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PIGMENT BINDERS

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The present invention relates to novel pigment binders suitable for use in printing textile materials and having improved pigment-carrying and binding properties rendering them resistant to the action of light as well as to oxidizing and bleaching agents.

The art is replete with proposals for fixing pigmentary colors solidly on fabrics. The pigmentary colors, as distinguished from dyes, are generally inert and fast to degradation agents such as sunlight and air as well as a common chemicals such as washing powders and the like to which textile fabrics are subjected in laundering and dry cleaning. Pigments in general have a high covering power and are relatively inexpensive to produce, and consequently many efforts have been made to apply them to textile fabrics in such a manner that the fabrics colored thereby will have light fastness and washing and cleaning resistant characteristics comparable to those colored with soluble dyes.

Many such attempts, however, have been unsuccessful. It has been proposed, for example, to use thermoplastic materials and the like to fix the pigment to the fabric. Fabrics so colored, however, become sticky when ironed and are therefore unsuitable for many purposes. It has also been proposed to use thermosetting resins to bind the pigment to the fabric. These attempts, however, have resulted in colored fabrics having a poor "hand," i. e., a certain objectionable stiff feeling of the cloth in handling, which is probably due to the fact that the pigment-containing composition applied covers the fabric with a continuous film that bridges the small interstices between the fibers.

An objection that is common to fabrics colored with many pigment-containing compositions heretofore proposed is the tendency of the printed fabric to yield color to another fabric or to the hand when rubbed against it. This phenomenon is usually referred to in the trade as crocking. Furthermore, many materials heretofore proposed for use in binding pigments have been found to be unsuitable when exposed to light or to the other severe conditions, such as laundering, to which finished textile fabrics are periodically subjected. The latter deficiency is not always immediately perceptible. Thus for example, a fabric printed with a pigment composition containing urea-formaldehyde resin as a binder may show no loss of color after it has been exposed to light for some time, but, upon subsequent washing, a considerable proportion of the pigment will wash out, apparently due to the fact that the binder was deleteriously affected by the exposure and therefore failed to bind the pigment to the fiber.

It is the salient object of the present invention to provide a pigment binder to securely fix insoluble pigments on textile fabrics so as to yield a coloring that is fast to light and to washing and that will not impair the "hand" of the fabric and is not subjected to crocking.

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This and other objects, the utility and advantages of the present invention will appear from the detailed description of the invention that follows hereinafter.

The pigment binder of this invention is designed to act as a vehicle for and to bind insoluble pigments to the fabric and may be used with conventional thickener, such as British gum, locust bean gum, starch and the like that is subsequently washed out of the fabric.

The pigment binder of this invention may be diluted or thinned readily with water to provide the viscosity desired for printing or light coloring operations and may readily be washed from the printing machinery, etc. and thus avoid fouling of the printing apparatus.

The pigment binder carrying the insoluble pigments may be applied to the fabric by means of any of the usual fabric coloring methods such as the rotary intaglio printing method or stenciling, and it may be applied successfully to all types of fabric including vegetable, animal, mineral and synthetic or mixed fabrics. The pigment binder does not detract from the brilliance, prominence and other inherent characteristics of the pigments that are available for textile coloring. Furthermore, the application of the pigment binders of this invention to fabrics may be combined with other textile processing, printing, dyeing or other coloring operations.

In accordance with the invention, any desired pigment or mixture of pigments may be dispersed in the aqueous phase in a pigment binder composition essentially comprising a chlorine-containing resin prepared by polymerizing compounds containing the vinyl group $H_2C : CH—$ or the vinylidene group $H_2C : C:$, preferably in combination with a plasticizer, such as synthetic rubber latex, and a water soluble, thermosetting urea-formaldehyde containing resin.

In addition to the substances referred to above, other materials, such as emulsifying, viscosity, and surface tension modifying agents and the like may be added if desired, as discussed more particularly hereinafter.

The term "chlorine-containing resin" as used in the description of the present invention, is intended to include vinyl chloride polymers, vinylidene chloride polymers, and vinyl-vinylidene chloride copolymers. These polymers and copolymers are well known in the art and, for the purposes of this invention, are preferably employed in the form of latices or aqueous dispersions. The dispersed resin is in the form of discrete spherical particles that have a negative charge. While the size of the individual spherical particles is not

believed to be particularly critical, it has been found that resins having a particle size of the order of 0.1 micron in diameter give excellent results. The dispersing medium is water, and small quantities of stabilizing agents are preferably also present to insure good colloidal stability. The concentration of solids in the dispersion may vary from a few percent up to a concentration of from 55% to 60%. At or near the upper limit of this concentration the viscosity increases very rapidly with concentration, and for this reason only higher concentrations are not practicable.

