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VESICULAR PRINTS AND PROCESS OF MAKING SAME

Clifford E. Herrick, Jr., Easton, Pa., and Ann K. Balk, Owego, N. Y., assignors to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

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This invention relates to methods of preparing a photosensitive vesicular print material by forming a dispersed mixture of a thermoplastic, hydrophobic resin such as polystyrene with an aqueous water soluble, gas impermeable colloid containing a stabilized photosensitive diazonium compound, coating it on to a support such as glass or black paper and drying. The invention also relates to the resulting photosensitive vesicular print material which comprises a substantially clear, continuous, hydrophobic resin layer having finely dispersed therein the colloid and photosensitive compound, to the method of preparing a stable vesicular print therefrom by irradiating it with actinic light through a design and then subjecting it to elevated temperatures to develop and stabilize the image, as well as to the resulting stable vesicular print.

The art is familiar with photographic vesicular images prepared from a light sensitive layer made up from a hydrophilic material such as gelatin and a photosensitive diazo compound which liberates nitrogen gas upon photodecomposition. The image is developed by treatment with steam or water, whereby the hydrophilic layer softens and the nitrogen gas therein expands forming minute vesicles which refract light which strikes the layer. This causes an appearance of whiteness by reflected light and darkness by transmitted light. Sometimes the resulting print is given a treatment with a coupling compound to render the unexposed diazo material non-photosensitive to prevent subsequent undesirable bubble formation in the unexposed or clear areas upon subsequent overall exposure to ordinary light and moisture.

Many disadvantages are inherent in this process and the resulting prints. The development operation is cumbersome and critical, and gives strong relief effects which are undesirable in photographic prints. In the treatment of the undecomposed diazo material with a coupling component an azo dye is formed, and this prohibits the use of foil vesicular prints as photographic negatives; furthermore, the white areas are badly colored thereby.

A particularly disadvantageous feature thereof is the instability of the vesicular prints in the presence of moisture; since the hydrophilic medium absorbs moisture and softens, the minute vesicles collapse, and the image is lost.

An improvement in this vesicular print process is the use of a single application of heat in the development step, giving clean whites, and improved tone gradation through the use of a non-reflecting, opaque backing for positive prints. However, even these improved prints leave much to be desired from the viewpoint of stability toward moisture.

It has been found, in accordance with the invention, that the above discussed drawbacks may be overcome and highly desirable vesicular print materials may be prepared by forming a dispersed mixture of 1 to 7 parts of a thermoplastic, hydrophobic resin and a water solution of 3 to 1 parts of a water soluble, gas impermeable colloid containing a stabilized photosensitive diazonium compound, preferably including an acidic diazo stabilizer and a plasticizer, coating it on a support and drying. The resulting layer comprises a substantially clear, continuous, hydrophobic resin phase having finely dispersed therein the water soluble resin or colloid and photosensitive compound. Upon irradiating this material with actinic light through a design, and then subjecting it to elevated temperatures for a short time, the image is developed. If desired, the resulting vesicular print may be re-exposed to the actinic or ultraviolet light to destroy remaining diazo compound. The resulting vesicular prints are substantially stable in the presence of moisture and exhibit good whites.

The objects achieved in accordance with the invention as described herein include the provision of vesicular prints which are stable to actinic light, moisture, and water at ambient temperatures; the provision of processes for making either positive or negative vesicular prints having the above-mentioned characteristics; the provision of a photosensitive vesicular print layer comprising a substantially clear, continuous, hydrophobic resin phase having finely dispersed therein hydrophilic colloid and photosensitive compound; the provision of methods for preparing photosensitive vesicular print materials by forming a dispersed mixture of 1 to 7 parts of a thermoplastic, hydrophobic resin and a water solution of 3 to 1 parts of a water soluble, gas impermeable colloid containing a stabilized photosensitive diazonium compound, preferably including an acidic diazo stabilizer and a plasticizer, coating it on a support and drying; the provision of a process of this type wherein the resin is polystyrene and the colloid is gelatin; the provision of a process of this type wherein the dispersed mixture contains the water soluble colloid in the continuous phase, and during the drying step this inverts so that the hydrophobic resin is in the continuous phase; and other objects which will become apparent as details or embodiments of the invention are set forth hereinafter.

