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TEXTILE DECORATING COMPOSITIONS

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1

This invention relates to textile decorating compositions, and is directed particularly to such compositions which contain pigments dispersed in resins of the type which are convertible to the insoluble and infusible state by heat or otherwise. Specifically, this invention relates to such compositions in which extremely good printing properties, high color value, and the like, are obtained by a conversion of the resin solution to the state of incipient gelation, in which the resin solution employed is no longer in a flowable liquid state.

Conventional textile printing is ordinarily done with water solutions of dyestuffs containing water soluble thickening agents in sufficient quantity to retard the spreading of the color on the fabric after printing. The dyestuff is fixed onto the fabric by some chemical process, and the thickening agent is then washed out of the fabric. The time and expense involved in this after treatment, added to the originally high color cost for light and tub-fast dyes, has been a major problem in textile printing. An unsolved problem has been the reproduction of very fine designs. Since the pastes spread on the fabric after printing when thin enough to be removed sharply from fine engravings, giving blurred designs, it has been found impossible to use photogravure cylinders or extremely fine mill and die engravings. Attempts to modify these pastes by addition of wetting agents and emulsification of oils therein have not solved the basic difficulties.

The use as printing pastes of colored lacquers (which, for the purpose of this application are defined as dispersions of color in vehicles consisting of a solution of a plastic or solid film-forming, water-resistant binder such as a cellulose derivative or a resin, in an organic solvent or mixture of solvents) has been attempted in order to overcome the difficulties with prior art pastes, but has not been successful commercially. Relatively few lacquer compositions withstand both dry cleaning and washing; and such compositions as are resistant have been generally unacceptable due to the fact that the fabrics, when printed with these lacquers, develop an undesirable stiff feel (known to the trade as "hand"), to the necessity for using large amounts of color to obtain deep shades, and to the tendency of colored markings to rub off onto other clothing and leave a mark (known as "crocking").

In the Jenett U. S. Patent No. 2,222,581, there is described a new type of textile printing paste which eliminates the disadvantages of the conventional dye printing pastes and avoids the dif-

2

ficulties which have been encountered in the prior art lacquer printing pastes. These new pastes are emulsions in which an outer continuous water-immiscible-lacquer phase is thickened by an inner aqueous phase which is at least 20 per cent. of the total emulsion, by weight. Preferably, the binder of the lacquer is one which is originally soluble in ordinary organic solvents and which can be converted into an insoluble state after printing—most desirably, a readily heat-polymerizable synthetic resin, best exemplified by urea formaldehyde and allied resins.

The use of pastes made in accordance with this invention permits of the use of cheap pigments and avoids the after treatment necessary with conventional printing pastes. Furthermore, these pastes separate sharply even from very fine photogravure cylinders, although thickened sufficiently to prevent any spreading on the fabric; this makes possible much finer printing than can be obtained with conventional pastes. The hand imparted to fabrics by these pastes is very much less than the hand imparted to similar fabrics by ordinary lacquer pastes having the same binder, the amount of color needed to produce deep shades is sharply reduced, and the crocking substantially eliminated.

We have discovered that pigmented pastes of the type described in the said patent can be markedly improved, particularly with respect to the color value obtainable therefrom, by treating the pastes, or the resin solutions used in making the pastes, to bring the resin solution to a state of partial gelation. In this state, the resin solutions are no longer true liquids, but have the peculiar mucilaginous consistency and flow characteristic of egg whites, in which smooth gelatinous masses appear to be dispersed through a rather thick liquid; and these pastes are thus essentially dispersions of gelled resin in resin solution.

Surprisingly enough, this type of printing paste wipes into, and separates from the cells of an intaglio engraving, just as smoothly and easily as a perfectly smooth flowing ink, even though the pastes may flow only fitfully through a tube because of the presence of gelled masses in the body thereof.

If the resin solutions are converted to harder gels, where they approach the consistency of egg whites which have been heated, thereby increasing the size and number of the smooth gelatinous masses dispersed therein, the pastes can be thickened sufficiently by the presence of this gelled resin-solvent combination so that the amount of

3

water necessary for optimum printing properties can be reduced, and in some cases the water can be eliminated.

In determining whether or not the gelation has been carried to a sufficient state to permit of the partial or total removal of water, the viscosity and yield value of the finished paste are of considerable value. The viscosity should be low (0.1 to 20 poises at 25° C.) and the yield value high (at least 50 dynes per square cm.) in order to get the desired printing properties. Preferably, we prefer to operate in a range of yield values between 100 and 800 dynes per square centimeter.

In some cases, the compositions show pseudoplasticity, and therefore have no true yield value and viscosity; however, the flow curves of these compositions reveal apparent values approximating those given above for true plastic compositions.

It is important that the gelation be controlled so that the entire mass does not set up to a stiff gel which cannot be dispersed in resin solution. This can be easily avoided by controlling the time of treatment, and the reactants employed.

