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PRINTING PASTES

Harry A. Toulmin, Jr., Dayton, Ohio, assignor to The Commonwealth Engineering Company of Ohio, Dayton, Ohio

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This invention is concerned with new compositions for use in printing textiles, paper, leather and the like. This application is a continuation-in-part of my application Ser. No. 369,943, filed July 23, 1953, now abandoned.

Textile printing, which may be defined as localized dyeing or pigmentation in which the color is restricted to definite parts of the fabric to form a design or pattern, may be accomplished by several different methods identified, respectively, as direct, dyed, discharge and resist. All of these methods involve the use of compositions of paste-like consistency.

In direct printing with a dyestuff, a dye substantive to the textile being printed is incorporated in the paste or putty.

In direct printing with a dyestuff by the intaglio method, a relatively free flowing printing paste containing the color is applied to an engraved printing roll, usually of copper, for example by means of a furnisher roller, the excess paste is scraped off the roll, leaving paste in the depressions only and the roller is then applied to the fabric in the printing machine.

In planographic printing with a substantive dyestuff the color is incorporated in the solid putty or block and a portion of the color is transferred when the fabric is contacted with the putty, to form a print.

In printing according to the dyed method, the mordant is included in the paste and printed and fixed on the fabric, after which the mordanted fabric is dyed with a suspension of the mordant dye.

Printing by the discharge method involves printing a dyed fabric with an aqueous paste-like composition, which on drying and ageing, destroys the dye in the printed pattern to produce the pattern in one color or in white on the ground of the initial color.

In resist (or reserve) printing using chemical resists, the fabric is printed with a paste containing a substance which resists the dye when the fabric is dyed subsequent to the printing.

In printing with pigments, a paste having the finely divided or pulverized pigment incorporated therein is used.

The printing pastes are usually made up with a thickener or binder and, in the past, starch and dextrin have been used as the thickening agent. These require cooking of the paste to obtain uniform, stable compositions of predetermined consistency and have the further disadvantage, particularly in the case of dextrin, that they tend to dry out at relatively low temperatures around 35° F., while becoming too soft for satisfactory printing at elevated temperatures of 100° F. or above, for instance between 100° F. and 125° F. The compositions, therefore, are not generally useful since they are not adapted to use over a wide temperature range such as may be encountered in textile printing.

Because the thickeners used in the past have been dependent on cooking under controlled conditions for control of the consistency of the final composition, considerable difficulty has been met in producing compositions

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useful under varying sets of conditions, as for instance under one set of conditions when a rather free flowing paste is required, and also under a different set of conditions such that thicker compositions, resembling a putty, produce the best results.

For example, when the paste has to be cooked at high temperatures to obtain a printing composition of the free flowing type, such as is preferred for intaglio printing, it often happens that the final product has a consistency which is so thin that it cannot be used in the intaglio method to produce sharp designs with extremely fine, close fitting, interwoven multi-colored lines without running or smudging of the lines. On the other hand, putties comprising the thickeners or binders of the prior art and which have been cooked in the process of their preparation, are often friable at relatively low printing temperatures and undesirably soft at the elevated temperatures.

One object of this invention is to provide improved pastes for use in different textile printing methods.

Another object is to provide new pastes, including putties, having a predetermined consistency which does not depend on cooking of the paste.

A specific object is to provide new improved pastes for use in intaglio printing and which result in sharp, clear, substantially non-smudging close prints.

Another specific object is to provide an improved planographic printing putty.

It was thought that dextran would have advantages over the known binders and thickeners for use in printing pastes, and further that the highly adhesive dextrans, such as that produced by the action on sucrose of the strain of *Leuconostoc mesenteroides* known as NRRL L. m. B-512 dextran, which are long-chain gumming materials would be best adapted to such use.

Surprisingly, it is now found that the highly adhesive, water-soluble native dextrans are not satisfactory thickeners and binders for inclusion in the printing pastes. Also surprisingly, it is found that only special dextrans are satisfactory and have advantages over the known binding agents.

