

[54] **IMAGING METHOD UTILIZING
CHEMICAL REACTIVITIES OF
PHOTOEXCITED STATES OF AROMATIC
HYDROXY COMPOUNDS**

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Primary Examiner—Charles L. Bowers, Jr.

[52] **U.S. Cl.**..... **96/27 R, 96/48 R, 96/49,**
96/90 R

[51] **Int. Cl.**..... **G03c 5/04**

[58] **Field of Search**..... **96/48 R, 49, 90 R, 91 R,**
96/48 HD, 27 R; 117/36.8, 36.9; 25/65 T

[57] **ABSTRACT**

An imaging process employing the excited state reac-
tivities of aromatic hydroxy materials to produce a vis-
ible image.

[56] **References Cited**

UNITED STATES PATENTS

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17 Claims, No Drawings

IMAGING METHOD UTILIZING CHEMICAL REACTIVITIES OF PHOTOEXCITED STATES OF AROMATIC HYDROXY COMPOUNDS

BACKGROUND OF THE INVENTION

This invention relates, in general, to a novel imaging process which utilizes the increased chemical reactivity of hydroxy aromatic compounds when they are subjected to photoexcitation and, more specifically, this invention relates to a novel imaging process in which hydroxy aromatic compounds are photoexcited in the presence of an inorganic or organic nitrite.

In the conventional diazo system, a substrate is coated with a composition comprising two components, a diazonium compound which is sensitive to light, and the other component is an azo coupler. In making a print, the substrate is exposed to ultraviolet rays through the master. The rays destroy or otherwise inactivate the print forming components in all areas of coated material which are not protected by the lines of design of the original. However, the problem of diazo-type materials is that they are notoriously difficult to store for long periods prior to use. The phenomenon known as "pre-coupling" invariably occurs even in the absence of a "developing agent" such as ammonia, etc. Moreover, because the diazonium compound and the azo dye coupling component react slowly to form an azo dye, it is less useful for subsequent copying purposes. Furthermore, diazo-type materials have almost invariably given images of poor light fastness.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to overcome the above-noted deficiencies.

Another object of this invention is to provide a simple, convenient imaging system.

Still another object of this invention is to provide photoprinting materials which have good storage stability prior to use.

A still further object of this invention is to accomplish the above objects through the utilization of the enhanced chemical activity of photoexcited aromatic compounds in the presence of inorganic or organic nitrites.

Other objects will be apparent to those skilled in the photoprinting art from the following description of the invention.

In general, the present invention comprises the discovery that an hydroxy aromatic compound in the presence of inorganic or aliphatic nitrites and in the absence of acid can be made to undergo a photoinduced coupling reaction when light is absorbed to produce a colored reaction product in an imaging configuration. In effect, what is occurring is that nitrous acid ordinarily required in the conventional method of producing a coupling reaction is now being generated via the photoexcitation of a hydroxy aromatic compound. The photoexcited aromatic specie has an increased acidity causing the formation of nitrous acid from nitrites as required for the coupling reaction.

Photoprinting materials employing the process of this invention have several advantages over previously utilized materials. The materials utilizing the process of this invention are quite stable in dark storage prior to use. In diazo-type materials a chemically energetic specie, the diazonium compound, is always present in the copying material as made. In the materials utilizing the

process of this invention, no chemically energetic specie is present until the material is "exposed," i.e., until the components are subjected to photoexcitation. With the process of this invention, very light fastness images can be obtained. Still further, no obnoxious developing agents such as ammonia, is required in the processing of the materials of this invention.

The process of this invention may be utilized to prepare negative print-out materials. In this embodiment the process of this invention may be compared to the "blue printing" process. But, in contrast to blue printing materials, no cyanide-containing light sensitive materials need be employed. In addition, the process of this invention provides means of producing images of an almost unlimited range of colors. It shares with blue printing the possible incorporation of very simple "fixing" methods, such as washing the photoprinting material with water.

Photoprinting materials utilizing the process of this invention require no complex or expensive machines for their exposure, development or fixing. This is in marked contrast to certain currently used photoprinting and copying methods. No equipment employing high voltages, powdered toners, developing fluids, fusing stations, etc., is required.