The carrying of the resin to the state of incipient gelation has still another value—it shortens the time required when the fabric is dried after printing to complete the conversion of the resins to the desired insoluble and infusible condition, so that unusually good wash-resistance can be obtained even in the absence of a prolonged cure of the resin.

Typical examples of our invention are the following:

Example 1

	Parts by weight
Solvent-soluble urea formaldehyde resin	3.75
Alkyd resin (glycerol phthalate modified with 35% soya oil)	11.25
Toluene	11.25
Solvent for urea resin:	
Xylene	1.50
Butanol	2.25
Pine oil	7.00
Solvesso #3 (hydrogenated petroleum naphtha—boiling range 182–210° C.)	53.00
Indanthrene Blue (vat pigment)	2.00
Alumina Aerogel	8.00

The ingredients are ball milled for 72 hours. After ageing for nine days, this paste showed:

Yield value at 25° C.—750 dynes per square centimeter

Viscosity at 25° C.—2.4 poises

This formulation has been reproduced with chlorinated copper phthalocyanine green and with a red pigment prepared by coupling diazotized dichlorbenzidine and the diethyl ester of phenyl methyl pyrazolone dicarboxylic acid.

The gelation in this case is probably caused by the exposure of the alkyd and urea formaldehyde resins to gelling reactants which are present in small quantities in all binders, in the presence of the alumina aerogel, which has an extremely high specific surface, and which may contain acid or similar adsorbed impurities. Similar results are obtained with other aerogels, such as silica aerogel; the aerogels may be produced in accordance with the disclosure of the Kistler Patent 2,093,454, September 21, 1937. Some gelation occurs with either the alkyd or the urea resin alone; but we prefer to use both, because the gelation occurs more rapidly and smoothly when both are present.

4

The paste prints well, and gives prints which may be set more rapidly than ungelled prints.

Example 2

	Parts by weight
Urea formaldehyde resin of Example 1	3.75
Alkyd resin of Example 1	11.25
Toluene	11.25
Solvent for urea resin:	
Xylene	1.50
Butanol	2.25
Pine oil	7.00
Solvesso #3	60.50
Indanthrene Blue	2.00
Trichloroacetic acid	0.50

The ingredients are ball milled for 72 hours, with the exception of the trichloroacetic acid, which is dissolved in part of the Solvesso #3 saved out for this purpose, and added at the end of the ball milling operation.

Four days after it was made, this paste showed:

Yield value at 25° C.—125 dynes per square centimeter

Viscosity at 25° C.—0.5 poises

When 11 days old, the yield value was 235 dynes per square centimeter, which shows the paste to be quite stable. The paste had the typical mucilaginous structure of a gel dispersed in a resin solution. On printing, the paste can be set by mere ageing, or by a very short heating.

This ink has been converted to the state of partial gelation by the use of trichloroacetic acid. Other acids can be used to replace it—for example, dichloroacetic, phthalic, tartaric, maleic, salicylic and similar acids soluble in the solvent employed.

The emulsion printing pastes of the Jenett Patent No. 2,222,581, can also be improved by converting the resin solution to the state of partial gelation, to get a dispersion of gelled resin in ungelled resin. The addition of acid as described in Example 2 is useful in this regard; the application of the method to emulsions has the advantage that the non-aqueous paste can be carried to the state of gelation desired, and water containing a neutralizing agent can then be emulsified into it to stop further progress of the gelation.

If desired, the resin solution may be gelled first, and the pigment pulp mixed in afterward. Thus—

Example 3

61 parts by weight of a 65% xylene solution of the alkyd resin of Example 1, 38 parts by weight of a 50% solution of the urea resin of Example 1 in 40-xylene-60-butanol, and 1 part by weight normal-butyl-hydrogen phosphate were heated to 65° C. for twenty minutes, and allowed to stand overnight to form a rather stiff solvent-dispersible gel. The gel is mixed to form a color by blending:

	Parts
Gel	30
Pine oil	20
Turpentine	20

and emulsifying the mixture with:

	Parts
20% copper phthalocyanine aqueous pulp	20
Water	10

This gives a blue paste containing 4% of color, which has a color value substantially higher than a similar ungelled emulsion paste containing ungelled resin with the same amount of water.

5

Similar gels to those of Example 3 can be prepared by heating with acetic acid, etc., and with aqueous solutions of some electrolytes (e. g.—20% sodium chloride solution).

Both the non-aqueous and aqueous emulsion pigmented partial gels may be blended with clear water-in-lacquer reducing emulsions (gelled or ungelled) to obtain finished pastes of very acceptable properties. Most desirably, they are blended with emulsions very low in solids content (of the order of 1%) which consist of water emulsified into lacquers consisting essentially of solvent and sufficient film-former to stabilize the emulsion, the solvent being of a type which is a solvent for the resin of the pigmented paste when used in limited quantities with relation to the resin, but which precipitates the resin when used in excessive amounts. When blended with substantial quantities of such low-solids emulsions, the resin-pigment-solvent aggregates separate out of the continuous phase, so that a three-phase emulsion comes into being. These emulsions consist of a continuous phase of resin solution rather low in solids, and a discontinuous aqueous phase, with resin-pigment-solvent aggregates in suspension in the continuous phase as well. Where a partially gelled pigmented material is used in accordance with our invention, the gelled resin exists, in combination with solvent and pigment, in suspension in this system.

