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OIL-IN-WATER EMULSION FOR VAT COLOR
PRINTING

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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, an oil-in-water emulsion.

Use of printing color-paste 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 also is 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 of a large amount of

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material. It is therefore necessary for the color to travel through a greater mass of paste than desirable to reach the fabric surfaces. Being starches and gums, they alter the hand of the material before finishing and must be removed in subsequent operations. Even more troublesome, the color yields are not always as good as might be desired. Particularly is this latter true in the background or "blotch" section of over-all 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 was quite unexpected in view of the fact that in successful printing with vat dyestuffs, it is necessary for the paste to contain 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 oil-in-water type.

Oil-in-water 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 for vat printing.

The exact technique for securing a suitable emulsion may vary. The outer phase may contain hydrophilic materials in solution to withstand the presence of the high salts content. It may 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 from about 15-60% of the internal oil phase. This internal phase serves primarily only to body the emulsion, i. e., to provide printing consistency.

In a preferred method of utilizing the invention, an oil-in-water emulsion is prepared as a "clear" vat 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

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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 internal oil phase, serving primarily to body the emulsion, may comprise a variety of water-insoluble nonsaponifiable oils. Hydrocarbons, particularly the more fluid petroleum fractions, are preferred because of their cost, availability, and relatively high volatility. The internal oil phase may be a single aliphatic hydrocarbon or mixtures thereof or with aromatics. An upper boiling range of 300-400° C. is satisfactory. Preferably, but not necessarily, the oil or mixtures should have a low viscosity, i. e., five centipoises or less and a distillation range 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 10 poises or even less may be desirable. On the other hand, conditions may be encountered in which a stiff paste of 100 poises or more may be needed. A viscosity of about 20-60 poises will cover most requirements. Viscosity, as discussed herein, is determined on a Brookfield Synchro-letric viscosimeter.

In addition to these materials, required in and forming the oil-in-water emulsion as such, 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. In addition, there may be dispersing agents, which are purposely incorporated, or become incorporated through their presence in the dye paste or dye powder, which is used to make up the printing paste.

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 a 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.

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

125 parts of a hydrocarbon solvent (distillation range 135-175° C. and containing approximately 92% of aromatics) is emulsified by means of an homogenizer into 60 parts of a mixture consisting of 50 parts of a 7.5% aqueous dispersion of the vat dyestuff 6,6'-dichloro-4,4'-dimethyl-bis-thionaphthene indigo (which dyestuff had been previously deflocculated in the presence of 1% of disodium disulfo dinaphthyl methane) and 10 parts of a 40% aqueous solution of sodium lignin sulfonate. Into this resultant emulsion is mixed 200 parts of a slurry consisting of 22.5 parts of anhydrous sodium carbonate, 22.5 parts of anhydrous potassium carbonate, 35 parts of sodium formaldehyde sulfoxylate, 30 parts of glycerine, and 90 parts water. Finally an additional 125 parts of the same hydrocarbon solvent is emulsified into the system.

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The above procedure produces a well-bodied, smooth, pink-colored O/W emulsion. Prints made from this color emulsion on bleached 80 x 80 cotton cloth are bright, strong, and well-defined. When finally aged, oxidized, soaped, and dried, they compare favorably with similarly finished prints made at the same color concentration, using a conventional starch thickener as the vat color carrier.

Example 2

200 parts of a hydrocarbon solvent (distillation range 135-175° C. and containing approximately 92% of aromatics) is emulsified by means of an Eppenbach homogenizer into 100 parts of a 20% aqueous solution of sodium lignin sulfonate. Into the resultant emulsion is stirred 400 parts of a slurry consisting of 45 parts of anhydrous potassium carbonate, 45 parts of anhydrous sodium carbonate, 70 parts of sodium formaldehyde sulfoxylate, 60 parts glycerine, and 180 parts of water. Finally 300 parts more of the above-mentioned hydrocarbon solvent is emulsified into the system in like manner. A well-bodied, smooth, tan colored oil-in-water emulsion clear results from this procedure.

A vat color printing emulsion is then prepared by stirring 10 parts of an aqueous dispersion of the vat dyestuff 6,6'-dichloro-4,4'-dimethyl-bis-thionaphthene indigo (previously thoroughly deflocculated in the presence of 1% disodium disulfo dinaphthyl methane) and containing approximately 15% real dye, into 90 parts of the above-mentioned oil-in-water emulsion clear.

The resulting color emulsion is machine-printed from an intaglio engraved copper roll onto bleached 80 x 80 cotton cloth and onto spun rayon cloth. The resulting prints, when dried, steam-aged, oxidized, soaped, and ironed dry, are found to be bright and strong, and to have as sharp a design as prints made at the same color concentration using a conventional starch printing thickener as the carrier for the deflocculated color dispersion.

Example 3

569 parts of a hydrocarbon solvent (distillation range 135-175° C. and containing approximately 92% aromatics) are emulsified by means of an Eppenbach homogenizer into a mix consisting of 38 parts of anhydrous potassium carbonate, 59 parts of sodium formaldehyde sulfoxylate, 51 parts of glycerine, 3.4 parts of sodium lignin sulfonate, and 247 parts of water. A smooth, light colored oil-in-water emulsion results.