The process of this invention yields well defined images. No thermal transfer steps are required. Thermal transfer almost invariably causes loss of definition and blurry images.

Finally, the process of this invention utilizes relatively low cost materials. No silver salts or other expensive components are required.

More specifically, the process according to this invention comprises forming a mixture of a hydroxy aromatic compound, e.g., 2-naphthol, inorganic or aliphatic nitrite, e.g., sodium nitrite, and optionally a polymeric matrix such as, polyvinyl pyrrolidone, dissolved in aqueous alcohol solvent to form a colorless solution. The polyvinyl pyrrolidone serves as a polymeric matrix for the hydroxy aromatic compound and nitrite when the solvent is evaporated producing a self-supporting colorless film or the mixture may be uniformly coated onto a suitable substrate. In the absence of light, proton transfer essentially does not take place between the hydroxy aromatic compound and the nitrite salt and no reaction occurs between the two components. However, when the hydroxy aromatic compound is photoexcited with light of a suitable wavelength corresponding to its ultraviolet absorption spectrum, proton transfer occurs rapidly and nitrous acid is generated. Reaction of nitrous acid with the ground state of 2-naphthol provides the highly colored 1-nitroso-2-naphthol.

The most probable mechanism of the reaction is that nitrous acid reacts with the ground state hydroxy aromatic compound as opposed to the excited species providing the colored nitroso derivative. This is based on the fact that the concentration of the excited state species is very much smaller than that of the ground state hydroxy aromatic material and that the probabilities of molecular collision are enhanced for the ground state material.

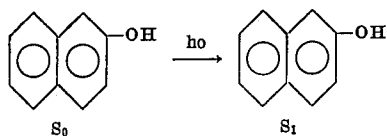
Additionally, if a metallic salt capable of reacting with the nitrosated naphthol, such as a ferrous salt, is also present, a darker colored image (e.g., blue-green) can be formed and this exhibits excellent light fastness.

Any suitable metallic salt may be used. Typical examples are the metal salts of copper, iron, cobalt and zirconium.

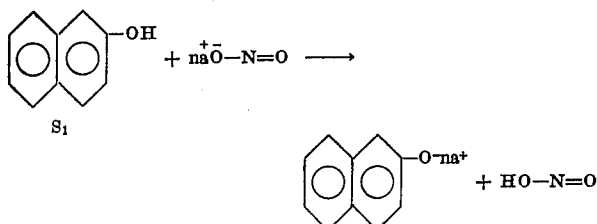
Any suitable hydroxy aromatic compound may be employed. Typical examples are hydroxy substituted: benzene, naphthalene, anthracene, phenanthracene, naphthacene, biphenyl, durene, acenaphthene, pyrene, chrysene, fluorene, fluoranthene and indene. Furthermore, the hydroxy aromatic compounds may carry other substituents such as, alkyl groups, halo, nitro, cyano, alkoxy, thio, carboxylic or sulfonic acids and salts thereof, esters and aldehydes.

Whereas coloration is produced by photoexcitation of a hydroxy aromatic compound in the presence of a nitrite, the physical consequences of the acidity enhancement are additionally utilized. If a primary aromatic amine is also present together with the combination of hydroxy aromatic compound and nitrite, then a highly colored azo compound can be formed upon photoexcitation. It may be assumed that the hydroxy aromatic compound, upon photoexcitation, liberates nitrous acid from the nitrite present, that the so-formed nitrous acid diazotizes the aromatic amine and that the resulting diazonium compound reacts with the hydroxy aromatic compound to yield an azo compound. But formally, it makes little difference if it is assumed that following the liberation of the nitrous acid it reacts with the hydroxy aromatic compound to produce a nitroso compound which, in turn, reacts with the aromatic amine to produce the azo compound. However, should the stoichiometry of the mixture be such that incomplete utilization of the nitroso derivative occurs, further color formation may be induced by addition of a metallic salt to the solution causing additional color changes. The following reaction sequence illustrates the transformation that takes place wherein S_0 represents the ground state and S_1 represents the excited state:

