United States Patent Office 3,463,638
Patented Aug. 26, 1969

3,463,638

HEAT-FIXABLE LIGHT-SENSITIVE COMPOSITIONS AND ELEMENTS

Eugene P. Damm, Jr., Poughkeepsie, N.Y., assignor to International Business Machines Corporation, Armonk, N.Y., a corporation of New York

No Drawing. Filed Aug. 20, 1965, Ser. No. 481,388
Int. Cl. G03c 1/58
U.S. Cl. 96—49 7 Claims

ABSTRACT OF THE DISCLOSURE

A light sensitive, heat-fixable negative diazotype composition, element and method of using, the composition consisting of a Rapidogen dye and a hydrolizable alkaline metal salt as an image fixing agent. The dye forming under the exposure to ultraviolet light and upon subsequent application of heat light insensitive alkaline hydrolysis products forming between the hydrolyzed alkaline metal salt and diazonium decomposition products of the dye.

This invention is related to a heat-fixable negative diazotype composition and element. More particularly, this invention is directed to a heat-fixable negative diazotype composition having incorporated therein an alkalin-fixing agent, a heat-fixable light-sensitive element coated with said composition and to a method of fixing images obtained by a negative diazotype process.

BACKGROUND

The art is familiar with negative diazotype processes which produce colored images when a light-sensitive, dye-producing composition is exposed to light. The exposed areas result in a permanent final condition, while the unexposced areas remain in a latent condition (i.e., on subsequent exposure to light, these areas react to produce additional dyestuffs). Therefore, in order to obtain a permanent image, it is necessary that the images be fixed.

Fixation of the image has been effected in the prior art by washing a developed document, thereby eluting the unreacted dye-producing composition. This method has proven to be cumbersome and time consuming. Further, the handling of wet copies is undesirable from a purely esthetic point of view.

Other prior art methods of fixing an image includes the coating of a developed image-bearing substrate with a solution containing a reducing agent or exposing the developed image to volatile acids. A limitation of these methods is that the volatile acids and reducing agents used are deleterious both to humans and to process equipment. Thus, relatively expensive equipment for the removal of the acid vapors is required.

Summarizing, the prior art has provided fixing methods for negative diazotype images which include the washing of the developed document to elute the unreacted dye-producing composition, coating the developed document with a reducing agent and exposing the developed document to volatile acids. These methods had the shortcomings of being cumbersome, time consuming, esthetically undesirable, expensive and harmful to humans and equipment.

OBJECTS

It is, therefore, an object of this invention to overcome the shortcomings of the prior art.

Another object of this invention is to provide a light-sensitive diazoic composition that is fixable by heat.

Another object of this invention is to provide a heat-fixable diazoic composition which may be employed in relatively simple negative diazotype copying devices.

Another object of this invention is to provide heat-fixable diazoic compositions which may be employed as coatings on various substrates to produce highly useful photosensitive copying means.

And yet another object of this invention is to a method of heat-fixing an image obtained by a negative diazotype process.

THE PRESENT INVENTION

Considered from one aspect, the present invention relates to heat-fixable, light-sensitive diazoic compositions for preparing light-sensitive heat-fixable elements comprising light-sensitive diazonium-generating agents, diazo couplers, alkaline-stabilizing agents, and alkali metal salts, which when heated, furnish alkaline hydrolysis products. The alkaline hydrolysis products thus produced react with unreacted diazonium compounds to form light-sensitive diazotates which can no longer undergo a dye-forming reaction.

Considered from another aspect, this invention is directed to a method of fixing an image on a light-sensitive element formed by a negative diazotype process. The image after having been developed by exposure to light is heated whereby unreacted diazonium compounds react with alkaline hydrolysis products and are thereby inhibited from undergoing further dye-forming reactions.

In still another aspect, this invention is directed to an improved negative diazotype process. The process is characterized by:

Exposing a light-sensitive heat-fixable element, prepared by coating a support with one of the light-sensitive heat-fixable compositions of this invention, to actinic radiation to develop a dyed image; and

Fixing the image by heating, thereby producing alkaline hydrolysis products which react with unreacted diazonium compounds, whereby said diazonium compounds are inhibited from undergoing further dye-forming reactions.

The element may simultaneously be exposed to actinic radiation and heat to obtain the developing and fixing of an image in a single step.

In the present description and the following claims, the expression "diazoic composition" is intended to include a diazonium-generating agent, a diazo coupler, and an alkaline-stabilizing agent. The term "diazonium-generating agent" is meant to include compounds which, when made reactive, rearrange or decompose to yield diazonium compounds. For purposes of this invention, light-sensitive element is meant to include substrates, supports or carriers coated with the compositions of this invention.

