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PRINTING TEXTILE FABRICS WITH A DYE PASTE COMPRISING A STYRENE-MALEIC ANHYDRIDE COPOLYMER CROSS-LINKED WITH DIVINYL BENZENE

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This invention relates to improved textile printing pastes and methods of printing fabrics therewith.

In the printing of textile fabrics, it is a common practice to increase the viscosity of the dye solution in order to obtain clear, well defined prints. This is accomplished by adding starch, gums or dextrans to the printing paste. Printing pastes prepared in this manner have the disadvantage that relatively large amounts of the thickening agent is required. This is expensive, causes excessive stiffening of the fabric and the thickening agent absorbs relatively large amounts of the dye, thus decreasing the color yield. Moreover, due to the excessive stiffening of the starch or dextrin and the fact that it will deteriorate on the fabric it must be washed out after the printing operation. Furthermore, these natural thickening agents are difficult to remove from the fabric, often requiring prolonged enzyme steeping.

It is the primary object of the present invention to provide printing pastes for use in printing fabrics, which require only relatively small amounts of synthetic thickener, give excellent color yields and are easily removed from the fabric.

A further object of the invention is to provide a printed fabric in which the print paste thickener remains on the fabric thereby providing a permanent finish.

Still further objects and advantages of the invention will appear from the following detailed description and appended claims.

In accomplishing the above objects the fabric is treated, as for example by a screen printing or roll printing process, with a printing paste, which consists of a mixture of a dye and an aqueous solution or dispersion of the ammonium, amine or alkali salt of copolymerized styrene-maleic anhydride which has been cross-linked with divinyl benzene. The concentration of the salt of styrene-maleic anhydride cross-linked with divinyl benzene in the printing paste, which is normally between 0.5 and 5%, should be adjusted to give a finished printing paste suitable for printing, while the amount of dye used depends on the depth of shade desired in the finished goods. For convenience, the printing operation is carried out at room temperature. However, appreciable changes in temperature will not deleteriously affect the results. The printed fabric is then dried and steam aged in order to transfer the dye from the print paste to the fabric. The time and temperature of the drying

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and the steam aging vary considerably depending upon the dye and the fabric printed. In some cases the drying operation may be eliminated. The printed and steam aged fabric is then washed in warm water to remove the print paste thickener.

When it is desirable to remove the synthetic resin from the fabric, the sodium or potassium salts of the resin are employed. However, a substantially permanent finish may be obtained by using the ammonium salt and in some cases the amine salt of the cross-linked styrene-maleic anhydride, which becomes insoluble on drying.

A very permanent finish may be produced by adding formaldehyde or formaldehyde-yielding chemicals to the ammonium salt of the anhydride, which substances interact with each other, probably cross-linking. The fabric printed with the above paste is then cured by heating between 200° to 300° F. Various aldehyde resins may also be used for this work, including melamine-aldehyde and urea-aldehyde resins and mixtures thereof, and alkylated derivatives of these resins.

Still another method of increasing the permanency of the thickening agent as a finish is to after-treat the printed fabric with a dilute aqueous solution of a heavy metal salt, as for example, the chloride, acetate or formate of copper, aluminum, calcium or zirconium.

The processes of this invention are applicable to a wide range of dyes, as for example, direct dyes, vat dyes, soluble vat dyes, azoic dyes and the like. The exact dye or class of dyes used is dependent on the fiber to be dyed and the shade and fastness required.

The copolymer or terpolymer of styrene, maleic anhydride and divinyl benzene used in accordance with this invention may be prepared by any one of several established ways. One of the well-known methods is mass polymerization, which involves heating styrene, maleic anhydride and divinyl benzene at temperatures between about 100 and 300° F. for several hours or more. A peroxide catalyst is often used and preferably the materials are heated cautiously as in a water bath. Another method which may be used is known as the solvent process which involves reacting the styrene, maleic anhydride and divinyl benzene at slightly elevated temperatures in the presence of a solvent which is capable of dissolving both the starting materials and the finished polymer, such as acetone. Still another method which can be used is the solvent-non-solvent method which involves carrying out the

reaction as above, but in a solvent which is capable of dissolving only the starting material and not the final copolymer.