Although any of a large number of plasticizers compatible with the foregoing chlorine-containing resins may be used in combination therewith, it has been found particularly preferable to use as a plasticizer appreciable proportions of an unvulcanized synthetic rubber latex comprising a polymer of a butadiene hydrocarbon and containing from about 30% to 70% by weight of solids. One such synthetic rubber latex that is particularly useful in accordance with the present invention is a copolymer of butadiene and styrene, wherein the relative proportion is 25% to 75% of butadiene and 75% to 25% styrene by weight. Others are copolymers of acrylonitrile with butadiene and of isoprene with isobutylene. These blends of vinyl resins and synthetic rubbers combine in various degrees sunlight resistance, ozone resistance, and solvent resistance, and have thermosetting properties. The rubber acts as a plasticizer and, as such, wholly or partially replaces the usual liquid plasticizer. It does not require vulcanization for the purpose intended in this invention. In fact, vulcanization is not desirable, since it tends to make the film hard and brittle. One advantage of this solid plasticizer over the usual liquid plasticizers is that it remains in the compound under certain severe conditions under which the liquid plasticizers would eventually dissipate or leach out.

To increase the thermosetting properties of the composition, it is desirable to add a water soluble thermosetting composition, such as urea-formaldehyde resin. It has been found particularly desirable to add water soluble protein alkylol amine reaction products such as a urea-formaldehyde-alkylolamine casein resin described, for example, in U. S. Patent No. 2,262,771. The advantage of a composition of this type over that of a straight urea-formaldehyde or melamine-formaldehyde resin is that the presence of the protein contributes to the stability of the resin dispersion and increases binding power of the film.

While the relative proportions of these preferred components of the pigment binder may, in accordance with this invention, be varied considerably, depending upon the particular application, it has been found generally preferable to combine them in the following ranges of proportions by weight:

	Per cent
Dispersion of chlorine-containing Resin	10–50
Plasticizer dispersion	5–40
Thermosetting composition	5 to 25

Although it is by no means necessary, the pigment binders of this invention may also contain relatively small proportions of formaldehyde, ammonia or an organic amine, and mineral oil. Excess formaldehyde may be added to help set the resin and harden the other components. Ammonia or an organic amine, such as, for example, triethanolamine, may be included in order to give it a pH within the range of 9 to 11. A light mineral oil generally known in the trade as "Mineral Spirits," or a heavy mineral oil such as that available under the name "Bayol," or both, may also be included. The former has the function of eliminating the tendency of pigment particles to stick in the engraving while the latter serves as a lubricant for the printing color. These optional ingredients may be added in the following proportions by weight, based on the weight of the final pigment binder composition:

	Per cent
Excess free formaldehyde	up to about 15
Ammonia or amine	up to about 10
Heavy mineral oil	up to about 10
Light mineral oil	up to about 15

and are preferably included in the following proportions:

	Per cent
Excess free formaldehyde	2–10
Ammonia or amine	3–8
Heavy mineral oil	2½–7½
Light mineral oil	2½–10

In use the pigment binder composition of the present invention is generally combined with thickeners, such as locust bean gum, British gum, starch and the like, the proportion of binder to thickener preferably being between 10% to 30% by weight of binder to 90% to 70% by weight of thickener. It has been found generally desirable to use a water-dispersible pigment in a binder-thickener combination of this type that goes into the aqueous phase. When such a binder-thickener combination containing the desired pigments is applied to the fabric, the solids go into a continuous film, inasmuch as the particles of rubber and resin are believed to merge together to form such a film that imprisons the pigment.

The pigment binder itself is generally in the form of a dispersion rather than in the form of an emulsion. The continuous film that is formed is continuous only in the sense that it is a continuous film enclosing the individual fibers of the fabric and not in the sense that it bridges the interstices between the fabric. When the composition containing the pigment binder thickener and the pigment color is applied to a highly capillary surface, such as a woven or knitted textile, the surface does not become a continuous film that bridges the interstices unless the material is coated over and over again until the capillarity is blocked and the spaces between the threads are filled in. The pigment binder carries the pigment and serves to bind the pigment to the fabric. The thickener is a carrier for the binder and is used only to give the necessary viscosity to the composition so that printing rolls can pick up the binder. In subsequent washing, the thickener will wash out.