In order to facilitate a clear understanding of the invention, the following preferred specific embodiments are described in detail:

Example 1

The following ingredients were used in this example (parts are by weight):

2 parts polyvinylidene chloride (Dow Saran latex F–122, A–20, 52.5% solids)
6 parts polyvinyl alcohol (50 parts of a 12% solution of Du Pont Elvanol RH 391A)
0.72 part diazo compound of 2-amino-1-naphthol-5-sulfonic acid
0.72 part citric acid.

The diazo and citric acid were dissolved in the polyvinyl alcohol solution, warmed to 40° C. and then poured slowly into the Saran latex with good stirring. The mixture was coated on black paper at a 15–20 mils wet film thickness and dried rapidly in subdued light. Exposure was made in a commercial Model F Ozalid machine, at speed 2, through a positive photographic transparency of very soft gradation. Then the image was developed by exposure to an infra-red heat lamp, 5 to 6 inches away, for a short time. The resulting print exhibited faithful reproduction of all half-tones, excellent whites, excellent maximum density and a complete absence of grain. It showed resistance to moisture at ambient temperatures.

Example 2

The following ingredients were used in this example:

4.8 parts polyvinylidene chloride (Saran latex 52.5% solids)
3.0 parts dextrose
6.0 parts water
0.36 part diazo compound of 2-amino-1-naphthol-5-sulfonic acid
0.36 part citric acid.

The solids were all dissolved in the water and slowly added to the Saran latex. A small amount of aqueous 8% hydroxy ethyl cellulose was added to thicken the emulsion. Coatings were made at 12 mils wet-film thickness, and prints were made as in Example 1; they showed superior resistance to moisture, and somewhat higher sensitometric contrast.

Example 3

The following ingredients were used in this example:

18 parts polyvinylidene chloride (Saran latex 52.5% solids)
12 parts polyvinyl alcohol (as 12% aqueous solution)
2.88 parts diazo compound of 2-amino-1-naphthol-5-sulfonic acid as a 10% aqueous solution
2.88 parts citric acid (as a 10% aqueous solution)
1–2 parts water.

A 20 mil coating was prepared by the method of Example 1. The layer was pre-heated briefly by two 5–6 second contact passages around an ironing mangle, at a temperature of about 190° F. This improved the gradation in the final print, and also improved its water resistance. Exposure was made first by giving the layer an all over flash of 9 seconds under an H–1 arc lamp. This gave a further improvement in the gradation in the shadow regions. Then a soft photographic positive transparency was used for a 3 minute exposure. At this time no printout occurred. Development by one passage around the rotary ironing mangle caused intensification of the latent vesicular image. The resulting print was a faithful reproduction of the original, extremely fine grained, and of excellent maximum density. It showed superior resistance to moisture.

Example 4

The following ingredients were used in this exmaple:

4.5 parts polyvinylidene chloride (Saran latex 52.5% solids)
3 parts polyvinyl alcohol (as 12% aqueous solution)
0.36 part diazo compound of 2-amino-1-naphthol-5-sulfonic acid as a 10% aqueous solution
0.36 part citric acid (as a 10% aqueous solution)
0.071 part graphite (as a 25% aqueous dispersion of Aquadag)

The coating mixture was prepared by the method of Example 1, the graphite being dispersed thoroughly in the polyvinyl alcohol solution before addition to the Saran latex. Coatings were made at a 20 mil wet-film thickness on a commercially prepared transparent Saran sheeting (any other suitable transparent or translucent base such as cellophane or transparentized paper is suitable). The layer was exposed through a rather dark photographic negative, after first being pre-heated and preflashed as in Example 3. Development in the rotary-ironing mangle caused the production of an accurate vesicular negative image, which, after re-exposure to the ultraviolet lamp to destroy excess diazo in the clear areas, could be used to make further positive diazo-type vesicular prints. It showed superior resistance to moisture.

