

UNITED STATES PATENT OFFICE

2,364,692

TEXTILE PRINTING EMULSIONS

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No Drawing. Application August 3, 1940,
Serial No. 351,206

7 Claims. (Cl. 260—29)

This invention relates to pigmented lacquer emulsions useful in the decoration of fabrics, and has particular reference to composite emulsions containing a plurality of dispersed phases.

The printing and dyeing of textile fabrics has been done for ages with soluble colors which are applied in solution, and fixed in or to the fibers by chemical action. Conventional textile printing is ordinarily done with water solutions of dye-stuffs containing water soluble thickening agents in sufficient quantity to retard the spreading of the color on the fabric after printing. The dye-stuff is fixed onto the fabric by some chemical process, and the binding 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 dye 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 ordinary colored lacquers (which, for the purpose of this application are defined as dispersion of color in vehicles consisting of a solution of plastic or solid film forming, water resistant binder such as a cellulose derivative or 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 lacquers have also been generally unacceptable due to the fact that the fabrics printed with 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"). The use of lacquers for dyeing has also been attempted, and has failed for the same reasons, and for the additional reason that pigments tend to flocculate and settle out in the very thin lacquers useful for penetrating cloth.

There has recently been developed a new type of textile printing paste which eliminates the disadvantages of the conventional dye printing pastes and avoids the difficulties 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 plasticized urea-formaldehyde type 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 new 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 new 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.

Emulsions of pigmented lacquers containing similar binders have also been suggested for the pigment dyeing of textile fabrics and have met with some success; but the problem of pigment distribution in such dye baths has been a major difficulty. Very often only a small amount of pigment is wanted in a dilute lacquer phase; and settling and aggregation of pigment makes the problem of uniform coloration unusually difficult.

I have invented a means of overcoming the problem of pigment distribution in dilute pigmented lacquer dye baths, and further improving the properties of water-in-lacquer emulsion printing pastes. My means comprises the use of multiple phase emulsions in which water is one phase, a concentrated pigmented resin-solvent aggregate is another phase, and a lacquer of very low solids content, which is only partially miscible with the pigmented resin-solvent lacquer from which the aggregate is formed, is the third phase.

The pigmented resin-solvent aggregate phase is made by dispersing pigment in a rather concentrated solution of a binder comprising a heat-convertible synthetic resin, so that the pigment will remain dispersed in the resultant lacquer. At least two volumes of binder to one of pigment should be used, since at least this much binder is required to hold the pigment tightly to the

fabric. The solvent mixture chosen should be water-immiscible, although a portion thereof may of itself be water-miscible. The solvent need not be one capable of infinitely diluting the resin solution; preferably, it is one which will produce some precipitation of the resin on substantial reduction of resin content.

The low solids lacquer should preferably contain a maximum of 10% non-volatile, particularly where economy and reduced hand are desirable, and most preferably the non-volatile content should be as low as possible consonant with the production of a stable emulsion, the non-volatile solute of this lacquer acting essentially as an emulsifying agent for the water employed. The important function of this lacquer is contributed by the solvent. It must be capable of diluting the pigmented lacquer phase when added in small quantities, but should cause cloudiness when added in larger quantities. This results in the formation of a dispersed phase of pigmented resin-solvent aggregate in the low solids lacquer; flocculation of the pigment with insufficient resin to protect it is prevented since the pigment is held tightly to the dispersed resin-solvent aggregate.

These dispersions of the pigmented resin-solvent aggregate in thin lacquer settle out very rapidly, and often are not easily redispersible; the function of the water in the emulsion is to prevent such a settling out, and to preserve the desired structure. Therefore, while the two lacquer phases can be mixed, and water then emulsified, I prefer to emulsify at least one phase, and preferably both, with water before mixing them.

Any heat-convertible resin may be used provided solvents are available with the desired properties. I have successfully used urea-formaldehyde resin (including resins made from its homologues and derivatives, such as thiourea, cyanuric acid, biuret, melamine, etc.), the soluble heat-convertible alkyd resins (those modified with low percentages of fatty acids), heat-convertible phenolic resins, and the like.

The solvents used will vary depending on the resin. Thus, with urea and the shorter oil alkyd resins, the original solvent may be a mixture of an alcohol and an aromatic hydrocarbon, with some terpenes if desired; the diluting solvent added in the low-solids lacquer may be aliphatic or aromatic hydrocarbons, or a mixture of aliphatic and aromatic hydrocarbons. With longer oil alkyds which are soluble in aromatic hydrocarbons, aliphatic hydrocarbons may be used as the diluent; those alkyds containing sufficient fatty acids to be soluble in aliphatic hydrocarbons are beyond the ready heat-convertible state, and cannot be used alone. With phenolic resins, alcohols may be used as the original solvents, various hydrocarbons as diluents. It should be observed that the tendency toward immiscibility is always increased by the incorporation of pigment into the resin lacquer; this should always be considered.