The copolymer of styrene-maleic anhydride and divinyl benzene produced by either of the above or by any other well-known method of manufacture is soluble in acetone, but insoluble in alcohol or benzene, and forms water-soluble or water-dispersible salts of ammonia or alkali metals. Instead of styrene, substituted styrenes including alkylated styrenes, such as methyl or butyl styrene, chlorstyrene or the like, may be used to prepare copolymers which are soluble or dispersible in dilute aqueous solutions of alkali or ammonia. Instead of maleic anhydride, partially esterified maleic anhydride, such as the half esters of methyl maleate, isopropyl maleate and secondary butyl maleate, may be used. It is also possible to prepare and use in accordance with this invention terpolymers of styrene, maleic anhydride and divinyl benzene which have been copolymerized with relatively small amounts of other unsaturated compounds, such as vinyl acetate, vinyl chloride, vinyl ethyl ether, indene, vinyl methyl ketone, acrylic esters and the like.

A further understanding of the invention will be obtained from the following examples, the parts being given by weight unless otherwise specified.

Example I

A solution of the sodium salt of cross-linked styrene-maleic anhydride resin was prepared by mixing together 320 parts of 50% caustic soda, 30,000 parts of water and 600 parts of cross-linked styrene-maleic anhydride copolymer. The 600 parts of cross-linked copolymer were prepared by heating 597.6 parts of a mixture consisting of equimolecular quantities of styrene and maleic anhydride with 2.4 parts of divinyl benzene at about 200° F. until the materials were copolymerized. The resulting mixture was then heated to 200 to 212° F. with stirring, and maintained at this temperature until a uniform, somewhat viscous, transparent solution or dispersion resulted, which required about one hour.

Five thousand parts of the above solution or paste was mixed with 5,000 parts of a dye solution prepared by dissolving 300 parts of Fastusol Blue LBRRA in 4700 parts of water. Samples of cotton fabric, rayon fabric and a mixed cotton wool fabric were screen printed with the above described printing paste and dried for 5 minutes at 220° F. and then aged in a steam chest for 5 minutes, washed for 10 minutes and dried. A clear, uniformly sharp print was obtained. Similar results were obtained using Fastusol Red (Rowe's Color Index, 1924, No. 278) and Fastusol Green.

Example II

A printing paste was prepared substantially as described in Example I to which were added 6% urea and 4% glycerine based on the total weight of the printing paste. On printing samples of cotton and rayon fabrics with the resulting print paste, and then aging and washing the printed fabric, excellent prints were obtained having a clear and sharp outline.

Example III

A solution of the ammonium salt of styrene-maleic anhydride which has been cross-linked with divinyl benzene was prepared by mixing together 333 grams of 26% ammonium hydrox-

ide, 24,000 cubic centimeters of water and 500 grams of copolymerized styrene-maleic anhydride cross-linked with 0.6% divinyl benzene. The resulting mixture was then heated to 200 to 212° F. with stirring and maintained at this temperature until a uniform, viscous, transparent solution resulted, which required about 1 hour.

Five hundred cubic centimeters of the print paste thickener prepared as described above were mixed with 500 cubic centimeters of a 5% solution of Fastusol Green. Samples of cotton and rayon fabric were then roll printed with the resulting printing paste, dried at 220° F. for 5 minutes, aged in a steam chest for 5 minutes at 200° F. and then dried at 250° F. for 10 minutes. The print paste thus obtained was resistant to washing and provided a relatively permanent finish on the fabrics. Moreover, a clear and uniformly sharp print was obtained.

Example IV

A solution of the ammonium salt of styrene-maleic anhydride which had been cross-linked with divinyl benzene was prepared by mixing together 500 grams of copolymerized styrene-maleic anhydride cross-linked with 0.45% divinyl benzene, 333 grams of 26% ammonium hydroxide and 24,000 cubic centimeters of water. The resulting mixture was then heated to 200 to 212° F. with stirring and maintained at this temperature until a uniform, viscous, transparent solution resulted, which required about 1 hour. After cooling the solution to about 120° F., a quantity of 35% formalin was added to the extent of about 10% on the weight of the previously cross-linked styrene-maleic anhydride used.

Five hundred cubic centimeters of the print paste thickener prepared as described above were mixed with 500 cubic centimeters of a 5% solution of Fastusol Blue LBRRA. Samples of cotton and rayon fabrics were screen printed with this printing paste, dried at 220° F. for 5 minutes, aged in a steam chest for 5 minutes at 200° F. and then cured at 280° F. for 4 minutes. A clear uniform print was obtained and the printed fabric was slightly stiffened. The print paste was exceedingly resistant to washing, thereby providing a substantially permanent finish and increasing the wash resistance of the dye.

Example V

A paste-like solution of the sodium salt of styrene-maleic anhydride which had been cross-linked with divinyl benzene was prepared by mixing together 320 parts of 50% caustic soda, 30,000 parts of water and 600 parts of cross-linked styrene-maleic anhydride copolymer. The 600 parts of cross-linked copolymer were prepared by heating 597.6 parts of a mixture consisting of equimolecular quantities of styrene and maleic anhydride with 2.4 parts of divinyl benzene at about 200° F. until the materials were copolymerized. The resulting mixture was then heated to 200 to 212° F. with stirring, and maintained at this temperature until a uniform somewhat viscous transparent solution resulted, which required about one hour.

