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AZIDO PHOTOHARDENABLE COLLOID CONTAINING AN IMMOBILE DYE AND PROCESS OF USING

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ABSTRACT OF THE DISCLOSURE

A light sensitive material containing a hardenable hydrophilic colloid, e.g., a gelatin, layer which contains a light sensitive aromatic azide and a coloring substance in the form of an immobile coloring matter or dye, or precursor capable of being transformed into an immobile coloring matter or dye by suitable treatment, such coloring substance being in homogeneous molecularly dispersed form in the colloid, said light sensitive material being substantially transparent and substantially free of opacity and light scattering characteristics and procedure for utilizing such material, which includes the steps of exposing said colloid layer to light under a pattern or negative, causing said azide to harden the colloid in proportion to the degree of exposure, and removing the unhardened colloid by dissolution with water, producing a dyed relief image which can be either a half-tone or a continuous-tone image.

The present invention relates to a material and process for the production of colored relief images.

It is general practice for the production of colored relief images to produce a relief image by differential tanning of a colloid such as gum, gelatin, glue or a synthetic colloid such as polyvinyl alcohol or the co-polymer of polyvinyl alcohol with acrylamide, acrylic acid and the like. Such colloid layers are sensitized with dichromate, or a diazonium compound. These sensitizers produce a differential hardening of the colloid upon light exposure, and after washing out the unhardened colloid the resulting colloid relief is subsequently dyed with a water-soluble dye or a dye solution in an appropriate solvent which penetrates into the colloid relief and results in a colored image.

This method which is capable of producing dye images has several serious disadvantages. It is time-consuming, difficult to control, and the dye images are not resistant to water or solvents. For the purpose of good color reproduction, especially for making color transparencies or for the making of graphic arts color proofing material, it is necessary that relief images are made which are in good color balance and in which the coloring matter or mixture of coloring matters are contained in a predetermined color density, in order to permit the uniform production of multicolor images by combination of the individual separation images.

It is also known to produce individual color separation images by incorporating insoluble pigments into the colloids. Such pigments are produced by comminuting pigment particles in a ball mill or the like. While such colloid layers containing a suspension of pigments are suitable for the production of half-tone images, they are unsuitable for the production of continuous-tone images where a gradation is produced ranging from full color density throughout a density scale down to pure white. Thus, such layers containing pigment particles produce a grainy and granular mottled image unsuitable for continuous-tone images in an image quality required for the production of continuous-tone graphic arts color proofing material, or for monochrome or multicolor composite color transparencies.

Monochrome prints containing pigmented relief images which represent the various aspects of the color separations for the purpose of making multicolor printing plates, are used in overlays and are viewed by reflected light. These overlays, however, show a varying degree of falsification of color values, and the color of their combined densities differ, depending on the order in which the layers are superposed. The distortion of tonal and color values is caused by the various degrees of opacity and light scattering, originating in the inhomogeneous distribution of particle sizes of the pigments.

Other drawbacks of the available commercial materials and processes are the cumbersome processing, which frequently requires flammable chemicals having obnoxious odors, or other chemicals which are often not readily available.

In the present invention I incorporate coloring matter or dyes which may or may not be water soluble, in a hardenable hydrophilic colloid containing an aromatic azide sensitizer compatible both which such coloring matters or dyes and with the hardenable colloid, such system being stable on storage. The coloring matters or dyes are of such nature that they are immobile and do not dissolve during processing, e.g., when the unhardened colloid is removed, as by washing. The combination of water-soluble or water-insoluble coloring matters or dyes which are immobile with respect to the processing liquid which dissolves the unhardened colloid, and which are homogeneously dispersed in the colloid, and an aromatic azide sensitizer which is capable of hardening the colloid upon exposure but which is non-reactive towards such coloring matters, constitutes an important feature of the invention. The use of bichromates or diazo compounds as sensitizers are not suitable to meet the necessary requirements for stability or inertness towards the colloids or dyes of the invention system. The colloid layer containing the light sensitive aromatic azide and the immobile coloring matter or dye in uniform homogeneous molecularly dispersed form in the colloid, is substantially transparent and substantially free of light reflecting or light scattering characteristics.

Thus, according to the invention there is provided a light sensitive material comprising a support having a hardenable hydrophilic colloid coating containing coloring matter, e.g., a dye, in substantially homogeneous molecular dispersion in said colloid, and a light sensitive aromatic azide which is compatible and non-reactive with said coloring matter or dye, said coloring matter or dye being immobile or non-transferable, and incapable of removal from the hardened colloid during processing of said material for production of a colored relief image, said azide being capable of hardening said colloid on exposure to light.

The term "immobile" or "non-transferable" coloring matter or dye as employed herein is intended to denote coloring matters or dyes, and excluding pigments, which will remain essentially fixed and will not migrate from or dissolve out of the hardened colloid by treatment of the colloid layer with water or other suitable solvents to remove unhardened colloid, following exposure to light.

The colored printing material of the invention containing coloring matters or dyes in molecular dispersion in a predetermined dye density in the hardenable colloid, has the advantage over prior art materials containing dispersed pigments, of being essentially transparent and having a negligible degree of opacity, thus permitting use of the individual color prints as overlays in any order without undue opacity or reflection, and permitting production of continuous-tone color images, heretofore not possible with present commercial materials.