The manner in which the foregoing objects and many other highly desirable objects have been achieved according to the present invention will be readily apparent in the light of the following description and claims, the description including certain detailed examples of preferred embodiments of the invention.

In the heat-developable diazotype systems of the prior art, a light-sensitive element coated with a diazoic composition, comprising a diazonium salt, a diazo coupler and a diazonium stabilizing acid, is exposed to light. The diazonium salt in the exposed areas are decomposed by light and are thus unable to further undergo dye-forming reactions. The unexposed area is then heated in the presence of an alkaline substance in order to develop a latent image. The alkaline substance neutralizes the acid so that the diazonium salt and diazo coupler may react to form a dye product.

In the present invention, a substrate is coated with a diazoic composition comprising a diazonium-generating agent, such as a diazoamino or triazene compound, a diazo coupler and an alkaline-stabilizing agent to prevent the preformation of the diazonium compound. Upon exposure to light, the diazoamino or triazene compound re-

arrange or decompose to form a diazonium compound. The diazonium already in an alkaline medium reacts with the diazo coupler to form a dye product. Thus, it can readily be seen that there is no necessity of heating a latent image in the presence of an alkaline substance to develop the image as in the prior art systems. After exposure to light, the image is fixed by heating to cause an alkali metal salt to form an alkaline hydrolysis product. The alkaline hydrolysis product reacts with unreacted diazonium to form diazotates which are passive.

Applicant does not wish to be limited by any theory as to the nature of the invention. However, it appears that the reaction mechanism for the fixation of the image may be illustrated by the following general equation:

$$(Ph{-}N{\equiv}N)^{+} + OH^{-} \xrightarrow{\text{heat}} Ph{-}N{=}NOH \overset{KOH}{\rightleftharpoons} Ph{=}NOK$$

where Ph is a phenyl ring; $(Ph—N\equiv N)^+$ representing a diazonium compound, and OH^- the alkaline hydrolysis product produced by heating of an alkali metal salt. The reaction products are passive and, therefore, unable to undergo dye-forming reactions with the diazo couplers that are present.

The diazoic compositions used to produce the dye-forming reaction in this invention are members of a class of materials listed in Table 5, p. 220 of "The Chemistry of Synthetic Dyes and Pigments" by H. A. Lubs, A.C.S. Monograph #127, Reinhold Publishing Corp., New York, 1955. These materials include both "Azoic Colors" (trade name of Charles Pfizer & Co., Inc. and "Rapidogen Colors" (trade name of General Aniline & Film Corp.)

These compositions are mixtures of a diazoamino or triazene compound having the general formula:

$$R{-}N{=}N{-}NH{-}R$$

where R is hydrogen and/or an aryl group; a "Napthol AS" coupling agent selected from the alkaline salts of 3 hydroxy 2-napthanilide derivatives, and stabilizing agents or buffer salts which serve to maintain the normally reactive diazoamino or triazene compound in a passive condition. These stabilizing agents are alkyl or aryl amine derivatives selected from the group consisting of sarcosine, N-methyltaurine, 2 amino-4-sulfobenzoic acid, N-ethyl-5-sulfoanthranilic acid and N-methyl-5-sulfoanthranilic acid. The proportion of diazoamino or triazene compounds, couplers and stabilizers in the diazoic compositions are fixed by the manufacturers.

In a preferred embodiment of this invention, a diazoic composition selected from a member of such compositions listed in Table 5, p. 220 of "The Chemistry of Synthetic Dyes and Pigments," hereinafter, the specific diazoic composition used in this invention will be referred to by the Color Index number of each composition, is admixed with an excess of an alkaline-fixing agent selected from the group of alkali metal salts consisting of sodium carbonate, sodium perborate, sodium hydroxide, lithium carbonate and potassium carbonate. The mixture is dissolved in a reagent grade solvent such as acetone or an acetone/water mixture or other suitable solvents.

The resulting solution may then be coated by any of the prior art techniques on a suitable support, substrate or carrier and dried. Suitable supports, substrates or carriers may include various types of paper, such as ordinary wood pulp paper, rag type paper or document paper, or various transparent films, such as cellulose acetate or "Mylar" (trade name of polyethylene terephthalate, E. I. du Pont Chemical Corp.). Alternately, the support may be coated by first applying a coating of a saturated aqueous solution of an alkali metal salt. The support is then dried. An acetone solution of the diazoic composition is then applied to the support and finally dried. When cellulose acetate films are used as the support, it is necessary to coat and dry the support rapidly since acetone is a solvent for the substrate material. Where it is desired that additional amounts of either the alkaline-fixing agent or the diazoic composition be applied to the support, the coatings can be layered in any combination; there may be applied one or more layers of either component or mixtures thereof in any combination.

