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VESICULAR PRINTS AND PROCESS OF MAKING SAME

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This invention relates to a method of preparing a photosensitive vesicular print material having high printing speed, by forming a spreadable aqueous solution of a hydrophilic colloid having thoroughly dispersed therein, a finely divided solid having an index of refraction substantially similar to that of the colloid together with a stabilized photosensitive diazonium compound, coating it on a support, and drying. The invention also relates to the resulting, substantially clear photosensitive high speed vesicular print material, to the method of preparing stable vesicular prints therefrom by irradiating with actinic light through a design and then subjecting to moisture or elevated temperatures for short times to develop and stabilize the images, as well as to the resulting vesicular prints.

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 photo decomposition. 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 when viewed by reflected light, and of opacity when viewed by transmitted light.

A disadvantage of these materials is their relatively slow printing speed which requires long exposures with a concurrent loss in the output of finished prints.

It is, accordingly, an object of this invention to provide vesicular print materials having a high printing speed.

Other objects will be apparent from the following description.

It has been found in accordance with the invention, that the above described drawbacks may be overcome, and superior vesicular print materials having high printing speed may be prepared by coating a support with an aqueous solution of a hydrophilic colloid having uniformly dispersed therein, a small proportion of a finely divided solid together with a stabilized photosensitive diazonium compound, and drying. The finely divided solid is one having an index of refraction substantially the same as that of the colloid. The resulting layer has high printing speed when exposed to actinic light through a design. The resulting printed layer contains a latent image, and this may be developed by short exposure to steam or heating to elevated temperatures. The image is fixed by drying or cooling so that the layer becomes hardened.

The objects achieved in accordance with the invention as described herein include the provision of methods for preparing high printing speed vesicular print materials by coating a support with an aqueous solution of a hydrophilic colloid having thoroughly and uniformly dispersed therein, a small proportion of a finely divided solid having an index of refraction substantially the same as that of the colloid together with a stabilized photosensitive diazonium compound; the provision of methods for making either positive or negative prints from the above type materials by irradiating with actinic light through a design and then developing by exposure to moisture or elevated temperatures for short periods followed by hardening the layer; 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 specific embodiment is described in detail:

Example 1

To 100 parts by weight of an aqueous solution containing 33% photographic gelatin, there is added about 15 parts of the following diazo solution:

	Parts
Water	100
Zinc chloride double salt of p-diethylamino benzene diazonium chloride	4
Thiourea	5
Citric acid	4

Then 5 parts of finely divided barium sulfate is thoroughly and uniformly dispersed therein. It is necessary to use freshly precipitated barium sulfate prepared by reacting barium chloride with sodium sulfate, and recovering the resulting finely divided barium sulfate. Commercially available barium sulfate cannot be used because it has a larger particle size and causes an overall white stain or haze. The colloidal solution is coated on black paper and dried. Then it is exposed to ultraviolet rays through a suitable positive transparency. Following this, it is developed by direct exposure to steam for 2 seconds, and allowed to cool to room temperature.

Using a GE–H5 lamp, 6 inches from the transparency, a print is obtained in an exposure of 30 seconds, followed by the above described development. In a similar exposure, using a comparative coated paper without any barium sulfate in the coating, an exposure of 70 seconds is necessary to produce prints of equal density.

Following an analogous procedure, except using a transparent support such as glass instead of the black paper, a negative print is obtained.

Comparable results to the foregoing are achieved by using the following variations.

The substantially clear hydrophilic colloid may be glue, gelatin, casein, fish glue, gum tragacanth, starch, dextrin, urea-formaldehyde resin or condensate, melamine-formaldehyde resin or condensate, albumin, polyvinyl alcohol, or mixtures thereof, and the like. The colloid is sufficiently impervious to gas to permit the formation of the fine vesicles; however, after formation of the image and hardening of the colloid, slow diffusion of gas therein is not objectionable. If desired, a plasticizer such as glycerol or the like may be included. A water binding material which releases water upon heating may be included; e.g., boric acid. This water may soften the colloid sufficiently to permit formation of the image. The colloidal material should be solid or semi-solid at ambient temperatures, but softened sufficiently to permit development of the image at elevated temperatures of the order of about 140 to about 250° F., or by exposure to a solvent, moisture or steam. The vesicular print materials do not contain couplers and do not require development with ammonia.