The processing of the colored light sensitive material of the invention is simple, and comprises exposing to light

predetermined portions of such colored light sensitive material, as through a negative or pattern, to cause the aromatic azide so exposed to light to harden the hydrophilic colloid selectively or differentially in such predetermined exposed portion in proportion to the degree of light exposure, and removing the unhardened colloid after such exposure without removing the exposed hardened colloid, by treatment with an aqueous solution which can be either cold or warm water, and if desired, solvents such as methanol, or salts such as alkali carbonate can be incorporated in the aqueous solution to regulate the dissolution of the unhardened colloid, leaving a colored relief image in proportion to the degree of light exposure.

By employing the light sensitive material and process of the present invention, color transparencies can be produced which are equally suited for use as high quality continuous-tone, or non-continuous half-tone, e.g., dot-like, color transparencies, and thus filling an important requirement of the graphic arts industry to obtain high quality results by a simple procedure. It is noted in this respect that Graphic Arts Monthly, March 1967, page 74, states: "At the present time there is no satisfactory means of proofing continuous-tone separations. Presently available color films have too high a contrast for this use and the colors available do not match graphic arts colors." Thus, employing the colored light sensitive printing material of the invention, incorporating the immobile or non-transferable coloring matters or dyes in homogeneous molecular dispersion together with the light sensitive aromatic azide sensitizer, in effect permits the production of colored colloid relief images by simple treatment in cold or warm water after printing.

The use of immobile coloring matters or dyes in a state of molecular homogeneous dispersion in a hardenable hydrophilic colloid according to the invention, in contrast to the use of pigments, results in a negligible degree of opacity or reflection. Such coloring matters or dyes are highly transparent, are capable of coloring a hydrophilic colloid homogeneously, permitting the production of continuous-tone relief images in excellent straight-line uniform gradation, including the region of low color densities, and such relief images are substantially free from graininess, granularity or mottle. A further important feature of the invention is that the immobile coloring matters or dyes employed are capable of forming colloidal solutions which do not stain the fingers, fabric, paper, and the like, when such dyes are contained in the processing solution used for dissolving the unhardened colloid during processing.

No printing material and process to my knowledge hitherto have been known which permit the production of colored relief images from pre-dyed and pre-sensitized materials which contain coloring matters in a transparent homogeneous molecularly dispersed immobile form, substantially free from light-scattering opaque matter, containing a combination of molecularly dispersed immobile coloring matter with light-sensitive, aromatic azide sensitizers which are inert toward such coloring substances and the colloid.

The coloring matters or dyes utilized in the colored light sensitive material of the invention and which may be water soluble or water insoluble, can be introduced into the colloid at any stage before coating the colloid solution, in contrast to the cumbersome and uneconomical manner of mechanical dispersion associated with the incorporation of pigments. Thus, for example, there can be employed in the light sensitive material of the invention soluble coloring matters or dyes in the form of monomers of a structure which makes them immobile or non-transferable so that they cannot be washed out from the colloid during processing, for example, monomeric dyes containing a high molecular weight substituent preventing diffusion thereof. Also, water soluble polymeric dyes which are non-diffusing due to their polymeric structure can be employed. Also, soluble dyes can be employed which are reactive with respect to the colloid but unreactive with respect to the aromatic azide sensitizer. The latter dyes have a reactive group capable of forming covalent bonds with the colloid. Further, dyes can be employed which can be made insoluble at any point of incorporation into the colloid by double decomposition or formation of an insoluble dye salt of an anionic or a cationic dye, such as by reaction of a soluble dye containing an anion with a quaternary nitrogeneous base.

Further, the immobile or non-transferable molecular dispersion can be formed employing dyes formed by chemical transformation of a dye precursor (dye forming substance) by coupling, hydrolysis, oxidation, reduction and the like, to form homogeneous molecularly dispersed coloration in the colloid. Such coloration of the colloid can be effected at any stage of the preparation of the material, either before or after the addition of a sensitizing aromatic azide compound, permitting a wide selection of suitable dyes and dyeing methods, by combination of one or more dyes or dye-formers.

Thus, the dye precursors can be present in the light sensitive material containing the azides in a hardenable colloid, and the final coloration can be developed subsequently at any stage compatible with the processing of the material. The dye precursors can be added to the solution of the hardenable colloid in admixture with the azide sensitizer, and have the advantage of simplicity and economy of procedure, because the precursors can be added in a predetermined concentration to form a stable mixture with the azide and such mixture is ready for coating without first developing the dye from the precursor. Such coating generally is practically colorless or weakly colored, making shorter exposures and higher speed possible. The permanent coloration can be effected after exposure at any point compatible with the processing of the exposed layer to a relief image, as will be apparent from the examples below. For example, for the production of insoluble azo dyes, this can be accomplished by incorporating into the hardenable colloid an azo coupling compound separately or together with the light sensitive azide, and reacting such azo coupler with a solution of diazo compound prior or subsequent to the coating of the colloid composition on a support, by procedures well known in the art.

Thus, coloring matters or dyes which can be employed according to the invention and which are of the types having the above characteristics generally comprise immobile azo dyes including azoic colors or dyes, vat, phthalocyanine, anthraquinone, oxazine, dioxazine, xanthene, triphenyl methane and premetallized dyes, examples of the latter being premetallized azo and anthraquinone dyes, and the like, which are stable metal complexes of such dyes. The precursors and the temporarily solubilized forms of these dyes can also be employed, and which are immobilized in the colloid by suitable treatment.

