United States Patent [19]

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[11] **3,772,017**

[45] **Nov. 13, 1973**

[54] **DIAZO-TYPE DEVELOPING PROCESS**

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[22] Filed: **Jan. 25, 1971**

[21] Appl. No.: **109,547**

[30] **Foreign Application Priority Data**

Jan. 27, 1970 Germany ..... P 20 03 542.1

[52] **U.S. Cl.** **96/49**

[51] **Int. Cl.** **G03c 5/18,** G03c 5/34

[58] **Field of Search** 96/49.75, 91; 250/65.1; 117/36.7, 36.8, 36.9

[56] **References Cited**

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[57] **ABSTRACT**

A diazo-type developing process, for light sensitive imaging material comprising a diazonium compound, employs a developer solution including an azo coupler compound and sodium sulfite. Contacting the exposed diazo-type material with the solution converts the image-wise disposed light-sensitive diagzonium compound to a diazo sulfonate, and subsequent heating effects development of an azo dye image while drying the sheet. The developer solution is resistant to oxidation and exhibits an extended useful life.

2 Claims, No Drawings

DIAZO-TYPE DEVELOPING PROCESS

BACKGROUND OF THE INVENTION

Diazo-type imaging processes have long been known and ordinarily employ diazonium compounds which are light-sensitive and readily decomposable by exposure to actinic radiation, generally ultraviolet light. Image-wise exposure of light-sensitive diazonium materials effects the formation of a diazonium compound image which may subsequently be coupled with azo components to form distinctly visible dye images.

Two diazo-type processes in common use include the "one-component" system which utilizes sheet material bearing only the light sensitive diazonium compound, the azo coupler component being applied subsequent to light exposure in a developing solution. A disadvantage inherent in the usual one-component system arises from the fact that the developing solution contains alkaline ingredients conductive to the coupling reaction. The inherent alkalinity, however, renders the developing solution particularly susceptible to aerial oxidation, thereby reducing its useful life.

The second process, a "two-component" diazo-type system, includes both the light-sensitive diazonium compound and the azo dye coupler together in the light-sensitive material along with acid stabilizers which prevent premature dye-forming coupling. Subsequent to light exposure the material is contacted with a developing medium of high alkalinity, usually moist ammonia gas, to effect the dye-forming coupling reaction. An obvious disadvantage of the two-component diazo-type system arises from the pungent and irritating nature of the gaseous ammonia developing agent.

Attempts have been made to supplant the disadvantageous gaseous and moist developing diazo-type systems with materials and processes which employ heat alone as a means of effecting azo dye image formation. Among such heat-developing materials are diazo-type compositions comprising diazo sulfonate compounds which, in general, are light-sensitive and possess the additional property of being capable of forming distinctive azo dyes when heated in the presence of azo dye coupler compounds. A system employing diazo sulfonate compositions is described in U.S. Pat. No. 2,217,189.

Although the disadvantages of the usual-one- or two-component diazo-type systems are avoided through the use of diazo sulfonate materials, additional disadvantages arise, particularly in the loss of light sensitivity as compared with materials employing diazonium compounds. The preparation of diazo sulfonate coating materials which possessed a practical degree of light sensitivity therefore was limited in the scope of useful light sensitive components and required close attention to the type of diazo compound employed in order to achieve acceptable results.

In addition to the inherent lower level of light sensitivity, the necessity of combining diazo sulfonate compounds with azo dye coupler components in a composition proved additionally disadvantageous due to the uncontrollable pre-coupling and instability of the composition. Attempts to improve the shelf life of these materials included the addition of various stabilizing materials such as described in U.S. Pat. No. 2,429,249 and U.S. Pat. No. 2,694,009. Incorporation of such stabilizers in the light-sensitive compositions represented, however, a further compromise to the light sensitivity of the material.

SUMMARY OF THE INVENTION

According to the present invention the various disadvantages encountered heretofore with diazo-type materials and processes are avoided by employing in a diazo-type process a light-sensitive material which utilizes the more highly light-sensitive diazonium compounds, and developing the characteristic azo dye image subsequent to light exposure by applying a developer solution which comprises an azo coupler component and sufficient amount of a sulfite compound to convert the image-wise disposed diazonium compound to the corresponding diazo sulfonate compound, and heating the resulting sheet to thereby effect dye-forming coupling of the diazo sulfonate with the azo coupler component. As a result of the present invention, advantage is taken of the high light sensitivity of diazonium compounds, the greater heat stability of diazo sulfonate compounds, and the resistance of the generally acidic developer solution to aerial oxidation.