The dextrans which are used in the present improved printing pastes are short, tough gums having a viscosity in the water at 25° C.=1.16-0.57 centipoises and the crumbly short gums having viscosity in water at 25° C.=1.36-0.50 centipoises, and which form aqueous solutions of marked turbidity. The short, tough gums are produced by the action on sucrose of the strains of *Leuconostoc mesenteroides* bearing the following NRRL (Northern Regional Research Laboratories) designations: B-1414, B-1208, B-1210, B-1308, B-1380, B-1307, B-1388, B-1500, B-1396, B-1419, B-1144, B-1411, B-1498-A, and B-1298. Native dextrans which are crumbly gums are produced by the strains bearing the NRRL designations: B-640, B-1066, B-1204, B-1255, B-1120, B-1429, B-1385. These native high molecular weight dextrans which are short, tough, or crumbly gums have the special advantage for use in the printing art that, used in the printing pastes, they do not form "legs" as do long stringy or plastic gums and the like.

The methods for obtaining these native dextrans by inoculating a sucrose-containing nutrient medium with the whole culture, or filtered enzyme, of the selected *Leuconostoc mesenteroides* strain, incubating the nutrient until the dextran is biosynthesized in maximum yield, and precipitating the dextran from the fermentate, are known in the art.

The pastes of this invention are best prepared by pasting the dyestuff with water, the dextran, a lower aliphatic alcohol, or a glycol ether such as the ethyl ether of ethylene glycol, and one or more liquids which are sol-

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vents for the dextran, such as formamide or morpholine, and which, in conjunction with the glycol, assist in controlling the viscosity and tack of the short, tough or crumbly gum dextrans.

When the dye or other printing agent is soluble in water, the compositions may be made up by pasting the dye and dextran in water but even in the case of the water-soluble dyes, it is advisable to include viscosity adjusting agent such as one of the lower alkyl ethers of the alkylene glycols up to propylene glycol, formamide, morpholine or other organic solvent for the dextran, or a mixture of the glycol ether and organic solvent. A sufficient amount of the short tough gum dextran, or of the even shorter, crumbly gum dextran, is used to give, with the water and alcohol, glycol ether and, preferably, organic solvent for the dextran, a paste having the required consistency for the given printing application. In general, the amount of dextran used may be between 20% and 75% by weight based on the total composition weight. The total proportion of liquid may be varied but, as an example, may be between 5% and 30%. Of this, the proportion of water may be from 2% to 50%, the balance of the 5% to 30% total liquid being made up of the alcohol or glycol ether and, preferably, the organic solvent for the dextran.

The short, tough and crumbly gum dextrans may be used in compositions in which the printing agent is any dyestuff or intermediate useful in the direct style of printing in which the color is applied directly in one operation, and fixed during ageing by penetration of the color into the fiber (substantive dyes), by chemical reaction (azoic dyes), by lake formation (mordant colors), by reduction and oxidation (vat dyes) or by hydrolysis and oxidation (Indigosols).

The paste may comprise a mixture of the mordant and a short tough or crumbly gum dextran and be used in the dyed style of printing in which the mordant paste is first printed on the fabric and fixed by drying, ageing, and removal of the dextran, followed by dyeing of the mordanted fabric in a suspension of the mordant dye.

In another embodiment, the printing composition may be a paste comprising a mixture of a dye solvent or stripper and a short, tough or crumbly gum dextran. Such pastes are used in discharge printing and when applied to dyed fabrics destroy the color at those portions of the fabrics to which they are applied.

In yet another embodiment, the paste may be of the kind used in printing methods in accordance with which a colored discharge is applied to a colored base to obtain color-on-color design effects.

The short, tough or crumbly gum dextrans are also very useful and satisfactory binders in pastes of the resist type comprising a substance which shields the printed portions of a fabric from coloration by a dye applied to or developed on a previously printed fabric.

The following examples in which parts are by weight illustrate specific embodiments and formulations of the invention.

Example I

About 10 parts of vat dye, 5 parts of chromium fluoride, 5 parts of ammonium oxalate and 50 parts of finely divided native *L. m.* B-1443 dextran, with 5 parts of water, 5 parts of the mono-ethyl ether of diethylene glycol, and 5 parts of formamide.

The paste is prepared at ordinary temperatures, the mixing being continued until a substantially completely uniform mass is obtained. Natural silk fabric is printed with the paste, dried, steamed in the "cottage steamer" for one hour, washed, soaked at 60° C., again washed and dried.