A soluble vat printing paste was prepared by mixing the following substances with 77 parts of the above print paste thickener in the proportions given:

4 parts Algosol Yellow GCA
4 parts glycerine
4 parts urea

4 parts of a 7% solution of sodium chlorate in water

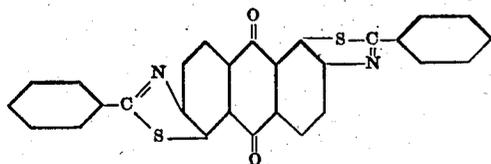
2 parts of a 1% solution of ammonium vanadate in water

1 part 26% ammonium hydroxide

4 parts ammonium sulfocyanate

Samples of cotton and rayon fabrics were printed with the above printing paste, dried at 220° F. for 5 minutes and steamed at 212° F. for 12 minutes. The samples were then rinsed well, washed with 0.25% soap solution at the boil for 15 minutes and dried. Clear vat prints with good color yield were obtained.

Algosol Yellow GCA is the leuco ester of a compound having the structural formula:



Example VI

A solution of the sodium salt of styrene-maleic anhydride cross-linked with divinyl benzene was prepared by mixing together 300 grams of copolymerized styrene-maleic anhydride cross-linked with 0.35% divinyl benzene, 140 grams of 50% caustic soda and 5614 cubic centimeters of water. The resulting mixture was then heated to 200 to 212° F. with stirring and maintained at this temperature until a uniform, viscous, transparent solution resulted, which required about 1 hour.

A printing paste was then prepared by adding the following substances to 735 parts of the above solution or print paste thickener in the amounts stated:

80 parts Rapidogen Golden Yellow R
8 parts caustic soda (30%)
30 parts sulfonated oil
147 parts warm water (85° F.)

A sample of cotton fabric was printed with this printing paste, dried for 5 minutes at 220° F., steam aged for 5 minutes, treated in successive baths of 1% acetic acid and 1% formic acid, both for 10 minutes, and then thoroughly rinsed, washed in 0.25% soap solution at 180° F. for 15 minutes, rinsed and dried.

Rapidogen Golden Yellow R is a mixture of B-hydroxy naphthoic acid anilide and acetoacetyl-tolidide coupled with diazotized dichlor aniline.

The amount of divinyl benzene used in accordance with this invention should preferably be between 0.1 and 1.0% on the weight of the styrene-maleic copolymer, as when appreciably larger amounts are used the printing paste tends to become too viscous.

Although the examples refer to the treatment of cotton, rayon and mixed cotton and wool fabric, equally good results can be obtained on all wool, cuprammonium rayon, acetate rayon, nylon, linen, synthetic protein, silk and hemp fabrics and fabrics consisting of mixtures or blends of any of the above materials.

It is customary in the printing of textile fabrics to add small amounts of urea, glycerine and oils, for example, sulfonated oils to the printing paste. These are commonly used agents in the art of textile printing and may be used with this invention as herein disclosed.

Although all of the examples herein described refer to the use of a pure synthetic print paste thickening agent, excellent results may also be obtained by combining the resins or copolymers described herein with other thickening agents such as for example, wheat starch, corn starch, potato starch, dextrin, British gum, locust bean gum, gum tragacanth, gum arabic, gum senegal, albumin, casein, various ethers and esters of cellulose and the like.

What is claimed is:

1. A method of printing textile fabrics which comprises treating said fabrics with a printing paste comprising a dye and an aqueous solution of a water-soluble salt of a copolymer prepared by copolymerizing a substance selected from the group consisting of styrene, methyl styrene, butyl styrene and chlorstyrene with a substance selected from the group consisting of maleic anhydride and partial esters of maleic anhydride, said copolymer being cross-linked with between 0.1 and 1% of divinyl benzene on the weight of said copolymer, said salt being selected from the group consisting of ammonium salts and alkali salts and being present in said paste in an amount between 0.5 and 5%, and then steam aging the fabric.

2. A method of printing textile fabrics which comprises treating said fabrics with a printing paste consisting of a dye and an aqueous solution of a water-soluble salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% of divinyl benzene on the weight of said anhydride, said salt being selected from the group consisting of ammonium salts and alkali salts and being present in said paste in an amount between 0.5 and 5%, and then drying, steam aging and washing the fabric.