The support may be glass, cellophane, cellulose acetate, or other suitable transparent material, to give a negative

print; or alternatively, black paper, metal, or opaque material of any desired color, to give a positive print.

Desirable light sensitive diazonium compounds are stabilized as diazo oxide, or as a metallic double salt such as the zinc chloride double salt, cadmium chloride double salt, or the like, and they may be derived from aromatic paradiamines, particularly N-mono or di-substituted benzene paradiamines, or from para-amino diphenyl amine, and 4-diethylamino diazonium chloride is preferred. Other suitable material are the zinc chloride double salt of 4-benzamido-2,5-diethoxybenzene diazonium sulfate, the zinc chloride double salt of diazotized 3-amino-carbazole, the cadmium chloride double salt of p-dimethylamino-benzene diazonium chloride, 2-hydroxy 4-sulfonaphthalene-1-diazo anhydride or the zinc chloride double salt of p-diethylamino-o-ethoxybenzene diazonium chloride. Other acidic stabilizers may be used, such as lower carboxylic acids, especially hydroxy carboxylic acids. If desired, other stabilizers of the thiourea type may be used.

Instead of the freshly precipitated barium sulfate, there may be used other finely divided inorganic solids such as bentonite, colloidal silica, calcium sulfate, calcium silicate, or mixtures thereof, or the like. The refractive index of the solid must be substantially similar to that of the colloid in order to provide substantially clear layers. In addition, only a small proportion of the solid is used, such as in the range of 3–10 parts of the finely divided solid to 30–40 parts of the hydrophilic colloid.

The particle size of these inorganic solids must be of the same order as that of freshly precipitated barium sulfate to give the desired speed increase without the formation of haze or stain. In general, the particle size of these finely divided solids should not exceed half of the wavelength of the viewing light and be below 0.4 micron.

It is extremely important that a very fine and uniform dispersion of the solid and of the light sensitive diazo in the hydrophilic colloid be obtained in order to assure that the vesicles take part in the formation of the image, and the gas formed in the decomposition of the exposed diazo does not escape unused from the colloid.

The heating or development step may be carried out by direct exposure to steam or a softening agent, exposure to radiant heat, or by contact with a heated surface for about 5–6 seconds at a temperature of about 140–250° F. The layer is hardened by cooling to ambient temperatures or by removal of softening agent. Colloids which are intermediate resin condensates may harden by further condensation.

The final prints may be coated with a hydrophobic wax or the like material to render them resistant to moisture under ambient conditions.

Instead of coating the final print with a hydrophobic wax, the unexposed and undeveloped material can be overcoated with a thin resin layer, for instance, an ethyl cellulose, vinyl chloride-vinyl acetate, or methyl methacrylate layer applied from a non-aqueous solvent mixture to give the vesicular print material added resistance to moisture.

This application is a continuation-in-part of the pending application Serial No. 261,754, filed December 14, 1951, now abandoned, which is a continuation-in-part of the application Serial No. 618,787, filed September 26, 1945, now abandoned.

Variations and modifications of the invention will be apparent to one skilled in the art in view of the foregoing disclosure. For instance, in place of the simple colloids disclosed, there may be used a mixture of zein and soluble polyamides, derived from a diamine and a dicarboxylic acid, which permits coating from organic solvent solutions. Accordingly, 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.

What is claimed is:

1. A process of making photographic vesicular print material having high printing speed which comprises forming a spreadable aqueous dispersion of 33 parts of gelatine, impervious to gas, 5 parts of finely divided barium sulfate having an index of refraction substantially the same as that of the gelatin and 4 parts of the zinc chloride double salt of p-diethylamino benzene diazonium chloride, coating it on a support and drying to a photo-sensitive, substantially clear, continuous layer having finely divided barium sulfate dispersed therein.