It has been found that textiles printed or otherwise pigmented with color pigments wherein the pigment binder of the present invention was used, do not require special curing, especially inasmuch as the application of pigments to textiles, in most instances, is done in conjunction with the application of other colors requiring acid aging for fixation. It has been noted that acid aging improves the fixation of the pigments slightly.

In order the describe the present invention still more specifically, the following examples are included for illustrative purposes only.

Example 1

32.5 parts by weight of vinyl chloride latex available on the market in the form of a water dispersion containing about 60% by weight of solids, 32.5 parts by weight of a synthetic rubber latex available on the market in the form of a water dispersion containing about 33% to 36% by weight of solids and believed to be a copolymer of butadiene and styrene prepared by copolymerizing one mol of butadiene with one mol of styrene, and 14 parts by weight of a urea-formaldehyde alkylolamine resin containing casein and made in accordance with the disclosure of U. S. Patent No. 2,262,771 were mixed until a homogeneous mass was obtained. To this mass were added 6 parts by weight of formaldehyde, 5 parts by weight of triethanolamine, 5 parts by weight of light mineral oil known as "Mineral Spirits," and 5 parts by weight of a heavy mineral oil known as "Bayol."

23 parts by weight of this pigment binder composition were then combined with 76.75 parts by weight of locust bean gum in the form of a 1.5% to 2% solution and 0.25 part by weight of phenol.

To this binder-thickener combination there were then added 3 parts by weight of W. D. Phthalocyanine Blue B 61–(Harmon). This pigment-containing composition was applied in the usual manner to a sample of 80 x 80 cotton fabric.

After the printed 80 x 80 cotton fabric was dried, it was exposed for 48 hours in a fadeometer. No perceptible loss of color was noted at the end of this time. The printed 80 x 80 cotton fabric was then given the No. 3 wash test (A. A. T. C. C. Standard). Examination of the printed fabric showed that practically no pigment had been lost and that the color value had remained substantially the same.

Another sample of 80 x 80 cotton fabric printed with this pigment-containing composition was subjected to the No. 4 wash test (A. A. T. C. C. Standard containing free chlorine as bleaching agent). Examination of the fabric after this test showed that the resistance of the pigment binder to reaction with chlorine was far superior to any that had previously been obtainable and that the color value was scarcely affected.

Another 50 parts by weight of the pigment binder composition prepared in accordance with this example were combined 150 parts by weight of locust bean gum in the form of a 1.5% solution.

To one-half of this binder-thickener combination there were then added 3 parts by weight of Monastral Fast Blue BWD. To the other half there were added 3 parts by weight of Monastral Fast Green GWD. These pigment-containing compositions were applied in the usual manner to samples of 80 x 80 cotton fabric.

Both samples of printed cotton fabric were boiled for one-half hour in a ½% soap solution. Examination of the boiled fabrics showed that practically no pigment had been lost and that the color value had remained substantially unaffected.

Example 2

10 parts by weight of vinyl chloride latex available on the market in the form of a water dispersion containing about 60% by weight of solids, 30 parts by weight of a synthetic rubber latex available on the market in the form of a water dispersion containing about 50% by weight of solids and believed to be a copolymer of butadiene and styrene prepared by copolymerizing one mol of butadiene with one mol of styrene,

and 25 parts by weight of a urea formaldehyde alkylolamine resin containing casein and made in accordance with the disclosure of U. S. Patent No. 2,262,771 were mixed until a homogeneous mass was obtained. To this mass were added 10 parts by weight of formaldehyde, 8 parts by weight of triethanolamine, 10 parts by weight of light mineral oil known as "Mineral Spirits," and 7 parts by weight of a heavy mineral oil known as "Bayol."

Samples of this pigment binder composition were then combined with the same thickeners and pigments as described in Example 1.

80 x 80 cotton fabric was printed with the resulting pigment-containing compositions and subjected to the same tests as described in Example 1. Examination of the fabrics after these tests showed substantially the same results as were obtained in Example 1.