Specific examples of the various types of coloring matters or dyes noted above which can be employed in the colored light sensitive material of the invention are given in the working examples below.

The aromatic light sensitive azides employed in producing the light sensitive material of the invention can be water soluble, such as mono-, bis- and polyazides. Specific examples are the alkali metal, e.g., sodium or potassium salts of:

4-azido-benzal-pyruvic acid
4,4'-diazido stilbene-alpha-mono-carboxylic acid
4,4'-diazido stilbene-2,2-disulfonic acid
4,4'-diazido diphenyl-2,2-disulfonic acid
4,3'-diazido benzalacetone-2-sulfonic acid

Alternatively, such azides can be water insoluble and incorporated in colloidal dispersion. Specific examples of such azides are the following:

azido-5-naphthol
4-azido phenol
4,4'-diazido-benzophenone
4,4',4''-trisazido-triphenylmethane

Various hydrophilic hardenable colloids can be employed in producing a light sensitive colored material containing immobile or non-transferable coloring matters or dyes in molecular dispersion, and a light sensitive aromatic azide, according to the invention. Examples of such hydrophilic colloids are gelatin, polyvinyl alcohol of various degrees of polymerization and viscosity, which can be partially esterified with acetyl groups or residues of any di- or poly-basic acid, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, cellulose glycolic acid, cellulose hydroxytheyl derivative of methyl, ethyl, benzyl cellulose, polymeric hydrophilic acrylates such as polyacrylic acid, and copolymers of hydrophilic acrylic compounds. If desired, mixtures of such colloids can also be employed, such as a mixture of gelatin and polyvinyl alcohol.

There is usually added to the hardenable colloid between about 0.1 and 1.0 gram of immobile coloring matter or dye, or its precursor, per 100 grams of colloid. The quantity of the coloring matter depends on the desired end use; for reflection images a maximum dye density of 1.0 to 1.5 is preferred, and for transparency images, a dye density of 2.0 to 3.0 is desirable. The quantity of the coloring matter or dye, or dye former for a certain dye density is determined in any manner well known in the art, and varies widely with the tinctorial power of the various dyes or dye precursors employed. The aromatic azide sensitizer generally is employed in amounts ranging from about 0.20 to about 10 grams per 100 grams of colloid.

The support or substrate to which the hardenable hydrophilic coating containing the immobile coloring matter or dye and light sensitive aromatic azide can be applied, can be opaque but is preferably transparent and can be, for example, paper, a plate, or plastic, e.g., transparent film, such as cellulose acetate, polyester or polystyrene film and the like. A coating composition which is applied to the support can contain, for example, from about 0.2 to about 20 mg. or more of the immobile coloring matter or dye per 100 square centimeters of coating.

The immobile or non-transferable coloring matters or dyes suitable for use in the present invention can be incorporated from solution into the liquid coating colloid solution, or they can be added in admixture with the aromatic azide sensitizer in a single solution to the colloid immediately preceding coating on the support. The solution of immobile coloring matter or dye is stable for an extended period of time, and the mixture of azide sensitizer and dye is stable and compatible. The process of manufacture of light sensitive material is thus simplified and the stock solution of sensitizer and coloring matter or dye can be added in any desired predetermined quantity and ratio to the coating colloid. Thus, homogeneously predyed and presensitized materials of reproducible quality can be produced according to the invention.

The following are examples of practice of the invention: In the examples below, the dyes are in large part identified by specifying the general type or dye class and including their Color Index number. The dyes are generally identified in the conventional way, as used in the Color Index, e.g., Color Index, Second Edition, 1956, vol. 3, p. 3009, or alternatively by the scheme of the dye formation. As an illustration, the dye obtained by coupling o-anisidine with p-tolylsulfonyl H acid, is identified as o-anisidine→p-tolylsulfonyl H acid.

EXAMPLE 1

A magenta azo dye is obtained by diazotization of one equivalent of 3-amino-4-methoxy benzene sulfonic acid in known manner and coupling the diazo solution with 1 equivalent of 8-stearoylamino-1-naphthol-3,6-disulfonic acid in sodium carbonate solution in known manner. The dye is isolated, and about 0.5 gram of the dye is dissolved and added to a 10 cc. 5% gelatin solution containing 0.1 gram 4,4'-diazido stilbene-2,2'-disulfonate disodium salt. Such gelatin solution is coated on one square meter of transparent subbed polyester film.

The dried coating is exposed through the base under a negative to light at a distance of one foot, for 5 to 10 minutes. The exposed material is immersed in warm water of a temperature between 32–40° C. In a few minutes (between 1–6 minutes) depending on the temperature of the water and nature of the gelatin, a continuous-tone magenta positive image is produced. The finished image is dried in a short time.

If a half-tone image is required instead of a continuous-tone image, the finished image can be produced in 15 seconds by washing out the unhardened gelatin in warm water of 45–50° C.

EXAMPLE 2

A yellow dye prepared by coupling thhe same diazo compound as in Example 1, with 1-phenyl 4'-palmitoylamino-3-carboxymethyl-5-pyrazolone, and isolated in the usual way, is incorporated in about the same quantity as the magenta dye above in a gelatin solution, as described in Example 1, sensitized with 0.2 gram of the disodium salt of 4,4'-diazido stilbene-2,2'-dicarboxylic acid. The resulting gelatin is coated on a polyester film and is exposed and processed as in Example 1. A yellow dye image is obtained.