An example of a clear reducing emulsion which will yield a three phase emulsion with the product of Example 3 is the following:

Example 4

A lacquer is made by mixing—

	Parts by weight
A solution of: 50 alkyd resin, 15 pine oil,	
35 Solvesso #3	1.20
A 15% rubber solution in Solvesso #2 (hydrogenated petroleum solvent—boiling range 135–177° C.)	1.00
Solvesso #2	22.00

Into this lacquer is emulsified a mixture of:

	Parts by weight
Sodium chloride	0.15
35% sulfonated tannin solution	0.12
Acetic acid	0.06
Water	75.47
	100.00

The alkyd resin is a 40% drying oil modified glycerol phthalate resin, which is freely soluble in hydrogenated petroleum solvents, as distinguished from the alkyd resin of Example 3.

This unpigmented emulsion contains 0.75% solids; the lacquer phase contains about 3% solids. It may be blended with the pigmented emulsion of Example 3 in ratios of 1 to 1 and higher, to produce a three-phase system in which a low-solids clear lacquer is the outer phase, and water and resin-solvent aggregates bearing pigment are the inner phases. Microscopic examination of the mixture indicates that the two disperse phases are in very close contact with one another. The mixtures are stable, and prints made therewith show the same resistance to washing and other influences as prints made from Example 3.

The new products we have described, when used for printing on fabric, give surface prints with unusually good color value; they can be converted to wash-fastness very much more rapidly than can ungelled materials.

6

These printing pastes can also be used for pigment dyeing; in this field, the pastes are used at relatively low binder content (preferably about 2½% or less) obtained by the use of low-solids reducing emulsions. The pastes are forced through the cloth by pressure; on drying, the resin-pigment aggregates stick to the fibers throughout the threads in an even fashion, without undue cementing. The use of water-in-lacquer emulsions notably reduces the migration of color on drying, and substantially eliminates this most serious difficulty in pigment dyeing; the partial gelation of the resin further increases this resistance to migration notably.

While the examples are restricted to urea formaldehyde and alkyd resins together, these resins may be gelled separately. Moreover, we have successfully obtained similar gels with various heat-convertible carbamide-aldehyde resins (made from carbamides such as urea and its derivatives and related compounds, including thiourea, guanidine, dimethylol urea, melamine, biuret, etc.); other heat-convertible alkyd resins, phenol formaldehyde resins and the like.

Similarly, the solvents and plasticizers may be changed as desired. The pigments should be chosen with care, having in mind the light-fastness and wash-fastness requirements of the particular problem. Furthermore, the water used in the emulsion may be replaced by non-miscible organic liquids in known manner.

Obviously, the examples can be multiplied indefinitely, without departing from the scope of the invention, which is defined in the claims.

In both the printing and pigment dyeing operations, it is noteworthy that the resultant fabric obtained is substantially like a dye-colored fabric, retaining its complete permeability to air, and to cleaning liquids. This result distinguishes the textile decorating compositions herein disclosed from the various textile coating compositions used to produce continuous films of fabric, for water-proofing, artificial leather production, and the like. We prefer to define our result as the production of microscopically discontinuous decorations on the cloth while producing visual continuity.

We claim:

1. A textile decorating composition of plastic consistency such that it can be applied to cloth by intaglio printing plates to produce, when admixed with pigment, visually continuous but microscopically discontinuous decorations on cloth, which comprises a vehicle comprising a heat-convertible synthetic resin and a solvent therefor, the resin being catalytically and non-uniformly advanced so that a part of it is gelled while part remains ungelled, the proportions of gelled to ungelled resin being such as to produce a vehicle having a marked yield value and variable flow characteristics in different parts thereof and containing smooth gelatinous masses of resin dispersed in a solution of resin not advanced to the gel point, the entire composition having a yield value of at least 50 dynes per square centimeter.

2. A textile decorating composition of plastic consistency such that it can be applied to cloth by intaglio printing plates to produce visually continuous but microscopically discontinuous decorations on cloth, which comprises pigment dispersed in a vehicle comprising a heat-convertible synthetic resin and a solvent therefor, the resin being catalytically and non-uniformly advanced so that a part of it is gelled while part remains ungelled, the proportions of gelled to

7

ungelled resin being such as to produce a vehicle having a marked yield value and variable flow characteristics in different parts thereof and containing smooth gelatinous masses of resin dispersed in a solution of resin not advanced to the gel point, the entire composition having a yield value of at least 50 dynes per square centimeter.

3. The composition of claim 2, in which the resin is a carbamide-aldehyde resin.

4. The composition of claim 2, in which the composition has water emulsified therein as a discontinuous phase.

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8

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