A vat color printing emulsion is prepared by stirring 10 parts of a commercial vat dye paste, containing approximately 15% of the vat dyestuff 6,6' - dichloro - 4,4' - dimethyl - bis - thionaphthene indigo into 90 parts of the above-mentioned oil-in-water emulsion.

When printed on 80 x 80 bleached cotton cloth and finished in the conventional manner, this printing color emulsion gives clear sharp prints which are brighter and stronger in color value than prints made at the same dye strength using a conventional starch thickener as the vat dye paste carrier.

Example 4

10 parts of a commercial vat dye paste, containing approximately 15% of the vat dyestuff of prototype No. 117, were stirred into 90 parts of the emulsion clear described in Example 3. Cotton prints made from this vat color printing

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emulsion were surprisingly clear, bright, and strong.

Example 5

An oil-in-water emulsion is prepared by emulsifying 480 parts of a hydrocarbon solvent (distillation range 135-175° C. containing 92% of aromatics) into an aqueous mix consisting of 4 parts sodium lignin sulfonate, 6 parts of a medium viscosity grade carboxymethyl cellulose, 41 parts of anhydrous sodium carbonate, 41 parts of anhydrous potassium carbonate, 64 parts of sodium formaldehyde sulfoxylate, 55 parts of glycerine and 319 parts of water. An Eppenbach high-speed homogenizer is used as the mechanism for producing the emulsion. The resulting product is a creamy white, smooth, well-bodied oil-in-water emulsion. 10 grams of the commercial vat dye paste containing approximately 15% of the vat dyestuff 6,6' - dichloro-4,4' - dimethyl - bis - thionaphthene indigo, are stirred into 90 parts of the emulsion clear prepared above. When the resulting color emulsion is printed on cotton cloth, the finished prints are found to be as strong and as clear as prints prepared at the same dye concentration using a conventional starch or gum thickener.

Example 6

An oil-in-water emulsion is prepared as directed in Example 5 except that 1 part of sodium alginate is substituted for the carboxymethyl cellulose. A well-bodied creamy oil-in-water emulsion is formed by this procedure. 10 parts of a commercial vat dye paste, containing approximately 15% of the yellow dyestuff of Color Index 1095, are stirred into 90 parts of the above described emulsion clear. Cotton prints prepared from this color emulsion possess good strength, clearness and sharpness of design.

Example 7

540 parts of a predominantly aliphatic hydrocarbon (distillation range 306-394° C.) is emulsified by means of an Eppenbach homogenizer into 510 parts of a mix consisting of 4 parts of sodium lignin sulfonate, 45 parts of anhydrous potassium carbonate, 45 parts of anhydrous sodium carbonate, 70 parts of sodium formaldehyde, 60 parts of glycerine and 280 parts of water. A creamy, yellowish-white oil-in-water emulsion results from this procedure.

10 parts of a commercial vat dye paste containing approximately 10% of the vat dyestuff of Color Index 1101 are stirred into 90 parts of the above-prepared emulsion clear. Finished cotton prints of this color emulsion are clear, bright and strong. They compare very favorably with prints made at the same dyestuff concentration using a conventional starch thickener as the vat color carrier.

Example 8

20.8 parts of Orange R powder, Color Index 1217 (prepared according to U. S. Patent Reissue No. 21,402) and containing about 18% sodium salt of lignin sulfonic acid, is dispersed by means of an Eppenbach mixer into a mix of 24 parts glycerine and 113 parts of water. 180 parts of a predominantly aliphatic hydrocarbon (distillation range 306-394° C.) are emulsified into the above dispersion. 64 parts of a pulverized mix consisting of 18 parts of sodium carbonate, 18 parts of potassium carbonate, and 28 parts of sodium formaldehyde sulfoxylate are then stirred into the above-described emulsion. The product

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is a smooth, well-bodied, oil-in-water emulsion which, when printed on bleached 80 x 80 cotton cloth and finished in the usual manner for vat prints, produces prints whose brightness and strength compare favorably with similar prints made at the same vat dye concentration using a conventional starchy-gum as the vat color carrier.

Example 9

45.5 parts of a predominantly aliphatic hydrocarbon solvent (distillation range 306-394° C.) is emulsified by means of a high-speed homogenizer into a mix consisting of 30.5 parts water, 2 parts calcium lignin sulfonate and 6 parts glycerine, 16 parts of a pulverized mix consisting of 4.5 parts sodium carbonate, 4.5 parts potassium carbonate, and 7 parts sodium formaldehyde sulfoxylate are then stirred into the above, formulated oil-in-water emulsion. 88 parts of the resulting well-bodied, tan colored emulsion are then mixed with 12 parts of an aqueous dispersion of the vat dyestuff Hydron Pink containing 1.8 parts of real dye and the resultant printing paste is printed on unbleached 80 by 80 cotton cloth and finished in the conventional manner. The resulting print compares favorably in color value, smoothness and sharpness of design with prints made at the same dye concentration made with a starch gum as the vat color carrier.