Example II

A paste is prepared by mixing together 10 parts of aluminum acetate, 40 parts of native *L. m.* B-1419, 10 parts

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of water and 10 parts of methanol, at ordinary temperature until a smooth product is obtained.

This mordant paste is printed on cotton fabric and fixed by ageing and washing to remove the dextran. The mordanted fabric is then dyed with a suspension of an Alizarin dye containing in the usual amounts, glue, Turkey red oil, chalk and tannin. The dyed fabric is washed, oiled, dried and again aged, the process being completed in the usual way by soaping and treatment with a bleaching powder solution to clear the whites.

The paste may be modified by substituting other metallic mordants for the aluminum acetate.

Example III

A discharge paste is prepared by intimately mixing 5 parts sodium sulfoxylate-formaldehyde, 3.5 parts zinc oxide, 4 parts potassium carbonate, 10 parts sodium N-benzyl sulfanilate (Solution Salt C-solubilizing agent), 0.5 part anthraquinone (reduction catalyst), 30 parts native *L. m.* B-1144 dextran, 40 parts water, 30 parts morpholine, and 30 parts of the mono-methyl ether of propylene glycol.

The resulting paste may be printed on a cotton fabric dyed an azoic red which is then aged and subjected to the usual after-treatments to obtain a white print on the red ground.

This paste can be modified to produce a color-on-color print. For instance, if a blue vat dye is substituted for the zinc oxide, a color discharge (blue print) on a red ground is obtained.

Example IV

A printing putty is prepared by pasting 120 parts of Calamine Fast Scarlet 4 BSY (C.I. 326) with 100 parts of water, 600 parts of the ethyl ether of ethylene glycol, and 1000 parts of native *L. m.* B-1118 dextran, in a dough mixer, until a uniform putty is obtained.

This putty may be printed by the planographic method on regenerated cellulose or cotton fabric to obtain a clear, sharp scarlet print.

Example V

About 1000 parts of native *L. m.* B-1298 dextran are pasted with 100 parts of water, 50 parts of the methyl ether of diethylene glycol, and 50 parts of formamide. About 40 parts of glycerol monostearate, 160 parts soap flakes, 10 parts of sodium di-isobutylsulfosuccinate, and 10 parts of trisodium phosphate are pasted with 120 parts of water and mixed with the dextran-containing paste. Following this, 120 parts of the dyestuff, Direct Sky Blue FF (C.I. 518) are pasted with 120 parts of water and 120 parts of ethylene glycol monethyl ether, and added to the mass. Mixing is continued until a uniform substantially homogeneous putty is obtained.

Cotton percale, preferably pre-moistened, is printed with the paste, dried, steamed for about 30 minutes in an open steamer, and then dried to obtain a clear, sharp, blue print.

The fabrics printed with the present pastes may comprise different materials and may be cotton, cellulose regenerated from viscose or cuprammonium, silk, synthetic fibers, etc. The pastes may also be used in printing paper, leather, and other bases.

Since various changes and modifications may be made in the details given, without departing from the scope of the disclosure and invention, it will be understood that it is not intended to limit the invention by the details given except as defined in the appended claims.

What is claimed is:

1. A printing paste composition consisting of the following constituents in parts by weight, 10 parts vat dye, 5 parts chromium fluoride, 5 parts ammonium oxalate, 50 parts native dextran in finely divided particles, 5 parts water, 5 parts monoethyl ether of diethylene glycol, and 5 parts formamide.

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2. A printing paste composition consisting of the following constituents in parts by weight—

1000 parts of native dextran	2,392,258
50 parts of methyl ether of diethylene glycol	2,416,145
50 parts of formamide	2,430,430
40 parts of glycerol monostearate	2,437,518
160 parts of soap flakes	2,503,623
10 parts of sodium di-isobutyl sulfosuccinate	2,725,303
10 parts of tri-sodium phosphate	2,756,160
120 parts of dyestuff	2,768,096
120 parts of ethylene glycol monoethyl ether	
340 parts of water	

the ingredients being admixed to form a homogeneous uniform paste.

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