When my invention is used in the water-in-lacquer emulsion printing pastes, it permits the dilution of the color to the desired shade with a very low-solids diluent lacquer, without danger of causing aggregation of the pigment. The pigment remains protected by the same amount of resin, and thus is as resistant to washing and rubbing. Furthermore, the pigment-resin aggregate is deposited in far more discontinuous

islands than in the concentrated form, while the diluting lacquer deposits little solids; as a result, the "hand" of the fabric is kept at a minimum.

In dyeing operations, where the fabric is impregnated throughout, reduction of resin deposited is even more important; and my method permits of effective pigment dyeing with an absolute minimum of resin deposition, while maintaining uniformity of pigment distributions.

Typical examples of my invention are the following:

EXAMPLE 1

Alkyd resin printing paste

A lacquer is made by mixing—

	Parts by weight
Alkyd resin solution—50% in toluene.....	20
Pine oil	8
Solvesso #3 (hydrogenated petroleum solvent—boiling range 175–210° C.).....	28

Into this lacquer is emulsified—

	Parts by weight
A 16½% aqueous pulp of Lithosol Blue G. L.	20
Water	24
	100

The alkyd resin of this lacquer is glycerol phthalate, modified with 33% soya oil fatty acids; it can be set by heat. It is soluble in aromatic hydrocarbons, and will precipitate on further dilution with aliphatic hydrocarbons, or with mixtures containing substantial quantities of aliphatics. The tendency of this lacquer toward immiscibility with added solvents is increased by pigmentation, as with all resin.

EXAMPLE 2

Reducing emulsion—water-in-lacquer

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 1.

This unpigmented emulsion contains 0.75% solids; the lacquer phase contains about 3% solids. It may be blended with the pigmented emulsion of Example 1 (13.2% solids—lacquer phase about 18% solids) 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 aggregate 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 1.

EXAMPLE 3

Urea formaldehyde resin

An emulsion was made from a lacquer containing—

	Parts by weight
Solvent-soluble urea-formaldehyde resin solution (50 resin, 30 butanol, 20 xylene)	12.0
Ethyl cellulose (47% ethoxy—10 centipoise viscosity)	10.0
Butanol	4.0
Solvesso #2	44.0

and an aqueous phase containing—

	Parts by weight
Benzidine yellow pulp (dry basis)	2.0
Water	28.0
	100.0

The lacquer contains about 23% solids, the emulsion 16%. It can be reduced with the diluting emulsion of Example 2, to give similar results. It may also be reduced with other unpigmented emulsions, such as the following.

EXAMPLE 4

Ethyl cellulose reducing emulsion

	Parts by weight
Ethyl cellulose (47% ethoxy—500 centipoise viscosity)	0.4
Pine oil	2.6
Solvesso #2	25.0
Water	72.0
	100.0

This clear has 0.4% solids; the lacquer phase has about 1.3% solids.

EXAMPLE 5

Urea-formaldehyde alkyd paste

A typical water-in-lacquer printing emulsion may be made as in Example 1 from—

	Parts by weight
Urea resin solution of Example 3	5.0
Alkyd resin solution of Example 1	15.0
Pine oil	5.0
Solvesso #3	34.0
20% pulp phthalocyanine green	30.0
Water	11.0
	100.0

This can be reduced with the unpigmented diluent of Examples 2 and 4, with results similar to Example 2.

EXAMPLE 6

	Parts by weight
Solvent-soluble melamine-formaldehyde resin (50 resin, 30 butanol, 20 xylene)	4.0
Alkyd resin solution (65 parts alkyd resin of Example 2, 35 parts xylene)	15.5
Solvesso #3	27.5
Benzidine yellow—dry basis, but used as pulp	1.6
Water	51.4
	100.0

Made as in Example 1; it may be reduced with the unpigmented emulsions of Examples 2 and 4.

All of the above examples may be made by first mixing the pigmented lacquers with the clear lacquers of Examples 2 and 4, provided water is immediately emulsified therein; or the clear lacquers of Examples 2 and 4 may be added to the emulsions with stirring. These methods, however, lack flexibility, since the pigmented emulsion and the diluting emulsion may both be made of printing consistency, so they can be mixed in any desired proportions before use.

The pigment may be added in pulp form as indicated, or it may be dispersed in conventional fashion.