Example 3

32.5 parts by weight of vinyl chloride latex available on the market in the form of a water dispersion containing about 60% by weight of solids, 32.5 parts by weight of a synthetic rubber latex available on the market in the form of a water dispersion containing about 33% to 36% by weight of solids and believed to be a copolymer of butadiene and styrene prepared by copolymerizing one mol of butadiene with three mols of styrene, and 14 parts by weight of a urea-formaldehyde alkylol amine resin containing casein and made in accordance with the disclosure of U. S. Patent No. 2,262,771 were mixed until a homogeneous mass was obtained. To this mass were added 6 parts by weight of formaldehyde, 5 parts by weight of triethanolamine, 5 parts by weight of light mineral oil known as "Mineral Spirits," and 5 parts by weight of a heavy mineral oil known as "Bayol."

Samples of this pigment binder composition were then combined with the same thickeners and pigments as described in Example 1.

80 x 80 cotton fabric was printed with the resulting pigment-containing compositions and subjected to the same tests as described in Example 1. Examination of the fabrics after these tests showed substantially the same results as were obtained in Example 1.

While but a few examples of the invention have been shown, it is obvious that innumerable changes in the relative proportions of the various ingredients of the pigment binder composition can be made without departing from the spirit of the invention. The relative proportions of the pigment binder and the thickeners can be varied to produce any desired viscosity suitable for the particular printing process used. It is to be understood that the invention is intended to be limited only by the scope of the appended claims.

We claim:

1. A pigment binder containing from about 10% to about 50% by weight of an aqueous dispersion containing from a few to about 60% by weight of a resin selected from the group consisting of vinyl chloride polymers, vinylidene chloride polymers and vinyl-vinlyidene chloride copolymers, said resin being in solid, dispersed form, from about 5% to about 40% by weight of an unvulcanized latex comprising a synthetic rubbery polymer of a butadiene hydrocarbon and containing from about 30 to 70% by weight of solids, and a water-soluble protein-alkylolamine-urea-

formaldehyde reaction product in an amount from about 5% to about 25% by weight.

2. A pigment binder containing from about 10% to about 50% by weight of an aqueous dispersion containing from a few to about 60% by weight of a resin selected from the group consisting of vinyl chloride polymers, vinylidene chloride polymers and vinyl-vinylidene chloride copolymers, said resin being in solid, dispersed form, from about 5% to about 40% by weight of an aqueous dispersion of an unvulcanized copolymer of butadiene and styrene containing from about 30 to 70% by weight of solids, and from about 5% to about 25% by weight of a water-soluble resinous product obtained by the addition of formaldehyde to an aqueous dispersion of urea and a protein solubilized with an alkylolamine.

3. A pigment binder containing from about 10% to about 50% by weight of an aqueous dispersion containing from a few to about 60% by weight of a resin selected from the group consisting of vinyl chloride polymers, vinylidene chloride polymers and vinyl-vinylidene chloride copolymers, said resin being in solid, dispersed form, from about 5% to about 40% by weight of an unvulcanized latex comprising a synthetic rubbery polymer of a butadiene hydrocarbon and containing from about 30 to 70% by weight of solids, a water-soluble protein - alkylolamine-urea - formaldehyde reaction product in an amount from about 5% to about 25% by weight, up to about 10% by weight of an amine, up to about 15% by weight of a light mineral oil, and up to about 10% by weight of a heavy mineral oil.

4. A pigment binder containing from about 10% to about 50% by weight of an aqueous dispersion containing from a few to about 60% by weight of a resin selected from the group consisting of vinyl chloride polymers, vinylidene chloride polymers and vinyl-vinylidene chloride copolymers, said resin being in solid, dispersed form, from about 5% to about 40% by weight of an unvulcanized latex comprising a synthetic rubbery polymer of a butadiene hydrocarbon and containing from about 30 to 70% by weight of solids, a water-soluble protein - alkylolamine-urea - formaldehyde reaction product in an amount from about 5% to about 25% by weight, from about 2% to about 10% by weight of formaldehyde, from about 3% to about 8% by weight of an amine, from about 2½% to about 10% by weight of a light mineral oil, and from about 2½% to about 7½% by weight of a heavy mineral oil.

5. A pigment binder containing from about 10% to about 50% by weight of an aqueous dispersion containing from a few to about 60% by weight of a resin selected from the group consisting of vinyl chloride polymers, vinylidene chloride polymers and vinyl-vinylidene chloride copolymers, said resin being in solid, dispersed form, from about 5% to about 40% by weight of an unvulcanized latex comprising a synthetic rubbery polymer of a butadiene hydrocarbon and containing from about 30 to 70% by weight of solids, and a water-soluble thermosetting urea-formaldehyde containing resin in an amount from about 5% to about 25% by weight.

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