Example 5

The following ingredients were used in this example:

5 parts polystyrene (as Dow latex 319, plasticized with 35% dibutyl phthalate)
5 parts polyvinyl alcohol (as 12% aqueous solution)
0.6 part diazo compound of 2-amino-1-naphthol-5-sulfonic acid as a 10% aqueous solution
0.6 part citric acid (as a 10% aqueous solution)
3 parts water

The solids were dissolved in the polyvinyl alcohol solution before adding to the plasticized polystyrene latex. Coatings were made as by the method of Example 1, at a 25 mils wet-film thickness, and dried rapidly with the aid of moving warm air. The emulsion was partially masked, exposed to an H–1 mercury arc lamp and developed in a rotary ironing mangle; this resulted in the formation of a vesicular image in the exposed areas.

Example 6

The following ingredients were used in this example:

6 parts A polyamid-type resin (General Mills B–200) (37% solids aqueous suspension)
6 parts polyvinyl alcohol (as 12% aqueous solution)
0.72 part 4-diethylaminobenzene diazonium chloride, zinc chloride double salt
0.72 part citric acid
6.5 parts butanol

The diazo and citric acid were dissolved in a few parts of water, and mixed thoroughly with the polyvinyl alcohol solution. The butanol was added slowly to rapidly stirring polyamid suspension, and the hot polyvinyl alcohol solution was then slowly poured into the stirring polyamid. Coatings were made at 20 mils on black paper as in the previous examples. Upon exposure and development, an image was produced.

Example 7

The following ingredients were used in this example:

4.5 parts polyvinylidene chloride (Saran latex 52.5% solids)
3 parts gelatin
10.6 parts water
0.36 part diazo compound of 2-amino-1-naphthol-5-sulfonic acid as a 10% aqueous solution
0.36 part citric acid (as a 10% aqeuous solution)

The gelatin is dissolved in water in a covered container over a steam bath. The diazo and citric acid are dissolved in water, and added to the gelatin. While still hot, this solution is added slowly, with good stirring, to the latex. Coatings are made at 12 mils on an opaque base and development is carried out as in previous examples.

Example 8

The following ingredients were used in this example:

15 parts polystyrene (50 parts of a 30% toluene solution)
3 parts melamine-formaldehyde resin (as as 60% aqueous solution)
0.5 part 4-diethylaminobenzene diazonium chloride, zinc chloride double salt
0.5 part citric acid
0.09 part di-ammonium phosphate [$(NH_4)_2HPO_4$]

The solids were dissolved in the aqueous solution and then added to the toluene solution and mixed gently, but thoroughly. It was coated on black paper at 25 mils wet-film thickness using a Bird type applicator. Some toluene was added to make the dispersion flow smoothly. The layer was dried at room temperature; then exposed to ultraviolet light for a few minutes, through a design, and developed by exposure to an infra-red heat lamp 5 or 6 inches away. Decided whitening appeared in the aera exposed to the actinic rays.

Example 9

The following coating mixture was made:

100 parts polystyrene
6 parts oleoyl polyoxyethylene glycol ester
363 parts toluene

A solution was made by warming and into it was mixed the following hot aqueous solution:

15 parts gelatin dissolved in
30 parts water
2.49 parts 4-diethylaminobenzene diazonium chloride zinc chloride double salt, and
2.49 parts citric acid wet with 1 part water

After thorough hand mixing, the emulsion was further refined by passing through an Eppenbach colloid mill for about one hour. An extremely fine dispersion resulted. A coating and print was prepared as in Example 8, using a positive photographic transparency when making the exposure to actinic rays.