The support now coated with the heat-fixable light-sensitive composition of this invention may be placed in an exposure apparatus which includes a vacuum frame printer and an actinic light source. The exposure apparatus may be a part of any of the various copying machines such as the Bruning, Ozalid diazo and the NuArc Printers. The light-sensitive support is exposed to light under a negative to develop a positive image. Subsequently, the developed image is heated by a hot air gun rated at about 300° F. The heating causes the image to be fixed, i.e., minimizes the dye-producing reaction of the unreacted diazonium compound and the coupler on subsequent exposure of the light-sensitive element to light. The developing and fixing processes may be carried out in a single step by simultaneously exposing and heating the light-sensitive element. It should be noted that when the element is placed in any of the above-mentioned printers, ammonia-developing stages are to be by-passed, since the image is formed when the light-sensitive element is exposed to actinic light and need not be further developed.

A number of variations of these basic techniques may be used and are suggested in the following examples. Other variations no doubt will occur to those skilled in the art.

In the following examples, the "Azoic" and "Rapidogen compositions referred to consist of prepared mixtures of a Napthol AS coupling agent and a diazotized and stabilized amine—i.e., diazoamino or triazene compound, the amine of which is indicated by its Color Index (C.I.) number. The generic composition of the mixtures has been indicated above.

EXAMPLES

Example I

A white base paper of weight 80 gm. is saturated with a saturated solution of sodium carbonate, dried and then coated by a solution containing 1.0 part by weight "Azoic Red NDS" Color Index #37150 in 100 parts of acetone. The coated paper is again dried and then exposed through a negative pattern to a light from an ultraviolet lamp, rated at about 80–100 watts, for about 1–2 seconds whereupon a stable red positive image is formed. The coated paper is then heated at a temperature of about 150° to 300° F. from about 30–60 seconds, whereupon a stable red image is fixed.

Example II

Example I was repeated except a saturated solution of sodium perborate was used in place of the sodium carbonate, there being substantially no change in the results obtained in Example I.

Example III

Example I was repeated except that a saturated solution of sodium hydroxide was used in place of the sodium carbonate, there being substantially no change in the results obtained in Example I.

Example IV

Example I was repeated except a saturated solution of lithium carbonate was used in the place of the sodium carbonate, there being substantially no change in the results obtained in Example I.

Example V

Example I was repeatd except a saturated solution of potassium carbonate was used in the place of the sodium carbonate, there being substantially no change in the results obtained in Example I.

Example VI

Example I was repeated except that "Azoic Scarlet NDR" Color Index #37090 was used in the place of

"Azoic Red NDS." The image was a deep scarlet of good visual density and light fastness on a light background.

Example VII

Example I was repeated except that "Azoic Red NDG" Color Index #37520 was used in place of "Azoic Red NDS." The image was a deep red of good visual density and light fastness on a light background.

Example VIII

Example I was repeated except that "Rapidogen Red R" Color Index #37120 was used in place of "Azoic Red NDS." The image was a deep red of good visual density and light fastness on a light background.

Example IX

Example I was repeated except that "Rapidogen Blue R" Color Index #37155 was used in place of "Azoic Red NDS." The image was a deep blue of good visual density and light fastness on a light background.

Example X

Example I was repeated except that "Rapidogen Green B" Color Index #37175 was used in place of "Azoic Red NDS." The image was a deep green of good visual density and light fastness on a light background.

Example XI

A white base paper is coated with a solution containing 1.5 parts of a saturated solution of sodium carbonate and 1.0 part "Azoic Red NDS" Color Index #37150 in 100 parts of an aqueous-acetone mixture. The coated paper is dried and then exposed through a negative pattern to a light from an 80 watt ultraviolet lamp for about 1 second whereupon a stable red positive image is formed. The developed image is then heated, at a temperature of from about 150° to 300° F. for 30 seconds, whereupon the stable red image is fixed.

Example XII

Example XI was repeated except that the heating and exposing steps were carried out simultaneously. The results being the same as though the light-sensitive element wsa exposed and heated in individual steps.

The diazoic compositions of this invention include not only those listed in the examples but may also include those Rapidogen and Azoic colors listed in "The Chemistry of Synthetic Dyes and Pigments" by H. A. Lubs, A.C.S. Monograph #127, Reinhold Publishing Corp., New York, 1955 and in the "Color Index," 2nd edition (1956) published jointly by The Society of Dyers and Colourists and the The American Association of Textile Chemists and Colourists, they being too numerous to list here.

While only a few alkali metal salts are herein listed, this is not to say that other alkali metal salts which form alkaline hydrolysis products upon heating are not encompassed by this invention.