The present invention additionally provides a greater choice in the available light-sensitive materials of practical imaging speed, a prolonged shelf life and stability of diazo-type materials which are devoid of the diazo/-coupler component combination, and a broad scope of color combinations available through the free selection of both the diazonium and azo coupler components; and further avoids the dangers and discomforts associated with the use of noxious, gaseous developers, such as ammonia.

DESCRIPTION OF THE INVENTION

The light-sensitive materials useful in the present invention include sheet-like supports such as paper, film or the like bearing a coating of a composition which comprises at least one light-sensitive diazonium compound. Such materials may be the commonly employed one-component or two-component diazo-type sheets, however, it is preferred to employ the one-component material to take advantage of the greater storage stability of compositions which are essentially devoid of the azo coupler component. In addition to the light-sensitive diazonium compound, the composition may include the usual diazo-type composition adjuncts such as buffers of aminoacetic acid; stabilizers such as 1, 3, 6-trisulfonic acid; napthalene-1,5-disulfonic acid; naphthalene-2,7-dissulfonic acid and their water soluble salts; antioxidants such as thiourea; metal salts such as aluminum sulfate; and binders such as gelatin, gum arabic, synthetic resins, silica dispersions and the like.

Diazonium compounds which are useful in the present invention are those commonly employed in one- or two-component diazo-type systems, in particular the benzene diazonium salts which are substituted in the benzene nucleus at a position para to the diazo group with any of a tertiary amino, acylamino, arylamino, alkoxy, alkylmercapto, arylmercapto groups, a halogen atom, or a heterocyclic substituent. The benezene nucleus of these diazonium compounds may additionally be substituted in the 2, 3, 2 and 3, or 2 and 5 positions with any of an alkyl, alkoxy, aryloxy, alkylmercapto, or arylmercapto group, or a halogen atom.

Some particularly useful diazonium compounds include 4-Ethoxy-benzene diazonium-; 3,4-Diethoxy-benzenediazonium-; 4-Chloro 2,5-dimethoxy-

benzenediazonium-; 4-Acetylamino-benzenediazonium-; 4-Benzoylamino-2,5-diethoxy-benzenediazonium-; 4-(Benzoyl-N-ethyl-amino)-benzenediazonium-; 4-Phenylamino-benzenediazonium-; 4-Ethylmercapto-benzenediazonium-; 4-Methylmercapto-2,5-diethoxy-benzenediazonium-; 2,4-Di-(ethylmercapto)-benzenediazonium-; 2,4-Di-(ethylmercapto)-5-methoxy-benzenediazonium-; 2-Phenylmercapto-4-ethylmercapto-5-ethoxy-benzenediazonium-; N-ethyl-carbazol-3-diazonium-; 4-Dipropylamino-benzenediazonium-; 2-Methyl-4-diethylamino-benzene-diazonium-; 4-Morpholino-2,5-dibutoxy-benzenediazonium-; and 3-Methoxy-4-dipropylamino-benzenediazonium salts.

The usual types of anions such as chlorides, sulfates and the like may be employed to form the useful salts of the various diazonium compounds.

The light-sensitive materials are prepared in the usual manner by combining the diazonium compound with the selected adjuncts in an appropriate solvent or dispersion and coating the mixture onto selected supports such as paper, cloth, metallic foils, transparent papers and films such as cellulose acetate, polyester or polycarbonate sheets, and drying the resulting coatings. Thus the preparation of the light-sensitive material does not differ significantly from that of one- or two-component diazo-type materials heretofore produced; in fact, commercial products of this type may be employed in the present process.

The developer solution employed in the process of the present invention includes any of the known rapid-coupling azo components found particularly useful in the common one-component moist developing diazo-type systems. Such azo coupler components include, for example, resorcinol; phloroglucinol; N-phenyl-pyrazolone-(5); acetoacetic acid amide; 2, 3 dihydroxy-naphthalene; and the like.