EXAMPLE 3

The magenta polymeric dye prepared by coupling diazotized anhydro-para-(m-amino-benzene sulphamino-) benzylalcohol, which is a polymeric compound, with 2-hydroxy-naphthalene-3,6-disulphonic acid, or the yellow polymeric dye produced by coupling the same polymeric diazo compound with 1-(p-sulphophenyl)-3-methyl pyrazolone-(5), prepared according to my U.S. Pat. 2,356,759, are utilized in the same combination of gelatin solution and azide sensitizer as in Example 1 or 2 above, in a concentration of 0.25 to 0.5 gram per square meter of applied coating. Magenta or yellow colored relief images are produced by the procedure as described in Examples 1 and 2.

Other polymeric dyes, e.g., prepared by tetrazotizing 34.4 grams benzidine-2,2'-disulphonic acid and coupling with 35.3 grams of 1,1'-[2,2'-disulpho-diphenylene-4,4'-bi-(5-pyrazolone-3-carboxylic acid], as described in my U.S. Pat. 2,470,769, Example 6 or 7, alternatively can be employed in combination with the azide sensitizer of Example 1 or 2 above.

Other examples of polymeric dyes which alternatively can be employed are described in my U.S. Pats. 2,470,769, 2,612,496, 2,644,753, 2,677,612 and 2,844,574.

EXAMPLE 4

The following dyes are incorporated separately into 100 cc. of 5% gelatin solution in a quantity of 0.2 to 0.5 gram per 100 cc. of solution:

Magenta dye

C.I. 18133: C.I. Acid Red 264—Monoazo dye. o-Anisidine→N-p-tolyl-sulfonyl H-acid

Yellow dye

C.I. 18890: Acid Yellow 34—Monoazo dye. Aniline→1-(2-chloro-5-sulfo-phenyl)-3-methyl-5-pyrazolone

Cyan dye

C.I. 74180: C.I. Direct Blue 86—Phthalocyanine dye. Copper phthalocyanine disodium sulfonate.

To each of these three solutions is added, dropwise, with stirring, 20 cc. of a 5% solution of the quaternary heterocyclic ammonium salt, 1-naphthoquinoline N-ethyl ethosulfate or 2-methyl naphthothiazole methyl methosulfate. A transparent insoluble dye salt in uniform molecular dispersion in each case is formed, which is completely insoluble in water.

To each of the resulting three solutions, 0.1 to 0.2 gram of the sodium salt of the azide compound of Example 1 is added, and the respective solutions are coated in the usual way on a transparent support and the coatings exposed and processed as in Example 1.

A magenta, yellow, and cyan relief image is formed in the respective materials. The coated colored materials containing the above specified combinations of immobile molecular dispersion of dye salt and azide are stable on extended storage.

Reactive dyes which are rendered immobile or non-transferable by reaction with the colloid are highly compatible in admixture with the light sensitive azides, so that stable solutions containing the azides and the reactive dyes can be formed, which can be added to the hardenable colloid solution at any stage of the dye fixation, that is, reaction of the dye with the colloid, without mutual interference.

It is therefore unnecessary to add the sensitizer only after completion of the dye fixation; the dye fixation can be effected at any point in the process. It is accordingly also possible to effect the dye fixation step in the presence of the azide sensitizer.

Suitable reactive dyes of this type are listed in the Color Index, pages 483–522, Supplement 1963.

The following is an example of the use of a reactive dye rendered immobile by reaction with the colloid.

EXAMPLE 5

0.25 to 0.5 gram of the yellow dye C.I. Reactive Yellow, described as a monoazo pyrazolone dichlorotriazinyl derivative, is dissolved in water and added to 100 cc. of a 5% gelatin solution which is made slightly alkaline at a pH above 7.5. The solution is digested at 50–60° C. for 20–30 minutes. 0.1 to 0.2 gram of sodium 4,4'-diazido stilbene-2,2'-disulfonate is added, either mixed with the solution of the reactive dye or at any point before or after the digestion. The dye, following digestion, becomes fixed to the gelatin and the solution is coated. After exposure and removal of the unhardened gelatin by treatment with warm water, a colored relief image is formed, permanently dyed in uniform molecular dispersion, with the maximum dye density unimpaired by dissolution of the non-hardenable colloid.

Alternatively, the dye solution and the sensitizing solution can be added to the gelatin solution directly without heating, and the fixing of the dyes is effected by heating the coated dry material for a few minutes to 90–100° C.

EXAMPLE 6

The yellow reactive dye of Example 5 can be replaced by other dichloro triazinyl dyes such as:

(A)

C.I. Reactive Red 1—Monoazo dye
C.I. Reactive Red 2—Monoazo dye
C.I. Reactive Blue 1—Anthraquinone dye

Similarly, reactive dyes with lower reaction rates, monochloro triazinyl derivatives such as those noted below, can be used in place of the yellow dye of Example 5. Examples of these are as follows:

(B)

C.I. Reactive Yellow 2—Monoazo dye
C.I. Reactive Yellow 3—Monoazo dye
C.I. Reactive Red 3 and 4—Monoazo dye
C.I. Reactive Blue 5—Monoazo dye
C.I. Reactive Blue 7—Anthraquinone dye

Furthermore, reactive dyes containing other reactive groups such as trichloro pyrimidyl groups of the types noted below, can be employed in place of the yellow dye of Example 5, such as:

(C)

C.I. Reactive Yellow 8—Azo dye
C.I. Reactive Yellow 11—Monoazo pyrazolone dye
C.I. Reactive Red 17—Monoazo dye
C.I. Reactive Blue 18—Monoazo copper complex
C.I. Reactive Black 6—Azo dye

Also, reactive dyes with vinyl sulfonyl groups as noted below can be employed in the procedure of Example 5.