For overall pigment covering of textiles, lacquer-in-water emulsions may be used. For example—

EXAMPLE 7

Pigment dyeing emulsions

	Parts by weight
Carbon black	5.0
are dispersed in—	
Alkyd resin solution (65 parts alkyd resin of Example 1, 35 parts xylene)	10.0
and	
Xylene	10.0
To the dispersion is added—	

	Parts by weight
Urea resin solution of Example 3	2.0
Alkyd resin solution of Example 1	5.0
Pine oil	10.0
Xylene	7.0

The lacquer is then emulsified into

	Parts by weight
Water	46.0
Sodium lauryl sulfate	2.0
Dry bentonite	3.0
	100.0

This emulsion contains about 10% resin solids; if applied to cloth direct, it will produce too stiff a hand. Reduction of the lacquer with solvent before emulsification produces pigment flocculation. It is possible to increase the non-aqueous phase and reduce the solids content by emulsifying the proper solvent into the emulsion with an emulsifying agent. This may be done by making an oil-in-water emulsion from—

	Parts by weight
Solvesso #2	69.00
Oleic acid	1.25
Triethanolamine	0.40
Water	29.35
	100.00

An excellent pigment dyeing bath is made from 1 part of the pigmented emulsion and 4 or more parts of the unpigmented material.

If desired, the same effect may be obtained by adding water to the pigmented emulsion, then adding the emulsifying agent to the water, and then adding the solvent.

All of the diluted examples, when examined under the microscope, showed the presence of three phases. In the case of the water-in-lacquer emulsions, however, the two dispersed phases—water and pigment-resin aggregate—are in such close association that they cannot be distin-

guished except in the initial stages of the admixture.

The examples might of course be multiplied, and changes made without departing from the scope of my invention, which is defined in the claims.

The choice of resins depends on the properties desired in the finished material—substantially all heat-convertible resins may be used to give some desired property, since volatile solvents are known to the art which will dilute solutions of these resins to a point and beyond that cause precipitation. The choice of the volatile solvents may be left to those skilled in the art, since the phenomenon of precipitation on dilution has been widely studied.

It is only necessary that the diluting solvent contain some emulsifying agent therein so that it may form a stable emulsion; and where high non-volatile (solids) content is undesirable, the solids of the diluting low-solids lacquer phase should not exceed about 10% by weight of that phase.

The minimum amount of aqueous phase needed to prevent separation of the two lacquer phases varies of course with the degree of incompatibility; but in general, 20% of aqueous phase, based on the complete emulsion, is sufficient. For reasons of economy, and for better working properties, higher amounts are preferable, as indicated in the examples.

The term "aggregate" as used to describe the pigmented resin-solvent aggregate phase, is used in its popular sense, and not in any technical sense.

I claim:

1. An emulsion comprising an aqueous phase, a phase consisting essentially of a volatile water-immiscible organic liquid having dissolved therein less than 10% of non-volatile, including an agent capable of producing a stable emulsion of water and said liquid, and a dispersed phase of pigmented resin-solvent aggregate derived from a heat-convertible resin lacquer which is miscible with limited quantities of said organic liquid, but immiscible with the quantities employed in the emulsion.

2. A textile decorating emulsion comprising a discontinuous aqueous phase comprising at least 20% by weight of the emulsion, a continuous phase consisting essentially of a volatile water-immiscible organic liquid having dissolved therein an agent capable of producing a stable emulsion of water and said liquid, and a dispersed phase of pigmented resin-solvent aggregate derived

from a pigmented heat-convertible resin lacquer which is miscible with limited quantities of said organic liquid, but immiscible with the quantities employed in the emulsion.

3. A textile decorating emulsion comprising a discontinuous aqueous phase comprising at least 20% by weight of the emulsion, a continuous phase consisting essentially of a volatile water-immiscible organic liquid having dissolved therein less than 10% of non-volatile, including an agent capable of producing a stable emulsion of water and said liquid, and a dispersed phase of pigmented resin-solvent aggregate derived from a pigmented heat-convertible resin lacquer which is miscible with limited quantities of said organic liquid but immiscible with the quantities employed in the emulsion.

4. The composition of claim 2, in which the heat-convertible resin comprises a heat-convertible alkyd resin.

5. The composition of claim 2, in which the heat-convertible resin comprises a plasticized urea formaldehyde resin.

6. A textile coloring emulsion comprising an outer continuous aqueous phase and two organic phases, one of which consists essentially of a volatile water-immiscible organic liquid having dissolved therein less than 10% of non-volatile, including an agent capable of producing a stable emulsion of water and said liquid, and the other of which consists of pigmented resin-solvent aggregate derived from a heat-convertible resin lacquer which is miscible with limited quantities of said organic liquid, but immiscible with the quantities employed in the emulsion.

7. The method of producing a textile decorating emulsion which comprises preparing a water-in-lacquer emulsion, the outer phase of which is pigment dispersed in a lacquer, the binder of which comprises a heat-convertible synthetic resin, the lacquer being of such body that pigment will remain dispersed in it, separately preparing a second water-in-lacquer emulsion, the outer phase of which is a lacquer consisting essentially of volatile solvent having dissolved therein an agent which renders the lacquer capable of emulsifying water therein, the second lacquer being only partially miscible with the first lacquer, and having a substantially lower non-volatile content than the first lacquer, and mixing the emulsions to produce an emulsion in which the outer phase consists essentially of the second lacquer, and the inner phases of which comprises water and the first lacquer.

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