydrogenated rosin	20
Mineral oil	6
Solvesso No. 2	126
Butanol	16

The above solution was then emulsified with 100 parts by weight of water containing 1.5 parts by weight of potassium oleate. The emulsion was stabilized by passing through a homogenizer. Printing pastes were than prepared with the proportion of ingredients shown in the following table.

Table 1

	1	2	3
Titanium dioxide	20	20	
Zinc oxide			20
Water	20	20	20
Sodium hydroxide (25% solution)	½	½	
Above ethyl cellulose emulsion	30	30	30
Potassium oleate (15% solution)			3
Corn starch (6% solution)		20	20

The printing pastes containing the above ingredients were prepared by mixing together the titanium dioxide or zinc oxide with the water to form a smooth paste and then adding the sodium hydroxide with stirring. In the case of the third example the potassium oleate was also added. After these ingredients were stirred to form a smooth paste, the aqueous oil-in-water type ethyl cellulose emulsion was mixed in with stirring and in the second and third examples the corn starch was then added. Each of the printing pastes were then printed on 80 x 80 print cloth and the fabric dried by passing over a series of heated rolls at a temperature of about 250° F. The printed fabrics obtained exhibited excellent resistance to laundering and crocking and the printed portion showed a high degree of whiteness.

EXAMPLE 3

The ethyl cellulose emulsion of the oil-in-water type prepared in accordance with the formulations shown in Example 2 was used in the preparation of a series of four printing pastes prepared according to the following formulation:

	1	2	3	4
	Parts by weight	*Parts by weight*	*Parts by weight*	*Parts by weight*
Monastral Fast Green GSF (Krebs)	4			
Monastral Fast Blue BNSF (Krebs)		4		
Chrome Yellow			4	
Ponsol Blue BCL Dbl. Pst.				4
Potassium oleate (15% solution)	2	2	2	2
Oil-in-water type ethyl cellulose emulsion (Example 2)	30	30	30	30

Each of the above printing pastes were prepared by mixing the pigment color and the potassium oleate and then adding the ethyl cellulose emulsion with stirring to form a smooth paste. Each paste was then printed on 80 x 80 print cloth and the printed fabric dried over heated cans at a temperature of about 250° F. The printed fabrics which were obtained were substantially resistant to washing and showed substantially no loss in color strength after being washed, for example, in a solution of 0.5% of soap and 0.2% of soda ash at 160° F. for one hour. The prints were also substantially resistant to crocking.

It will be understood that the details and examples given hereinbefore are illustrative only and that the invention as broadly described and claimed is no way limited thereby.

What I claim and desire to protect by Letters Patent is:

1. A textile printing paste comprising an inert water-insoluble pigment dispersed in an aqueous oil-in-water type emulsion of solids content from about 2% to about 20% by weight, the said emulsion comprising a solution of ethyl cellulose in a volatile water-immiscible organic solvent, the amount of pigment being sufficient to give the desired color and the total solids content of the said textile printing paste being not in excess of about 45% by weight.

2. A textile printing paste comprising an inert water-insoluble pigment dispersed in an aequeous oil-in-water type emulsion of solids content from about 2% to about 20% by weight, the said emulsion comprising a solution of ethyl cellulose and a plasticizer therefor in a volatile water-immiscible organic solvent, the amount of pigment being sufficient to give the desired color and the total solids content of the said textile printing paste being not in excess of about 45% by weight.

3. A textile printing paste comprising an inert water-insoluble pigment dispersed in an equeous oil-in-water type emulsion of solids content from about 2% to about 20% by weight, the said emulsion comprising a solution of ethyl cellulose and a suitable synthetic resin compatible therewith in a volatile water-immiscible organic solvent, the amount of pigment being sufficient to give the desired color and the total solids content of the

said textile printing paste being not in excess of about 45% by weight.

4. A textile printing paste comprising an inert water-insoluble white pigment dispersed in an aqueous oil-in-water type emulsion of solids content from about 2% to about 20% by weight, the said emulsion comprising a solution of ethyl cellulose in a volatile water-immiscible organic solvent, the amount of pigment being sufficient to give the desired color and the total solids content of the said textile printing paste being not in excess of about 45% by weight.

5. A textile printing paste comprising a titanium dioxide pigment dispersed in an aqueous oil-in-water type emulsion of solids content from about 2% to about 20% by weight, the said emulsion comprising a solution of ethyl cellulose in a volatile water-immiscible organic solvent, the amount of pigment being sufficient to give the desired color and the total solids content of the said textile printing paste being not in excess of about 45% by weight.

MALCOLM C. MOORE.