(D)

C.I. Reactive Yellow 13—Monoazo dye
C.I. Reactive Red 21 and 22—Monoazo dye
C.I. Reactive Blue 19—Anthraquinone dye
C.I. Reactive Blue 21—Phthalocyanine dye
C.I. Reactive Black 5—Disazo dye

Finally, reactive dyes containing reactive dichloro quinoxaline groups as follows, can be employed in the procedure of Example 5:

(E)

C.I. Reactive Yellow 10—Monoazo dye
C.I. Reactive Blue 11—Phthalocyanine dye
C.I. Reactive Green 1—Anthraquinone dye
C.I. Reactive Black 2—Violanthrone dye

Reactive dyes of the B and D types above require somewhat longer reaction time and somewhat higher pH, but they are all equally well suited for the manufacture of stable pre-dyed material of uniform coloration, dyed fastly in molecular dispersion according to the invention.

The following examples illustrate production of light sensitive materials of uniform coloration by generating the dyes, which are immobile and preferably insoluble, in molecular dispersion at any stage of the production of the light sensitive materials or the making of the relief image. These examples particularly illustrate the utilization of dye precursors for the preparation of a permanently dyed sensitized printing material for the production of dyed relief images.

EXAMPLE 7

About 0.6 gram of the dye precursor or color former C.I. 67301 C.I. Solubilized Vat Yellow 2 is dissolved in 100 cc. water and the solution is added with stirring to 50 cc. of 10% gelatin solution. To the mixture is added sufficient dilute hydrochloric acid to adjust it to pH 3.8 (bromocresol green indicator turns yellow). To this solution is added, dropwise, with stirring, a sodium nitrile solution in small portions containing about 20–25% by weight of the dye precursor. The insoluble vat dye is formed by oxidation in the colloid and is distributed therein in molecular dispersion. The acid reaction is maintained and the soluton is tested with iodide starch paper for the small excess of nitrous acid. The gelatin solution is kept at 35–38° C. and after about 20 minutes stirring, a small quantity of urea solution is added to destroy the free nitrous acid. The excess acid is neutralized, if desired, and one of the sensitizers 0.1–0.2 gram disodium-4,4'-diazido-2,2'-disulfonate or 0.2–0.4 gram of disodium-4,4'-diazido-diphenyl-2,2'-disulfonate, is added. The solution is coated on a polyester base. The above quantity of coating composition is used for 1 square meter surface.

EXAMPLE 8

The above yellow color former of Example 7 is replaced by a corresponding quantity of each of the following respective color formers, using essentially the same procedure as noted in Example 7:

C.I. 73361: C.I. Solubilized Vat Red 1—Indigoid Vat Dye—Leuco sulfuric ester salt of 6,6'-dichloro-4,4'-dimethyl thio indigo

C.I. 67001: C.I. Solubilized Vat Red 10—Anthraquinone Vat Dye—Leuco sulfuric ester salt of indanthrene red FBB

C.I. 60011: C.I. Solubilized Vat Violet 1—Anthraquinone

Vat Dye—Leuco sulfuric ester salt of chlorinated iso violanthrone

C.I. 70306: C.I. Solubilized Vat Blue 7—Anthraquinone Vat Dye—Leuco sulfuric ester salt of indanthrene blue green FFD

C.I. 73076: C.I. Solubilized Vat Blue 48—Indigoid Vat Dye—Leuco sulfuric ester salt of hexabromo indigo

C.I. 73661: C.I. Solubilized Vat Black 6—Indigoid Vat Dye—Leuco sulfuric ester salt of indanthrene printing black BGL

The following examples describe the coloration of a hydrophilic colloid with an insoluble azoic color (azo dye) in homogeneous molecular dispersion.

EXAMPLE 9

25 cc. of a 0.1 normal solution (a) of diazotized C.I. 37125 C.I. Azoic diazo component 5-(4-nitro-2-methoxy-aminobenzene), or (b) of the isodiazotate of the latter compound, or (c) of the stabilized diazo salt thereof (which is a triazene), is added dropwise with rapid stirring, to 100 cc. of 5% gelatin to which 0.3 gram C.I. 37505 Azoic coupling component 3-hydroxy-1,2-naphthanilide was added, dissolved in 25 cc. 50% methanol made alkaline with .05–0.1 gram NaOH or 0.1–0.2 gram dimethylaminoethanol.

To the mixture to which the solution of diazo compound (b) or (c) was added, a small quantity of acetic acid was added to bring the pH to 3.5, and the solution stirred cold or may be heated.

In each case employing (a), (b), and (c) above, a magenta red color develops in homogeneous molecular dispersion.

After the development of the color, 0.1–0.2 gram of disodium-4,4'-diazido-stilbene, 2,2'-disulfonate is added to each of the colored colloid solutions, and the above quantity of colloid sufficient for a coating surface of 1 square meter, is coated on a polyester base or support.