Example 10

A mixture of

40 parts styrene-isobutylene copolymer, and
138 parts toluene

was rolled in a closed jar until in solution, then the following solution was mixed in thoroughly, including 3 passages through a hand-operated mill:

20 parts melamine-formaldehyde resin (in 60% aqueous solution)
0.6 part di-ammonium phosphate [$(NH_4)_2 HPO_4$]
1.0 part citric acid
4.0 parts 4-diethylaminobenzene diazonium chloride, zinc chloride double salt
5 parts water
2.45 parts of an alkyl aryl polyoxyethylene glycol (Glim)

Coatings were made on black paper at 12 mils; and the Example 9 procedure was followed.

Example 11

Separate mixtures of

40 parts styrene-isobutylene copolymer
138 parts toluene, and
10 parts gelatin
20 parts water

were dissolved on a steam bath. A mixture of

4.0 parts 4-diethylaminobenzene diazonium chloride, zinc chloride double salt
1.0 part citric acid
0.3 parts di-ammonium phosphate [$(NH_4)_2$ HPO_4]
5 parts water

was also dissolved on a steam bath and thoroughly mixed with the gelatin solution while both were still hot. After cooling to 35° C., 10 parts melamine-formaldehyde resin (as a 60% aqueous solution)(Resloom M–75) was added. The entire solution was then thoroughly mixed with the toluene copolymer solution, put through a hand colloid mill three times and then processed as in Example 10.

Comparable results to the foregoing are achieved by using the following variations: Instead of the black paper, a transparent support such as glass, cellophane, or other suitable transparent material may be used to give a negative print. Alternatively, an opaque material such as metal or the like may be used to give a positive print. The opaque material may be of any color, as desired and if indicated, an adhesive interlayer may be used.

The thermoplastic hydrophobic resins are known, and one type may be typified by polystyrene, styrene-isobutylene copolymers, vinyl acetate-vinyl chloride copolymers, poly methylmethacrylate, polyvinyl acetate, ethyl cellulose, hydrolyzed interpolymers of vinyl acetate and ethylene, and the like. For the present purposes, these are dissolved in a suitable solvent such as toluene, benzene, acetone, and the like. Other types of resins may be used in the form of their water suspensions, and these may be typified by polyvinylidene chloride latex (Saran), natural rubber latex, polystyrene latex, and polyamid resin latices. In order to form the dispersions with the above mentioned first type of resin, a wide range of oil-soluble and water-soluble emulsifying agents may be used such as sodium N-oleoyl-N-methyl taurate, oleoyl methyl tauride, sodium salt, oleoyl polyoxyethylene glycol amine, an alkyl aryl polyoxyethylene glycol, oleoyl polyoxyethylene glycol ester, sorbitan sesquioleate, and the like.

The water soluble, gas impermeable colloidal materials are known, and these may be typified by polyvinyl alcohol, gelatin, partial (e. g. 10–20%) aceto acetic acid ester of polyvinyl alcohol which is obtained by reacting polyvinyl alcohol with diketene, melamine formaldehyde resin, or intermediate condensate, dextrose-urea formaldehyde resin, dextrin, albumin, and the like.

Desirable light sensitive diazonium compounds are stabilized as the diazo oxide or as a metallic double salt such as zinc chloride double salt or the like and are derived from aromatic paradiamines, N-mono or di-substituted benzene paradiamines or from para-amino diphenyl amine. For the solvent solution methods or compositions, the preferred diazonium compound is 4-diethylaminobenzene diazonium chloride. For the latex type methods or compositions, diazonium derivatives of naphthols are especially useful, and of these, the diazonium derivative of 2-amino-1-naphthol-5-sulfonic acid is preferred.

Desirable diazo stabilizers are acidic materials, such as lower carboxylic acids, especially hydroxy carboxylic acids. If desired, other known plasticizers may be used provided they are compatible in the present resin systems. Thiourea or the like material may also be included with the diazo compound.