2. A vesicular print material having high printing speed consisting of a support carrying a substantially clear layer comprising a continuous body of 33 parts of gelatine, impervious to gas, and having uniformly dispersed therein, 4 parts of the zinc chloride double of p-diethylamine diazonium chloride and 5 parts of finely divided barium sulfate having an index of refraction substantially similar to the gelatin.

3. A vesicular print material of claim 2 wherein the support is black paper.

4. A process of preparing a vesicular print which comprises irradiating through a design with actinic light, the material of claim 2 to make a latent image thereon and then subjecting it to an elevated temperature to develop the image.

5. A process of making photographic vesicular print material having high printing speed which comprises forming a spreadable aqueous uniform dispersion of (1) from 30 to 40 parts of a hydrophilic organic colloid impervious to nitrogen gas and selected from the group consisting of gelatin, fish glue, dextrin, polyvinyl alcohol, urea-formaldehyde condensate, and melamine-formaldehyde condensate; (2) from 3 to 10 parts of a finely divided solid selected from the group consisting of bentonite, barium sulfate, calcium sulfate and calcium silicate, said solid having an index of refraction substantially the same as that of the colloid; and (3) a stabilized photo-sensitive diazonium compound, coating said dispersion on a support and drying it to a photo-sensitive, substantially clear, continuous layer having finely divided solid dispersed therein.

6. A vesicular print material having high printing speed consisting of a support carrying a substantially clear layer comprising a continuous body of from 30 to 40 parts of a hydrophilic organic colloid impervious to nitrogen gas and selected from the group consisting of gelatin, fish glue, polyvinyl alcohol, dextrin, urea-formaldehyde resin and melamine-formaldehyde resin and having uniformly dispersed therein a stabilized photo-sensitive diazonium compound and from 3 to 10 parts of a finely divided solid selected from the group consisting of bentonite, barium sulfate, calcium sulfate and calcium silicate, said solid having an index of refraction substantially the same as the colloid.

7. A process of making photographic vesicular print material having high printing speed which comprises forming a spreadable aqueous uniform dispersion of from 30 to 40 parts of gelatin, from 3 to 10 parts of finely divided barium sulfate having an index of refraction substantially the same as that of the gelatin, and of a stabilized photo-sensitive diazonium compound, coating it on a support and drying to a photo-sensitive, substantially clear, continuous layer having finely divided barium sulfate dispersed therein.

8. A vesicular print material having high printing speed consisting of a support carrying a substantially clear layer comprising a continuous body of from 30 to 40 parts of gelatin, impervious to nitrogen gas, and having uniformly dispersed therein, in addition to a stabilized photo-sensitive diazonium compound, from 3 to 10 parts of finely divided barium sulfate, having an index of refraction substantially similar to the gelatin.

9. A vesicular print material of claim 6 wherein the support is black paper.

10. A vesicular print material of claim 8 wherein the support is black paper.

11. A vesicular print material of claim 2 wherein the support is a transparent cellulose material.

12. A vesicular print material of claim 6 wherein the support is a transparent cellulose material.

13. A vesicular print material of claim 8 wherein the support is a transparent cellulose material.

14. A vesicular print material as defined by claim 6 wherein said finely divided solid has a particle size below 0.4 micron.

15. A vesicular print material as defined by claim 8 wherein said finely divided barium sulfate has a particle size below 0.4 micron.

16. A process of preparing a vesicular print which comprises irradiating through a design with actinic light, the material of claim 6 to make a latent image thereon and then subjecting it to an elevated temperature to develop the image.

17. A process of preparing a vesicular print which comprises irradiating through a design with actinic light,

the material of claim 8 to make a latent image thereon and then subjecting it to an elevated temperature to develop the image.

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