In summary, a support is coated with a composition comprising a stabilized diazoic composition and an alkali metal salt. The coated sheet is dried and exposed through a negative pattern to actinic light whereupon a positive image is formed. The exposed document is then fixed by heating said document at a temperature sufficient to cause the alkali metal salt to form hydrolysis products which react with unreacted diazonium, thereby inhibitng further dye formation upon subsequent exposure of the image to light.

To increase printing speed, i.e., accelerate the dye-forming reaction a humectant such as glycerine may be added to the coating solution. Other additives of the prior art used to improve the overall quality and speed of copying may also be used in the compositions of this invention.

This invention has the advantage of resulting in a dry negative diazotype copying process, thus eliminating the need for handling corrosive liquids. The process produces documents having high contrast. Another feature of this invention has the added advantage that the need for ammonia, acids or other deleterious materials for developing or fixing an image is eliminated.

While this invention has been particularly described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of my invention.

What is claimed is:

1. A method of fixing a negative azo dye image of a diazotype material after imagewise exposure to actinic light, said diazotype material carries a layer comprising an azo-coupling component, an alkaline-fixing agent, and a light-sensitive component, said light-sensitive component selected from the diazo amino compounds having the formula

$$R—N=N—NH—R$$

where R is selected from the group consisting of hydrogen and aryl groups; the method which comprises heating the imaged diazotype material to cause the production of alkaline hydrolysis products from said alkaline-fixing agent, said alkaline hydrolysis products reacting with the diazonium compound formed by decomposition of the diazoamino compound and thereby inhibit the azo-dye components from undergoing a dye-forming reaction on subsequent exposure to light.

2. A method of fixing a negative azo dye image of a diazotype material after imagewise exposure to actinic light, said diazotype material carries a layer comprising an azo-coupling component, an alkaline-fixing agent, and a light-sensitive component, said light-sensitive component selected from the diazoamino compounds having the formula

$$R—N=N—NH—R$$

where R is selected from the group consisting of hydrogen and aryl groups, said alkaline-fixing agent selected from at least one member of group consisting of sodium carbonate, sodium perborate, sodium hydroxide, lithium carbonate and potassium carbonate; the method which comprises heating the imaged diazotype material to cause the production of alkaline hydrolysis products from said alkaline-fixing agent, said alkaline hydrolysis products reacting with the diazonium compound formed by decomposition of the diazoamino compound and thereby inhibit the azo-coupling components from undergoing a dye-forming reaction or subsequent exposure to light.

3. The method of claim 2 wherein the heating is continued from about 30–60 seconds at a temperature of from about 150° F. to 300° F.

4. A process for preparing negative diazotype reproduction comprising the steps of:

exposing a light-sensitive, heat-fixable element to actinic radiation imagewise to form an azo dye in the exposed areas of the element image, said element having a layer comprising a diazoamino compound selected from those compounds having the formula

$$R—N=N—NH—R$$

where R is selected from the group consisting of hydrogen and aryl groups; an azo coupling component and an alkaline fixing-agent capable of generating alkaline hydrolysis products; and

fixing the developed image by heating the unexposed areas of the element thereby causing the formation of alkaline hydrolysis products which inhibits further dye-forming reactions upon subsequent exposure to actinic radiation by reacting with the diazonium compound formed by the decomposition of the diazoamino compound.

5. The process of claim 4 wherein the light-sensitive, heat-fixable element is exposed to actinic radiation from

an ultraviolet lamp rated at from about 80–100 watts for about 1–2 seconds.

6. The process of claim **5** wherein heating is at a temperature of from about 150° F.–300° F. and is continued from about 30–60 seconds.

7. The process of claim **6** wherein the light-sensitive, heat-fixable element is simultaneously developed by exposing to actinic radiation and fixed by heating.

References Cited

UNITED STATES PATENTS

1,882,561	10/1932	Haller	8—45
1,926,322	9/1933	Von der Grinten et al.	96—91 XR
1,997,507	4/1935	Akintievsky	96—49
2,088,506	7/1937	Chambers	8—45
2,995,465	8/1961	Richey	117—36.8
2,995,466	8/1961	Sorensen	117—36.8
3,003,844	10/1961	Jelinek	8—45
3,322,541	5/1967	Reichel	96—33
2,290,130	7/1942	Parker et al.	8—45

OTHER REFERENCES

Landau et al.: "Diazo Compounds in the Photocopying Industry," The Journal of Photographic Science, vol. 13, May–June 1965, paper presented Oct. 31, 1964 (p. 150 relied on).

Saunders, K. H.: "The Aromatic Diazo-Compounds and Their Technical Application," Edward Arnold & Co., London, 2d ed., 1949 (pp. 170–175 relied on).

NORMAN G. TORCHIN, Primary Examiner

C. BOWERS, Assistant Examiner

U.S. Cl. X.R.

8—45; 96—91; 117—36.8; 250—65.1