In addition to the azo coupler component, the developer solution includes a substantial amount of a sulfite salt, such as sodium sulfite. Application of a layer or thin film of the developer solution to a light-exposed sheet of the diazo-type material directly forms, by the action of the sulfite, a diazo-N-sulfonate disposed in image-wise fashion according to the diazonium compound remaining in the sheet material after exposure. While the sheet remains moistened at its surface with the developer solution, the sheet material is heated, such as by passing in contact with rollers maintained at a temperature of between about 130° and 150° C. The effect of heating the material is to convert the diazo-N-sulfonate compound into an active coupling form whereupon immediate dye-forming coupling with the azo coupler compound takes place with formation of the distinctive dye image. Concurrently the sheet is dried and the imaged material is ready for use without further fixing, or aeration which is often required, particularly with ammonia-developed two-component diazo-type systems.

PREFERRED EMBODIMENTS

Example 1

A paper sheet previously coated with a 10% solution of zinc acetate was coated in the usual manner with an aqueous solution containing, in one liter, the following compounds:

24.6 grams 4-phenylamino-benzene diazonium sulfate
20.0 grams aminoacetic acid
20.0 grams thiourea

Subsequent to drying, the resulting sheet was exposed under an original in an ordinary diazo-type copying device having a ultraviolet light source and the remaining diazo composition was lightly moistened with a developer solution containing, in one liter of water, the following compounds:

50.0 grams sodium sulfite
7.5 grams 2,3-dihydroxy-naphthalene
30.8 grams magnesium salicilate
20.0 grams sodium benzoate.

While the material remained moistened with the developer solution, it was heated by passing through rollers at a temperature of between about 130° and 150° C There was immediately developed a deep blue-violet image on a white background.

Substitution in the developing solution of 10 grams of resorcinol for the 2,3-dihydroxy-naphthalene yielded a deep brown-red image on a white background when the exposed sheet material was treated in the foregoing manner.

EXAMPLE 2

A common diazo-type paper base sheet was pre-coated with zinc acetate as in Example 1 and then coated with an aqueous solution containing, in one liter:

22.5 grams N-ethyl-carbazol-3-diazonium chloride-zinc chloride
20.0 grams aminoacetic acid
40.0 grams thiourea

The dried sheet was image-wise exposed under an original in the usual manner and was moistened with an aqueous solution containing, in one liter:

50.0 grams sodium sulfite
10.0 grams resorcinol
30.0 grams magnesium salicilate
20.0 grams sodium benzoate

The moistened sheet was developed by heating as in Example 1, yielding a deep red brown dye image.

EXAMPLE 3

The pre-coated paper of Example 2 was coated with an aqueous solution containing in one liter:

24.0 grams 4-dipropylamino-benzene diazonium chloride - zinc chloride
20.0 grams aminoacetic acid
40.0 grams thiourea

The dried sheet was exposed under an original, as previously described, and subsequently moistened with an aqueous solution containing, in one liter:

50.0 grams sodium sulfite
8.0 grams 1-phenyl-3-methyl-pyrazolone-(5)
30.0 grams magnesium salicilate
20.0 grams sodium benzoate.

The moistened sheet material was developed with heat as described in Example 1 to yield a deep red dye image. Substitution of 8.0 grams 2,3-di-hydroxy-naphthalene or 7.5 grams phloroglucinol for the pyrazolone compound of Example 3 yielded upon development respectively blue and deep blue-violet images on white backgrounds.

EXAMPLE 4

A cellulose acetate film, superficially hydrolysed to provide a more coatable hydrophillic surface, was coated with an aqueous solution containing, in one liter:

24.0 grams 2-methyl-4-diethylamino-benzene diazonium chloride - zinc chloride
20.0 grams aminoacetic acid
40.0 grams thiourea

The dried sheet was exposed under an original as in the previous examples, and then moistened at the coated surface with an aqueous solution containing, in one liter:

50.0 grams sodium sulfite
7.5 grams phloroglucinol
30.0 grams magnesium salicylate
20.0 grams sodium benzoate

The moistened sheet was heated, as in Example 1, and developed a deep blue-violet colored image on a transparent background.

I claim:

1. An imaging process comprising:
a. forming on a suitable support a coating of a composition comprising:
1. a light-sensitive benzene diazonium compound,
2. aminoacetic acid, and
3. thiourea;
b. exposing said coating imagewise to light thereby forming an image-wise disposition of said composition on said support;
c. moistening said image-wise disposed composition with an acidic solution comprising:
1. an azo coupler compound normally coupling with said diazonium compound under alkaline conditions to form an azo dye, and
2. an alkali sulfite salt, and
d. heating said moistened composition in excess of about 100° C, thereby effecting formation of an azo dye image.

2. An imaging process according to claim 1 wherein said sulfite salt is sodium sulfite.

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