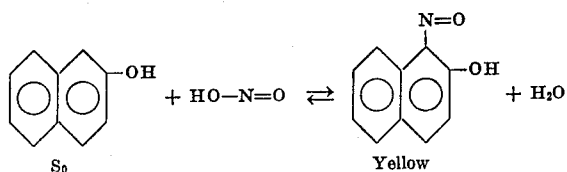
1. Photoexcitation



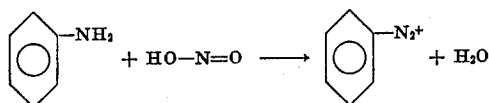
2. Proton Exchange



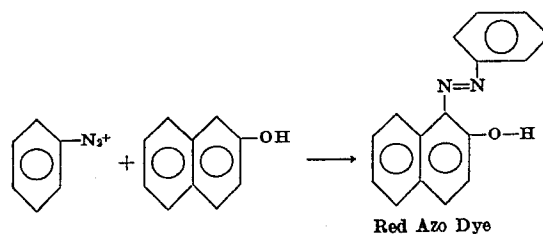
3.



4. Diazotization



5. Coupling



The above reaction sequence does efficiently utilize the photogenerated acid since one mole of product is formed per mole of acid consumed. A further increase in the overall efficiency of such systems could be realized by employing reaction sequences that respond in a catalytic fashion to the presence of acidic protons. Thus, many conversions could be effected following a single photo-chemical event.

Although the solutions which are used to coat substrates to prepare photoprint materials according to the process of this invention are prepared in the dark, care must be taken to avoid acidity. Any acidity introduced except that resulting from imagewise photoexcitation will obviously negate the principles upon which this invention is based. In maintaining the pH of the requisite coating solutions at approximately 7 or slightly above, buffers may be advantageously used.

In practicing another specific aspect of the present invention, an amino hydroxy aromatic compound has been found to undergo diazotization and self-coupling after being exposed imagewise to give a colored image. Accordingly, 8-amino-1-naphthol-3,6-disulfonic acid disodium salt is mixed in an aqueous solution of sodium nitrite which is coated onto paper, air dried and then exposed imagewise with a suitable light source; nitrous acid is again produced in the system causing a diazotization and self-coupling reaction which results in the formation of a colored image.

Any suitable hydroxy aromatic compound also containing a primary amino function may be employed. Typical examples of the amino substituted aromatic hydroxy compounds such as, benzene, naphthalene, anthracene, phenanthracene, naphthacene, biphenyl, durene, acenaphthene, pyrene, chrysene, fluorene, fluoranthene, and indene. Moreover, the amino aromatic hydroxy compound may be further substituted with derivatives such as, alkyl groups, halo, nitro, cyano, alkoxy, thio, acids, esters and aldehydes.

In preparing photoprinting materials utilizing the process of this invention certain coating aids may be added to the coating solutions. Thus, polymer thickening or sizing materials such as, polyvinyl pyrrolidone, polyvinyl alcohol, gelatin, crosslinking agents such as, starch anthranilate, modified starch, etc., or the like may be advantageously employed in order to obtain rapid print out, scuff resistant, optically attractive coatings. Likewise, colloidal materials such as, fillers or pigments, may be added. Among these are finely divided silica, titanium dioxide, clays and the like. Any suitable substrate may be used. Typical examples of substrates may consist of paper, either coated or uncoated; plastic sheeting, either transparent or opaque; metallic sheets, foils, laminates, etc.

The coating process employed may include roller coating, knife coating, nib coating, dip coating, spraying, brushing, etc.

Since the active materials are usually coated from solution or suspension in a liquid rather than from the dry powdered state, it is usually necessary to dry the photoprint material so prepared prior to cutting and packaging. It is possible, of course, to apply the requisite combination of materials as dry particulate materials to suitable substrates.