3. A method of printing textile fabrics which comprises treating the fabric with a printing paste consisting of a dye and an aqueous solution of the sodium salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% of divinyl benzene on the weight of said anhydride, said salt being present in said paste in an amount between 0.5 and 5%, and then drying, steam aging and washing the fabric.

4. A method of printing textile fabrics which comprises treating said fabrics with a printing paste consisting of a dye and an aqueous solution of a water-soluble salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% of divinyl benzene, said salt being selected from the group consisting of ammonium salts and alkali salts and being present in said paste in an amount between 0.5 and 5%, drying and steam aging the fabric, and then treating the fabric with a dilute aqueous solution of a heavy metal salt.

5. A method of printing textile fabrics which comprises treating the fabric with a printing paste consisting of a dye and an aqueous solution of a water-soluble alkali salt of copolymerized styrene-maleic anhydride cross-linked with from 0.1 to 1% of divinyl benzene on the weight of said polymer, said salt being present in said paste in an amount between 0.5 and 5%, and then drying, steam aging and washing the treated fabric.

6. A method of printing textile fabrics which comprises treating the fabric with a printing paste consisting of a cotton direct dye and an aqueous solution of a water-soluble alkali salt of copolymerized styrene-maleic anhydride cross-linked with from 0.1 to 1% of divinyl benzene on

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the weight of said polymer, said salt being present in said paste in an amount between 0.5 and 5%, and then drying, steam aging and washing the fabric.

7. A method of printing textile fabrics which comprises machine roll printing the fabric with a printing paste consisting of a dye and an aqueous solution of a water-soluble salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% divinyl benzene on the weight of said polymer, said salt being selected from the group consisting of ammonium salts and alkali salts and being present in said paste in an amount between 0.5 and 5%, and then drying and steam aging the fabric.

8. A printing composition for textile fabrics which comprises a dye and an aqueous solution of a water-soluble salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% of divinyl benzene on the weight of said polymer, said salt being selected from the group consisting of ammonium salts and alkali salts and being present in said composition in an amount between 0.5 and 5%.

9. A textile fabric printed with a printing paste comprising a dye and a water-soluble salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% of divinyl benzene on the weight of said polymer, said salt being selected from the group consisting of ammonium salts and alkali salts.

10. A method of printing textile fabrics which comprises treating the fabric with a printing paste consisting of a dye and an aqueous solution of the ammonium salt of a copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% of divinyl benzene on the weight of said polymer, said salt being present in said paste in an amount between 0.5 and 5%, and then drying and steam aging the fabric.

11. A method of printing textile fabrics which comprises treating the fabric with a printing paste consisting of (1) a dye, (2) an aqueous solution of the ammonium salt of copolymerized styrene-maleic anhydride cross-linked with from 0.1 to 1% of divinyl benzene on the weight of said polymer and (3) a substance selected from the group consisting of formaldehyde and formaldehyde-yielding substances, said salt being present in said paste in an amount between 0.5 and 5%; drying and steam aging the fabric, and then heating the fabric for a short period of time at 200 to 300° C.

12. A method of printing textile fabrics which

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comprises treating the fabric with a printing paste consisting of (1) a dye, (2) an aqueous solution of the ammonium salt of copolymerized styrene-maleic anhydride cross-linked with from 0.1 to 1% of divinyl benzene on the weight of said polymer and (3) a substance selected from the group consisting of melamine-aldehyde resin and urea-aldehyde resin, said salt being present in said paste in an amount between 0.5 and 5%; drying and steam aging the fabric, and then heating the fabric for a short period of time at 200 to 300° C.

13. A method of printing textile fabrics which comprises treating the fabric with a printing paste consisting of a soluble vat dye and an aqueous solution of an alkali salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 to 1% of divinyl benzene on the weight of said polymer, said salt being present in said paste in an amount between 0.5 and 5%; and then drying, steam aging and washing the fabric.

14. A method of printing textile fabrics which comprises treating the fabric with a printing paste consisting of an azoic dye and an aqueous solution of an alkali salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% of divinyl benzene on the weight of said polymer, said salt being present in said paste in an amount between 0.5 and 5%, and then drying, steam aging and washing the fabric.

15. A method of printing textile fabrics which comprises screen printing the fabric with a printing paste consisting of a dye and an aqueous solution of a water-soluble salt of copolymerized styrene-maleic anhydride cross-linked with between 0.1 and 1% of divinyl benzene on the weight of said polymer, said salt being selected from the group consisting of ammonium salts and alkali salts and being present in said paste in an amount between 0.5 and 5%, and then drying and steam aging the fabric.

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