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PRINTING PASTE COMPRISING A VAT DYE CARRIED IN A WATER-IN-OIL EMULSION, SAID OIL BEING A LIQUID HYDROCARBON IN WHICH AN ALKYD RESIN IS DISSOLVED

Frederick Fordemwalt, Bound Brook, N. J., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

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This invention relates to a novel composition for printing with vat dyestuffs, to the printing with such compositions, and to the products so produced. In particular, the invention is concerned with a novel type of textile printing paste. More specifically, it deals with such pastes containing, as a thickener, a water-in-oil emulsion.

Use of printing-color-pastes containing dyes, particularly in printing operations using vat dyes, is sufficiently well known so that the procedure has become almost standardized. The actual color source may be either a dye paste or a dye powder. In addition to the real color, a dye paste usually contains agents to prevent drying out, settling, and/or freezing. Dye powders, not being subject to these difficulties, do not require these agents, but they usually contain agents, or are so processed, as to promote dispersibility.

In either case, the dye paste or dye powder must be made up into a printing paste. In so doing, it is customary to admix the real color with a suitable thickener to form a paste which is suitable for application. In the past, this thickener has usually consisted of a gum and/or starch dispersion.

In the case of vat dyestuffs, it is further necessary to add a reducing agent and, usually, also an alkali. Because the color yield from printing color pastes often decreases rapidly as the paste ages after being made up, these printing color pastes are usually prepared by the fabric finishers just before they are to be used.

The printing color pastes, however compounded, are then applied to textile, paper, or other fabric materials for decorative or protective purposes. The printed pieces are dried, aged in a steam ager, treated with an oxidizing agent, rinsed, and finally dried. Usually, in processing textiles, the printed fabric is also soaped at or near the boil with about a 0.1% soap solution; and again rinsed before the final drying operation.

As has been outlined above, the conventional practice has become almost standardized in its use of a thickener or "carrier" in preparing a printing paste which contains the dye paste or dye powder. In fact, these thickeners or "carriers" have themselves become substantially standardized in the form of starch-gum compositions which do not vary greatly in composition, wherever or however used. In spite of the almost universal adoption of such starch-gum carriers, their use has a number of drawbacks. For example, they require the deposition on the fabric

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of a large amount of material. It is, therefore, necessary for the color to travel through a greater mass of paste than necessary to reach the fabric surfaces. Being starches and gums, they alter the hand of the material before finishing and must be removed in the finishing operations. Even more troublesome, the color yields are not always as good as might be desirable. Particularly is this latter true in the background, or "blotch," sections of overall prints.

There is, therefore, an existing demand for an improved method of preparing and using printing paste compositions. They should not be subject to the outlined drawbacks above, which are inherent in the use of conventional starch-gum thickeners or carriers. It is, therefore, a principal object of the present invention to develop such compositions and devise methods for their use.

Surprisingly, compositions fulfilling the objects of this invention have been successfully prepared without the use of any starch-gum composition. This is particularly surprising in view of the necessity, in successful printing with vat dyestuffs, for the presence in the paste of various electrolytes. In general, this result is accomplished by substituting, for the usual carrier of the art, not a paste but an emulsion of the water-in-oil type.

Water-in-oil emulsions, as prepared for the purposes of the present invention, can be made to contain all the ingredients required for successful vat printing. It is a significant development that such emulsions are stable, despite their containing the high electrolyte content required.

The exact technique for securing a suitable emulsion may vary. The inner phase may contain hydrophilic materials in solution to withstand the presence of the high salts content. It may also contain one or more surface-active agents without thickeners. The various proportions and the sequence followed in the addition of the components to the emulsions may be varied. Preferably, however, the emulsion will contain about 15–25% by volume of the oil phase. It may go as low as 10% or up to 50%.

In a preferred method of utilizing the invention, a water-in-oil emulsion is prepared as a printing "clear" or carrier. It contains all the chemicals commonly present in the conventional starch-gum vat-printing clear or carrier paste. It is used in application exactly as are the starch clears. The color may be present when the emulsion is formed, if so desired. The final colored

emulsion, in any case, is printed on the fabric, and the print then finished, as in the current trade practice using a conventional clear.

The external oil phase may comprise a variety of water-insoluble nonsaponifiable liquid hydrocarbons in which is dissolved a small amount of a suitable resin. As to the hydrocarbons used, the more fluid petroleum fractions are preferred because of their cost, availability, and relatively high volatility. However, the oil phase may comprise one or more aliphatic or aromatic hydrocarbons or mixtures thereof. A boiling range of 380°–400° C. is satisfactory. Preferably, but not necessarily, the oil or mixture should have a low viscosity, i. e., five centipoises or less and a boiling point of 100°–300° C.

The amount of oil or oil mixture used will depend on the requirements of the printing paste in which it is incorporated, i. e., the surface to be printed, nature of the pattern, and the like. For a shallow, fine-patterned roll, a printing-paste viscosity of ten poises or even less may be desirable. On the other hand, situations may be encountered wherein a stiff paste of 100 poises or more may be needed. About 20–60 poises will cover most requirements. Viscosity, as discussed herein, is determined on a Brookfield Syncholetric viscosimeter.

The liquid hydrocarbon for the oil phase having been selected, it is prepared for use. As noted above, a resin is usually dissolved therein. As to the resin used, an alkyd resin is used, but it may be varied both as to type and amount. Any polyester of a polyhydric alcohol, a polycarboxylic acid, and drying oil acids in which the total alcoholic hydroxyl groups and the carboxyl groups are about equimolar, and having a drying oil acid content of about 35–80% by weight, may be used. Preferably, the drying oil acids should comprise about 45–65% by weight.