In one modification of the present invention, an oil-in-water type emulsion of the thermoplastic, hydrophobic resin is prepared and for this, a commercial latex such as Saran latex may be used. The water soluble, gas impermeable colloid is dissolved in the continuous aqueous phase together with the light sensitive diazo compound and diazo stabilizers. The resulting emulsion is coated on to the support, and then dried. It has been found that an inversion results, whereby the dispersed resin particles of the emulsion become the continuous phase of the dried film, with the water soluble colloid and diazo compound dispersed therein in the form of minute particles. This inversion occurs more readily at the higher ratios of the resin to the colloid, but has been found also at high ratios of colloid to resin, such as two parts of the colloid per part of the resin.

In another modification of the invention, a water solution of the water soluble, gas impermeable colloid and the stabilized light sensitive diazo compound is finely dispersed in a solvent solution of the thermoplastic, hydrophobic resin, using an emulsifying agent if desirable, e. g. as described above. The resulting emulsion is coated on to the support and dried. The resulting layer consists of a substantially clear continuous resin phase having finely dispersed therein the water soluble colloid and stabilized diazo compound.

The heating or development step is preferably carried out by direct contact with a heated surface, e. g. at about 140–190° F. However, other heating means, such as radiant heat may be used. For some applications, where water resistance is not critical, direct steam heat may be used. In the printing step, the exposure to actinic light or ultraviolet rays may be for about 30 seconds to 3 minutes depending upon the strength of the light source. After development, the vesicular prints may be re-exposed to the actinic light at ambient temperatures to destroy any remaining diazo compound.

The resin and colloid are sufficiently hard to resist deformation by any gas liberated therewithin at ambient temperatures, even on the hottest summer days so that no image change can occur. The resin intermediate or condensate type of colloid may further condense or harden in the image development step. The vesicular print is also resistant to moisture, inasmuch as the hydrophobic resin surrounds and protects the dispersed particles of water soluble colloid.

The resulting vesicular print may be re-exposed to the actinic or ultraviolet light to destroy remaining diazo compound.

A particular advantage of the new compositions is the adjustability of their sensitometric characteristics. These can be varied within wide limits by varying the ratio of the colloid to the resin. The higher ratios of colloid to hydrophobic resin result in materials having extremely soft gradation so that details in shadows and highlight areas are both easily reproduced. Materials containing higher proportions of the hydrophobic resin relative to the colloid, show increased contrast, and those with a very high ratio of resin to colloid are especially suitable for black and white line reproductions.

The sensitometric properties of a layer containing a high ratio of resin to colloid, such as is suitable for line drawings, may be varied by a short heating for 2 or 3 seconds at about 190° F. before exposure or printing (e. g. in an ironing mangle). The resulting material has softer gradation properties, so that it can be used for accurate half-tone production. Thus, a particular layer formulation may serve for many uses, by adjusting its sensitometric characteristics by means of a preliminary heat treatment.

The hydrophobic resin and the water soluble resin or colloid are selected to give final compositions which are substantially clear, thermoplastic at elevated temperatures (e. g. about 140–200° F.), and of good physical stability at ambient temperatures even under the hottest weather conditions. Generally the amount of the hydrophobic resin is in the range of 1 to 7 parts and the corresponding amount of the water soluble, gas impermeable resin is in the range of 3 to 1 parts. The gas impermeability characteristic is such that the liberated gas is substantially entrapped in the form of bubbles or vesicles in the colloid, in the printing step and especially in the development step. After the development and cooling or image fixation, any residual excessive gas pressures may be relaxed by the slow passage of the gas through both the colloid and the hydrophobic resin, and this tends to give a more stable vesicular print.

It is indeed surprising that the processes of the invention are so practical, and yet give vesicular prints combining good whites, with substantial stability in the presence of moisture.

Variations and modifications of the invention will be apparent to one skilled in the art in view of the foregoing

disclosures, and it is intended to include within the invention all such modifications and variations except as do not come within the scope of the appended claims.