Example 10

An emulsion clear is prepared as directed in Example 9 except that 2 parts of the chromium salt of lignosulfonic acid are substituted for the calcium salt. 12 parts of a commercial vat color paste containing about 15% of the Jade Green dyestuff of prototype No. 117 are mixed with 88 parts of the above prepared emulsion and printed on 80 x 80 unbleached cotton cloth. Bright smooth prints, which compare favorably with starchy-gum prints, are obtained in this process.

Example 11

Into an aqueous mix of 1.8 parts sodium lignin sulfonate, 6 parts glycerine and 28.5 parts water are emulsified 43.7 parts of predominantly aliphatic hydrocarbon solvent (distillation range 306-394° C.) by means of an homogenizer. To the resultant oil-in-water emulsion are stirred in a pulverized mix consisting of 5 parts sodium carbonate, 5 parts potassium carbonate, and 13 parts sodium formaldehyde sulfoxylate. When 88 parts of the thickened emulsion thus formed are mixed with 12 parts of a commercial dye paste containing about 15% of the green vat dyestuff of prototype No. 117, a colored emulsion is formed which when printed on spun rayon produces good strong prints.

Example 12

A water dispersion is prepared by mixing together 50 parts of a 10% aqueous suspension of bentonite, 15 parts of glycerine, 5 parts of a 40% aqueous dispersion of sodium lignin sulfonate and 90 parts water. Into this mix is emulsified by means of a high-speed stirrer 50 parts of a predominantly aliphatic hydrocarbon of distillation range 306-394° C. A pulverized mix consisting of 11 parts sodium carbonate, 11 parts potassium carbonate and 17 parts sodium formaldehyde sulfoxylate are then mixed into the oil-in-water emulsion formed by the foregoing procedure. The resulting product is a thick, smooth oil-in-water emulsion clear suitable for vat color printing. 12 parts of a commercial dye paste containing about 17% of the blue vat dyestuff of Color Index

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1184 are mixed with 88 parts of the above-formulated emulsion clear and the color paste so formed is printed on 80 x 80 unbleached cotton cloth and the prints finished in the conventional manner. The finished prints compare favorably in strength and brightness to prints at the same dye concentration made with a starchy-gum as the vat color carrier.

Example 13

The procedure of Example 12 is followed except that 50 parts of a 1% aqueous dispersion of sodium alginate are substituted for the bentonite suspension. Prints obtained with this product are strong and bright.

From the foregoing examples, it will be seen that the use and practice of the present invention has a number of advantages. In many cases, stronger value color prints are obtained. In general, smoother prints are obtained, particularly in the background or "blotch" areas. A greatly reduced solids content is deposited on the fabric during printing. The fabrics have a soft hand even before finishing. There are no starches, gums, and the like present to be washed from the print during finishing.

It is also an advantage of the present invention that the printing color compositions, so prepared and used, are applicable to substantially all situations wherein vat dyestuffs are printed in fabrics. Particularly printing on cotton, rayon, and the like is the invention of particular utility.

Further, because of the nature of the materials, they are more quickly and easily applied. There is improved opportunity for printing one vat color over another to secure mixed shades, and a multiplicity of colors, with the use of only a very few engraved rolls. Finally since all the formulations are dispersible in water the equipment in which they are used is easily cleaned.

While the illustrative examples given above are concerned with vat dyes, it should be noted that soluble vat dyes may also be used. This may in some cases increase the ease of formulation and application. It may also in some cases increase the available color range.

It should be noted, also, that in the above examples neutralized lignin sulfonates have been employed in forming oil-in-water emulsions. These are preferred to other types of dispersing and stabilizing agents. Emulsions prepared with these materials are very stable. Among those suitable for use are the sodium, potassium, ammonium, calcium, magnesium, and chromium

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lignin sulfonates. Similarly, lignin-containing products from wood wastes, for example some of the distillation concentrates from which the lower molecular weight fractions are removed, as shown in U. S. Patent No. 2,201,812, may also be useful.

We claim:

1. A stable color printing composition comprising a water-insoluble vat dyestuff disseminated through a water-dispersible oil-in-water type emulsion paste, said paste containing (a) water-soluble electrolytes including alkali metal carbonates and a water-soluble formaldehyde sulfoxylate salt (b) an aqueous bodying material consisting of a liquid hydrocarbon suspended therein as the internal phase, and (c) a water-soluble salt of a lignin sulfonate.

2. A composition according to claim 1 in which the oil-in-water emulsion comprises as its internal phase a mixture of aliphatic and aromatic hydrocarbon oils.

3. A composition according to claim 1 in which the oil-in-water emulsion comprises as its dispersed phase a petroleum distillate solvent having a viscosity not over about five centipoises and a boiling range of 100-400° C.

4. A method of printing with vat colors which comprises printing with a printing paste composition comprising a water-insoluble vat dyestuff disseminated through an oil-in-water emulsion, said emulsion containing water-soluble electrolytes including alkali metal carbonates and a water-soluble reducing agent and a thickener consisting of liquid hydrocarbon suspended therein as the internal phase, and (c) a water-soluble salt of a lignin sulfonate.

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