In amount, the resin used will depend to some extent on the nature of the resin and the oil, the nature of the vat color, the nature of the surface to be treated, and the alteration in hand which is permissible. Usually, the amount will be about 4–8% by weight of the oil.

In many cases, it will be found desirable to add a small amount of dispersing agent. These may be water-soluble or not, their primary purpose being to aid in forming and stabilizing the dispersion of the inner or water phase. Salts of lignin sulfonic acids, i. e., the alkali-metal, alkaline-earth metal, and chromium lignin sulfonates are highly suitable. These may be dissolved in a small amount of water and thoroughly disseminated in the hydrocarbon before forming the final clear or the final printing-color-paste. Other commercial wood product dispersants may also be used. The exact amount of dispersant used will vary with its molecular nature. Ordinarily, about 0.1–0.5% by weight of the final emulsion will be satisfactory with about 0.2–0.3% being the average practice.

A good practice is to emulsify a solution of the dispersant in a separate solution of the resin to be used in a small amount of the hydrocarbon. This mixture may then be readily blended into the remainder of the hydrocarbon. In this way, superior results in the form of smoother, more stable emulsions, and more uniform color deposition, may be obtained.

In addition to these materials, usually required or added in the oil phase, there are certain other ingredients required for successful printing of the vat dyestuffs themselves. In standardized practice, these will include, for example, an alkali or alkaline material, and a reducing agent. There may be present additional dispersing agents, either purposely incorporated or incorporated through their presence in the dye paste or dye powder used to make up the final printing paste. Printing assistants and the other agents to prevent drying, settling, and/or freezing may be used.

For example, it is customary to use, as the alkaline material, sodium carbonate and/or potassium carbonate. Ordinarily, both are used. These being soluble in water, they may be added at any point in the preparation of the emulsion. In the same way, the customary reducing agent is sodium formaldehyde sulfoxylate or its chemical equivalent. This too may be added at any stage in the formation of the emulsion. If a printing assistant such as glycerin and the like is desired, it too may be added as and when necessary. Preferably, however, they are dissolved in the water prior to its dissemination in the oil.

Preparation and use of emulsions in the common practice of the present invention will be more fully illustrated in conjunction with the following examples. These examples are intended as illustrative only. Unless otherwise noted, all parts are by weight.

Example 1

0.8 parts of sodium lignin sulfonate were dissolved in 1.2 parts of water and this solution then stirred by a mechanical stirrer into 8.0 parts of a 50% solution of a medium oil-oxidizing resin containing 33% phthalic anhydride and 55% linseed oil in a hydrocarbon solvent having a distillation range of 135°–175° C. and an aromatic content of approximately 92%. This mix was placed on an Eppenbach homogenizer and 60 parts of the hydrocarbon were then added to complete the oil phase. While this oil phase was strongly agitated on the homogenizer, there were slowly added 260 parts of a solution composed of:

	Per cent
Sodium carbonate	5.45
Potassium carbonate	5.45
Sodium formaldehyde sulfoxylate	8.50
Glycerine	3.55
Water	77.05
Total	100.00

and the stirring continued to emulsify thoroughly the water solution into the oil. There were then added 36.4 parts of a commercial printing paste color composition containing the vat dye of Color Index 1184, and the stirring was continued on the Eppenbach homogenizer until the color was thoroughly and smoothly incorporated into the emulsion.

Example 2

The emulsion formed in Example 1 was printed on 80 x 80 bleached cotton cloth and the resulting print finished by a conventional process for vat prints: i. e., dried, steamed, oxidized, and soaped. A bright, strong, sharp print was secured, being both brighter and stronger than a corresponding print prepared at the same time from a mix of 36.4 parts of the same commercial printing color in 330 parts of a commercial type vat carrier paste prepared from starch materials.

Example 3

A paste was prepared as described in Example 1, except that the vat color paste was mixed with

the water solution before this was emulsified into the oil phase. Prints made as in Example 2 were equally as strong, sharp, and bright as those prepared in Example 2.

Example 4

A print was prepared as described in Example 3, using, instead of the blue vat dyestuff, a commercial vat scarlet printing paste color that contained a mixture of 6,6'-dichlor-4,4'-dimethyl-bis-thionaphthene indigo, and the vat orange dye of Color Index 1217. The resulting print on 80 x 80 bleached cotton was strong, sharp, and bright, being superior in strength and brightness of shade to a corresponding print prepared at the same time with the same dyestuff in a commercial type of vat carrier paste from starch products.

Example 5

A print was prepared as described in Example 3 using, instead of the blue vat dyestuff, a commercial vat yellow printing paste color that contained the yellow dye of Color Index 1095. The resulting print was bright and sharp.

Example 6

A print was prepared as outlined in Example 4. This was lightly dried and then over-printed with the emulsion described in Example 4. When the final print was dried and finished in the regular manner, an excellent smooth, clear, orange-colored print was produced. Thus a successful over-print was obtained with the final color the additive shade of the two dyes used.

I claim:

1. A stable, color-printing paste having a viscosity of 10–100 poises and comprising a water-insoluble vat color disseminated through a carrier; said carrier comprising a water-in-oil type emulsion having an aqueous inner phase containing water-soluble electrolytes, including (*a*) a member selected from the group consisting of the alkali metal hydroxides and carbonates, (*b*) a water-soluble, formaldehyde-sulfoxylate salt, and (*c*) a water-soluble lignin sulfonate salt, suspended in an external oil phase comprising 10–60% by weight of the printing paste, said oil being selected from the low-viscosity liquid hydrocarbons having a distilling range of from 80°–400° C., and having dissolved therein from 4–8% by weight of the oil of an oil-soluble, drying-oil-modified, thermosetting alkyd resin.

2. A color printing paste according to claim 1 in which the distillation range of said low viscosity liquid hydrocarbon is about 135–175° C.

FREDERICK FORDEMWALT.

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