We claim:

1. A process of making photographic vesicular print material which comprises forming a dispersed mixture of 1 to 7 parts of a thermoplastic, hydrophobic resin and a water solution of 3 to 1 parts of a water soluble gas impermeable organic colloid containing a stabilized photosensitive diazonium compound, coating the mixture on a support and drying to a clear, continuous, hydrophobic resin layer which is thermoplastic at temperatures on the order of from 140° F. to about 200 F. and has finely dispersed therein water soluble colloid and photosensitive diazonium compound.

2. The process of claim 1 wherein the dispersed mixture contains a solvent solution of the hydrophobic resin in the continuous phase.

3. The process of claim 2 wherein the diazonium compound is 4-diethylaminobenzene diazonium chloride zinc chloride complex.

4. The process of claim 3 wherein the resin is polystyrene and the organic colloid is a water soluble melamine-formaldehyde condensation product.

5. The process of claim 3 wherein the resin is polystyrene and the organic colloid is gelatin.

6. The process of claim 1 wherein the dispersed mixture contains the water soluble organic colloid in the continuous phase, and during the drying step this inverts so that the hydrophobic resin is in the continuous phase.

7. The process of claim 6 wherein the diazonium compound is derived from 2-amino-1-naphthol-5-sulfonic acid.

8. The process of claim 7 wherein the resin is polyvinylidene chloride and the organic colloid is water soluble polyvinyl alcohol.

9. The process of claim 7 wherein the resin is polyvinylidene chloride and the inorganic colloid is gelatin.

10. A vesicular print material having a support carrying a substantially clear hydrophobic layer which is thermoplastic at temperatures ranging from about 140° F. to about 200° F., said layer comprising a continuous body of 1 to 7 parts of a thermoplastic, hydrophobic resin having finely dispersed therein 3 to 1 parts of a water soluble, gas impermeable organic colloid and a stabilized photosensitive diazonium compound.

11. The vesicular print material of claim 10 wherein the diazonium compound is 4-diethylaminobenzene diazonium chloride zinc chloride complex.

12. The vesicular print material of claim 11 wherein the resin is polystyrene and the organic colloid is a water soluble melamine-formaldehyde.

13. The vesicular print material of claim 11 wherein the resin is polystyrene and the organic colloid is gelatin.

14. The vesicular print material of claim 10 wherein the diazonium compound is derived from 2-amino-1-naphthol-5-sulfonic acid.

15. The vesicular print material of claim 14 wherein the resin is polyvinylidene chloride and the organic colloid is a water soluble polyvinyl alcohol.

16. The vesicular print material of claim 14 wherein the resin is polyvinylidene chloride and the organic colloid is gelatin.

17. The process of preparing a vesicular print which comprises exposing through a transparency with actinic light, a vesicular print material carrying on a support a substantially clear hydrophobic layer which is thermoplastic at temperatures ranging from about 140° F. to about 200° F., said layer comprising a continuous body of 1 to 7 parts of a thermoplastic, hydrophobic resin having finely dispersed therein, 3 to 1 parts of a water soluble, gas impermeable organic colloid and a stabilized photosensitive diazonium compound, to form a latent image in said layer and then heating the exposed material to develop the vesicular image.

18. The process of preparing a vesicular print which comprises irradiating through a design with ultraviolet light, a vesicular print material carrying on an opaque support a substantially water insoluble clear hydrophobic layer which is thermoplastic at temperatures ranging from about 140° F. to about 200° F., said layer comprising a continuous body of 1 to 7 parts of a thermoplastic, hydrophobic resin having finely dispersed therein, 3 to 1 parts of a water soluble, gas impermeable organic colloid and a stabilized photosensitive diazonium compound, to form a latent image in said layer and then heating the exposed material to develop the vesicular image, and then re-exposing the resulting print to actinic light to destroy the remaining diazonium compound.

19. The process of preparing a direct duplicate vesicular print which comprises heating the material of claim 10 briefly to a temperature at which it becomes thermoplastic, flashing it with actinic light, exposing the layer through a pattern with actinic light to form a latent image therein and then developing the exposed material by heating it to the thermoplastic temperature level.

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