In practicing the process of this invention, in contradistinction to the conventional diazo system, the substrate is exposed to light in a negative working system and in the areas where light strikes coloration is effected. Light, as previously stated, causes the hydroxy aromatic compound in its excited state to produce nitrous acid from an inorganic or aliphatic nitrite which causes the coupling reaction to occur. The wavelength of light usable in this invention must be absorbed by the hydroxy aromatic compound.

In a "print-out" image forming procedure of this type, a means of stabilizing or "fixing" must be provided, otherwise the entire sheet of photoprint material slowly becomes colored upon exposure to room light. It has been found that simply washing the substrate with water, thereby dissolving away the nitrite, constitutes one effective fixing procedure. By suitable choice of hydroxy aromatic compound, the remaining unreacted aromatic compound may also be removed by water washing from those areas where it has not been utilized in image formation. The colored image, being much less water soluble, usually remains on the substrate. On the other hand, when hydroxy aromatic compound and nitrite esters are present, fixation may be accomplished by sublimation or heating the substrate to a temperature which causes the unreacted material to sublime therefrom. Other fixing procedures will be obvious to those skilled in the art.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following preferred examples further define, describe and compare preferred materials, methods and techniques of the present invention.

EXAMPLE I

Equal molar quantities of 2-naphthol, aniline and sodium nitrite (0.001 mole) are dissolved in 100 ml of water previously adjusted to pH=7.0 being careful not to expose the solution to ultraviolet irradiation. The mixture must be prepared and kept in the dark to avoid color formation prior to the exposure step. The water solution is then applied to a hydrophilic paper substrate, and the water is allowed to evaporate so that the substrate is dry to the touch. The coated substrate is then exposed in an imagewise fashion through a target for 30 seconds using a 100 watt UV source positioned 1 inch away from the substrate. After exposure the excess sodium nitrite is then removed in the fixing step by washing the substrate with water. The paper can then be dried in room light.

EXAMPLE II

Equal molar quantities of 2-naphthol, aniline and sodium nitrite (0.001 mole) and polyvinylpyrrolidone are dissolved in 100 ml of 50/50 water-ethanol mixture being careful not to expose the solution to ultraviolet irradiation. The mixture must be prepared and kept in the dark to avoid color formation prior to the exposure

step. The solution is then applied in an imagewise fashion through a target for 30 seconds using a 100 watt UV source positioned 1 inch away from the substrate. After exposure a mylar film is placed over the image to prevent further development of the background areas.

EXAMPLE III

8-amino-1-naphthol-3,6-disulfonic acid monosodium salt (1g) is dissolved in 50 cc of water and the solution adjusted to pH=7.0 with either dilute (10 percent) hydrochloric acid or sodium hydroxide solution (10 percent) as required. Sodium nitrite (1.0 gm) is then dissolved in 1.0 cc of water. The two solutions are then mixed in the dark and applied to a sheet of plain white paper with a brush. The water solvent is allowed to evaporate at room temperature by passing dry air over the coated sheets. The dried paper, positioned 1 inch from an ultraviolet (100 watt) light source is then exposed in an imagewise fashion for 30 seconds and the blue image fixed by washing away any unreacted sodium nitrite with water.

EXAMPLE IV

Equal molar quantities of 2-naphthol and isoamyl nitrite (0.001 mole) are dissolved in a 50/50 ethanol-water mixture (5 cc) along with 2.0 gm of polyvinylpyrrolidone being careful not to expose the solution to ultraviolet irradiation. The solution is applied to a sheet of aluminum, the solvent allowed to dry and the coating exposed to ultraviolet irradiation in an imagewise fashion for 30 seconds using a 100 watt (3,000A) light source. Fixing of the yellow image is accomplished by at least one of the reactants by sublimation.

EXAMPLE V

Starch anthranilate (I) is prepared by heating potato starch (6.0 gm), sodium carbonate (0.012 gm) and isatoic anhydride (0.012 gm) in 9 ml of water for 4 hours at 70°C. Plain white paper is then coated with the starch (I) and the water solvent allowed to evaporate. The coated paper is then treated with a water solution of 2-naphthol-6-sulfonic acid sodium salt and sodium nitrite (0.1 gm of each in 5 cc of water) under red light conditions. The water is allowed to dry before being contact exposed to ultraviolet light in an imagewise fashion (100 watt ultraviolet light source [3,000A]) for 60 seconds. The resulting orange image is fixed by washing away unreacted naphthol and nitrite salts.