After drying, the material is printed under a negative through the base with ultraviolet or arc light. The unexposed parts are washed out in 1–2 minutes in warm water of 38–45° C. temperature and a positive colored relief image results.

The development of the color in the coating mixture by addition of the acetic acid as noted above can be omitted, and the gelatin mixture containing the coupling compound, the diazo compound and sensitizer, can be coated immediately. After drying and exposure, the coated material formed using azoic components (b) and (c) can be treated with a cold 3% acetic acid solution for 5 minutes and the color develops in homogeneous molecular dispersion. Thereafter, by treatment in warm water as above, the colored relief image is produced. Thus, a simplification in the preparation of the coating liquid is achieved, representing economy in time and labor, and furthermore the so-prepared material is of higher speed and requires less exposure.

EXAMPLE 10

In a procedure similar to that of Example 9, other azoic diazo components, e.g.:

C.I. 37070: C.I. Azoic Diazo Component 26—5-chloro-2-phenoxyaniline hydrochloride

C.I. 37075: C.I. Azoic Diazo Component 33—5-chloro-2(p-chlorophenoxy)aniline hydrochloride

C.I. 37155: C.I. Azoic Diazo Component 24—4'-amino-2'5'-dimethoxybenzanilide

C.I. 37190: C.I. Azoic Diazo Component 38—p-nitro-benzene-azo-2'5'-dimethoxyaniline

can be combined with azoic coupling components, e.g.:

C.I. 37565: Azoic Coupling Component 7—3-hydroxy-N-2-naphthyl-2-naphthamide

C.I. 37610: Azoic Coupling Component 5—4,4'-bis-O-acetoacettoluidide

C.I. 37585: Azoic Coupling Component 36—3-hydroxy-2-O-anthratoluidide

and will result in dyes of various other colors.

The production of azoic coloration for the preparation of the materials of the present invention can be achieved by incorporating the finished azoic dyes into the hydrophilic colloid solution in a temporarily solubilized form by known methods which are described in the American Chemical Society Monograph #127, H. A. Lubbs (1955), pages 224–225 and also in U.S. Patents 2,095,600; 2,199,-048; 2,276,187. These dye compounds are highly compatible with the hydrophilic colloids and are stable in combination with the azide sensitizers employed according to the invention.

EXAMPLE 11

The azoic dye which is produced employing (a), (b) or (c) in Example 9 above, that is, the 4-nitro-2-methoxy-benzene-azo-1'-2'-hydroxy-3'-naphthanilide, is solubilized by converting it into the 2'-benzoic acid-3,5-disulfonic acid ester, as described in U.S. Patent 2,095,600. The water soluble sodium salt of this solubilized azoic dye is added to 5% gelatin solution in a quantity of about 0.2 gram per 100 cc. of gelatin solution.

The dye is developed by heating the solution to 50–60° C. with a small quantity of ammonia or with sodium hydroxide added, and subsequently neutralizing the solution before coating. The same dye formed utilizing (a) to (c) of Example 9 above is developed in the colloid in homogeneous molecular dispersion. The azide sensitizer noted in Example 9 is then added, the colored gelatin solution coated on a support, and the coated material is exposed and processed to form a colored relief image as in Example 9.

EXAMPLE 12

The material of Example 11 containing the solubilized dye component can be coated with the gelatin solution of the solubilized dye and azide sensitizer, and the coated material exposed before the dye is developed. Since such material is stable, it can be exposed and the dye developed subsequent to the exposure. This affords a simple, economical procedure, and also a higher light sensitivity of the material results in the same manner as described in Example 9 above.

Thus, the material, after exposure, is treated with a 3% acetic acid solution for 5 minutes. The relief image is developed in warm water and the final coloration is developed by immersion in a dilute solution of NaOH or ammonia.

Similar results can also be obtained with a variety of other solubilized azoic dyes.

The following example illustrates use in my invention of water soluble dyes which form stable metallic complexes, preferably chromium, copper and nickel complexes.

EXAMPLE 13

0.3 gram of each of the respective dyes listed below is added to 100 cc. of 5% gelatin solution to which the azide sensitizer of Example 9 is added and the gelatin solution is coated on a polyester base, the above quantity of solution being sufficient for 1 square meter area of base. Very stable light sensitive materials especially suitable for the production of black relief images are thus produced.

C.I. 15711: C.I. Acid Black 52—Monoazo Dye metallized. Metallized chromium complex of 6-nitro-2-naphthol-4-sulfonaphthalene-azo-1-2-naphthol

C.I. 15691: C.I. Acid Black 43—Monoazo Dye metallized. Chromium complex of 6-nitro-1-phenol-2-azo-1-2-naphthol

C.I. 14885: C.I. Acid Black 54—Monoazo Dye metallized. Chromium complex of 6-nitro-2-naphthol-4-sulfo 1-azo-2, -1 naphthol-8-sulfonic acid

C.I. 14006: C.I. Acid Yellow 98—Monoazo Dye metal-

lized. Chromium complex of 3-sulfo-benzene-azo-4'-salicylic acid

C.I. 18810: C.I. Acid Red 18—Monoazo Dye metallized. Chromium complex of 2-naphthol-4-sulfo-azo-4'-3'-methyl-1-(m-sulfophenyl)-5-pyrazolone

C.I. 13425: C.I. Acid Green 12—Monoazo Dye metallized. Chromium complex of 4-nitro-2-hydroxy-azo-1,2-amino-5-sulfo naphthalene

C.I. 15050: C.I. Acid Blue 158A—Monoazo Dye metallized. 4-Sulfo-2-naphthol-azo-2-1-hydroxy naphthalene-8-sulfonamide

The following example illustrates the preparation of light sensitive materials colored homogeneously in molecular dispersion with phthalocyanine dyes produced from phthalocyanine dye precursors according to the invention.

EXAMPLE 14

To 100 cc. of a 5% gelatin solution are added, respectively:

(a) 0.25–0.5 gram of the phthalocyanine precursor C.I. 74240 C.I. Ingrain Blue 1, a derivative of chloromethylated copper phthalocyanine, dissolved in a 50% methanol containing 5% acetic acid, added to 100 cc. of 5% gelatin solution and heated to 60° C. for 25 minutes and finally made alkaline with ammonia, heated further for 20 minutes and neutralized. To this solution 0.1–0.2 gram disodium salt of 4,4'-diazido stilbene-2,2'-dicarboxylic acid is added.

(b) 0.25–0.5 gram C.I. 74160 C.I. Ingrain Blue 2, phthalocyanine precursor, is dissolved in a solvent as in (a) above, added to 100 cc. of 5% gelatin solution, neutralized, and 10 cc. of a 3% sodium bisulfite solution is added, and the solution heated to 55° C. for 25 minutes. After neutralization, the azide sensitizer noted above is added.

(c) 0.25–0.5 gram of the phthalocyanine precursor C.I. Ingrain Blue (Phthalogen Blue 1B) is dissolved in 10 cc. dioxane to which is added 1 cc. water and 1 cc. of 0.1 normal HCl, and the resulting solution is added to 100 cc. of 5% gelatin, to which 2 cc. of 5% isoascorbic acid is added. The mixture is heated for 10 minutes at 65° C., neutralized, and the above azide sensitizer is added.

Each of the gelatin solutions (a), (b) and (c) above, containing the respective phthalocyanine dye precursors is coated on a surface, the amounts of sensitized gelatin solution noted above in each case being coated on 1 square meter of surface. The coatings in each case are exposed and treated with warm water to remove unhardened gelatin. The final coloration is developed after printing and completion of the relief image by immersing the materials in an acid solution of a reducing agent, e.g., hydroquinone, sodium bisulfite, sodium hydrosulfite, isoascorbic acid and the like.

The following examples describe the coloration of a hydrophilic colloid with salts of cationic (basic) dyes, forming immobile coloration in homogeneous molecular dispersion.

EXAMPLE 15

To 100 cc. of a 5% gelatin solution containing 0.4 gram sodium polystyrene sulfonate of a molecular weight of 10,000 to 50,000 is added with stirring, a 50% methanolic solution containing 0.3 gram of each of the respective following dyes:

(1) C.I. 49005: C.I. Basic Yellow #1 (Thiazole dye)
(2) C.I. 48055: C.I. Basic Yellow #11 (Methine dye)
(3) C.I. 48015: C.I. Basic Red #15 (Methine dye)
(4) C.I. 52015: C.I. Basic Blue #9 (Thiazine dye)

The solution of sodium polystyrene sulfonate can be added after the dye solution has been added to the gelatin solution.

To each of these respective solutions 5 cc. of a 3% aqueous solution of disodium 4,4'-diazido stilbene-2,2-disulfonate is added.

Dyes 1 and 2 produce a yellow colored colloid; 3 a magenta and 4 a cyan colored colloid.

Instead of the above polystyrene sulfonate salts, other immobile high molecular weight anionic salts of the above dyes can be provided, such as the dye salts of the interpolymer of ethylenesulfonic acid with methyl methacrylate, the sulfonate of anisolformaldehyde condensation product, and the like. If desired, dye salts of heteropoly inorganic acids such as phosphotungstic, phosphomolybdic, or silico tungstic acid, or other inorganic precipitating acids can be used.

The above respective gelatin solutions of the immobile dye salts can be coated on one square meter of any suitable support and exposed and processed as described in the previous examples.

The following example describe the coloration of a hydrophilic colloid with water insoluble dye dissolved in a water immiscible liquid or solvent. These dyes are thus homogeneously distributed in microscopic droplets in high molecular dispersion. The solvents may or may not contain, in addition to the dyes, plastics, resins, and the like. The solvents preferably should have the same refractive index as the gelatin. Such solvents are, e.g., methyl phthalate, n-butylphthalate veratrole, and tri-o-cresyl phosphate.

EXAMPLE 16

0.5 gram of each of the following dyes, respectively, are dissolved with heating in 3–10 times its quantity of one of the above listed solvents, e.g., methylphthalate:

For yellow:
C.I. 11855: Disperse Yellow—Monoazo dye
C.I. 11860: Solvent Yellow 12—Monoazo dye
For magneta:
C.I. 261251: Solvent Red 27—Disazo dye
C.I. 12715: Solvent Red 8—Monoazo dye
For cyan:
C.I. 74360: Solvent Blue 25—Phthalocyanine dye

To facilitate dispersion, a water miscible solvent e.g., a quantity of acetone equal to the above solvents, may be added. To the dye solution a small quantity of emulgant such as sodium dodecyl sulfate or sodium oleate is added and mixed in an emulsifying apparatus of any suitable type.

To the respective dye solutions, various quantities of any resin such as cellulose acetate butyrate, polyvinylacetate or methylstyrene can be added.

The above colored gelatin emulsions are sensitized with 0.2 gram disodium, 4,4'-diazido-stilbene, -2,2'disulfonated azide sensitizer.

For one square meter of surface, there is applied 100 cc. of a 5% gelatin emulsion containing 0.5 gram of the above dyes dissolved in the above solvents and emulsified as described above, and the coatings exposed and processed as described in the previous examples.

It is understood that the coloring matters or dyes described above can be used singly, or if desired employed in mixtuers in predetermined quantity, in order to match the shades of various printing inks if applied to provide color proofing materials for use in the graphic arts industries.

It is also understood that the printing of the above colored light sensitive materials if coated on a transparent support can be effected as described in the examples above by exposure to light either through the base, especially when a relief image is desired which adheres to the base, or it can be exposed from the coated side. If a half-tone image is desired, the exposure is adjusted to a degree such that the light penetrates through the entire thickness of the coated light sensitive layer. In the event that the relief image is to be subsequently transferred from the original support to a different support, the exposure is carried out only to a degree which permits the formation of an image in the outer surface, and the transfer of the image is effected by dissolving the unhardened deeper strata of the

layer. This can be further facilitated by utilizing an unsubbed base, that is, a base without an anchoring layer preparation.

Alternatively, the invention coatings can be applied to an opaque support provided with a plastic coating which facilitates the removal and transfer of the relief image at any stage of the processing. The support, e.g., transparent or opaque film or paper, can be provided with a stripping sublayer, either hydrophilic soluble or non-hydrophilic solvent soluble, or with a thermoplastic stripping layer.

The relief image formed on the surface can be transferred to any other temporary or permanent support. The unhardened portions of the colored colloid following exposure can be removed after or during image transfer, and permitting the production of composite color images on a transparent or reflecting base, affording simplification for the production of transfer images by methods heretofore difficult to control.

The surface of each coating can carry a hydrophilic or non-hydrophilic adhesive layer and the processing can be effected after contacting another support during or subsequent to the transfer. A preferred embodiment in this respect is the application of a pressure sensitive adhesive layer on top of the light sensitive coating and the addition of a thin transparent protective foil, so that the material can be printed. The protective foil is removed after printing and before the layer is brought in contact with the support to which it is to be transferred and subsequently processed. In this manner consecutive layers can be transferred to a common support and a composite image can be produced.

Although various modifications of my invention have been described for purposes of illustration, the invention is not to be taken as limited except by the scope of the appended claims.

I claim:

1. A method of producing a dyed relief image which comprises exposing predetermined portions of a light sensitive material comprising a support having a photohardenable hydrophilic colloid coating substantially free of light scattering opaque matter, said coating comprising:

(A) a photo-hardenable hydrophilic colloid;

(B) a light sensitive aromatic azide compound capable of hardening said colloid on exposure to light; and

(C) an immobile dye coloring material selected from the group consisting of azo, vat, phthalocyanine, anthraquinone, oxazine, dioxazine, xanthene, triphenyl methane, and premetallized dyes, said dye being in substantially homogeneous molecular dispersion in said colloid, and said dye characterized by being compatible and non-reactive with said aromatic azide and incapable of removal from the hardened colloid by aqueous solutions during processing of said material for production of a colored relief image, to cause said hydrophilic colloid to harden in said predetermined exposed portions, treating said hydrophilic colloid with an aqueous medium to remove unhardened colloid without removing hardened colloid, to form a colored relief image.

2. A process as defined in claim **1**, said coloring matter being a water soluble immobile dye.

3. A process as defined in claim **1**, said coloring matter being a water insoluble salt of a water soluble dye.

4. A process as defined in claim **1**, said coloring matter being an immobile azo dye.

5. A light sensitive material comprising a support having a photo-hardenable hydrophilic colloid coating substantially free of light scattering opaque matter, said coating comprising:

(A) a photo-hardenable hydrophilic colloid;

(B) a light sensitive aromatic azide compound capable of hardening said colloid on exposure to light; and

(C) an immobile dye coloring material selected from the group consisting of azo, vat, phthalocyanine, anthraquinone, oxazine, dioxazine, xanthene, triphenyl methane, and premetallized dyes, said dye being in substantially homogeneous molecular dispersion in said colloid, and said dye characterized by being compatible and non-reactive with said aromatic azide and incapable of removal from the hardened colloid by aqueous solutions during processing of said material for production of a colored relief image, and wherein said colloid and said azide compound are different compounds.

6. A light sensitive material as defined in claim **5**, said dye being a water soluble azo dye containing a substituent rendering said dye immobile in said colloid.

7. A light sensitive material as defined in claim **5**, said coloring matter being a water insoluble salt of a water soluble dye.

8. A light sensitive material as defined in claim **5**, said coloring matter being a water insoluble salt of a water soluble anionic or cationic dye.

9. A light sensitive material as defined in claim **5**, said coloring matter being a water soluble dye reactive with said colloid to form an immobile dye.

10. A light sensitive material as defined in claim **5**, said coloring matter being a non-diffusing polymeric dye.

11. A light sensitive material as defined in claim **5**, said light sensitive material being essentially transparent and having a negligible degree of opacity.

12. A light sensitive material as defined in claim **5**, said colloid being gelatin.

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