While the invention has been described with reference to its preferred embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents substituted for elements thereof without departing from the true spirit and scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from its essential teachings.

What is claimed is:

1. An imaging process which comprises exposing in an imagewise manner a composition comprising an aromatic hydroxy compound and an inorganic or aliphatic nitrite salt in aqueous solution to light of a suitable wavelength corresponding to the ultraviolet absorption pattern of the hydroxy aromatic compound, said process being further described in that the composition is

supported by a suitable substrate and that said solution contains no ingredient which produces acid in the absence of light of the above-described wavelengths to thereby produce a colored image in exposed areas of said composition on a substrate.

2. The process of claim 1 wherein the solution contains an aromatic amine in addition to the aromatic hydroxy compound and the nitrite salt.

3. The process of claim 1 wherein the aromatic hydroxy compound is substituted with an amino radical.

4. The process of claim 1 wherein the solution contains a metallic salt in addition to the aromatic hydroxy compound and the nitrite salt.

5. The process of claim 1 wherein the solution has a pH within the range of from 6 to 8.

6. An imaging process employing the excited state reactivities of an aromatic hydroxy material comprising the following steps:

- a. providing an aromatic hydroxy compound;
- b. combining said hydroxy compound with an inorganic or aliphatic nitrite salt in aqueous solution, said solution being characterized in that it contains no ingredient which produces acid in the absence of light of a suitable wavelength corresponding to the ultraviolet absorption spectrum of the aromatic hydroxy compound;

c. coating a substrate with said solution, and

d. exposing said coated substrate to light of a suitable wavelength corresponding to the ultraviolet absorption pattern of the hydroxy aromatic compound in an imagewise fashion to produce a colored image in the exposed areas.

7. A process according to claim 6 wherein the image is fixed to said coated substrate.

8. A process according to claim 6 wherein an aromatic amine is included in said solution.

9. A process according to claim 6 wherein the hydroxy aromatic compound is substituted with an amino radical.

10. A process according to claim 6 wherein additionally a metallic salt is added to said solution.

11. A process according to claim 6 wherein said solution has a pH of about 6-8.

12. A process according to claim 6 wherein a cross-linking agent is included in said solution.

13. A process for producing a colored image comprising:

- a. forming a solution by dissolving a hydroxy aromatic compound, a material selected from the group consisting of an inorganic or aliphatic nitrite or mixtures thereof, and a resinous polymer in a solvent, said solution being characterized in that it contains no ingredient which produces acid in the absence of light of a suitable wavelength corresponding to the ultraviolet absorption spectrum of the aromatic hydroxy compound;

b. evaporating said solution to form a self-supporting colorless film, and

c. exposing said film in an imagewise fashion to light of a suitable wavelength corresponding to the ultraviolet absorption pattern of the hydroxy aromatic compound to thereby produce a colored image in the exposed areas.

14. A process according to claim 13 wherein said image is fixed in said film.

15. A process according to claim 13 wherein an aromatic amine is included in said solution.

16. A process according to claim 13 wherein the hydroxy aromatic compound is substituted with an amino radical.

17. A process according to claim 13 wherein a metallic salt is added to said solution.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,801,319 Dated April 2, 1974

Inventor(s) Franklin D. Saeva and Donald E. Sargent

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

1. Column 1, line 16, omit "the other component is".
2. Column 1, line 18, "the master" should be "a master".
3. Column 1, line 49, "an hydroxy aromatic" should be "a hydroxy aromatic".
4. Column 2, line 6, "agents" should be "agent".
5. Column 2, line 11, "process. But" should be "process, but".
6. Column 7, line 1, "solution" should be "composition".
7. Column 7, line 4, "in" should be "in the".
8. Column 7, line 5, "a substrate" should be "the substrate".

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents