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3,062,650

PHOTOGRAPHIC PRINTOUT SYSTEM COMPRISING AN ORGANIC AZIDE

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7 Claims. (Cl. 96-90)

This invention relates to novel photographic reproduction methods and materials and particularly to new photographic print-out materials comprising certain organic azides in conjunction with p-phenylenediamine color developing agents and certain color-forming coupler compounds.

Various organic azide compounds are known to be light sensitive and have been previously employed in photographic applications. For example, certain light sensitive azido compounds have been incorporated in layers of albumin, starch and the like in which they act to harden or tan the colloid under the influence of light. The untanned areas of the colloid layer are then dissolved away to produce an image useful in photomechanical reproduction methods. It is also known that when an exposed silver halide photographic emulsion is developed in the presence of p-phenylenediamine color developing agents and color-forming coupler compounds containing reactive methylene or methine groups that the couplers react with the oxidation products of the color developing agent to form indoaniline or azomethine dyes. It has now been discovered that the light sensitivity of the organic azides and the familiar photographic color development dye-forming reaction can be employed in a dry photographic print-out system. The need for a system capable of producing colored print-out images without the necessity for wet processing has long been recognized in the art.

It is therefore an important object of the present invention to provide a dry photographic system capable of producing colored print-out images.

It is another object of the invention to provide photographic print-out materials capable of forming indoaniline or azomethine dyes directly on exposure to light without further processing.

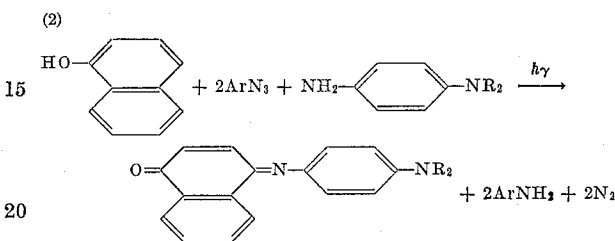
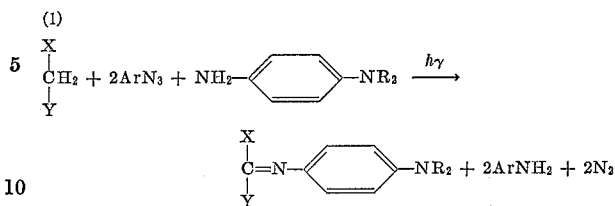
It is a further object of the invention to provide a novel means for initiating the reaction of p-phenylenediamine color developing agents with color-forming coupler compounds to form indoaniline and azomethine dyes.

These and other objects of the invention which will become apparent from the detailed description below are attained by providing a photographic element comprising either a conventional photographic support coated with a colloid layer in which certain light sensitive organic azido compounds, p-phenylenediamine color developing agents and certain color-forming coupler compounds are dissolved or dispersed or a similar photographic material in which the several named active components are incorporated in a self-supporting layer. Photographic elements of this type, including films, plates, photographic printing papers, copying papers and the like, when sensitized with the azide-developer-coupler compositions of the present invention and given an image-wise exposure to actinic light produce the desired print-out images.

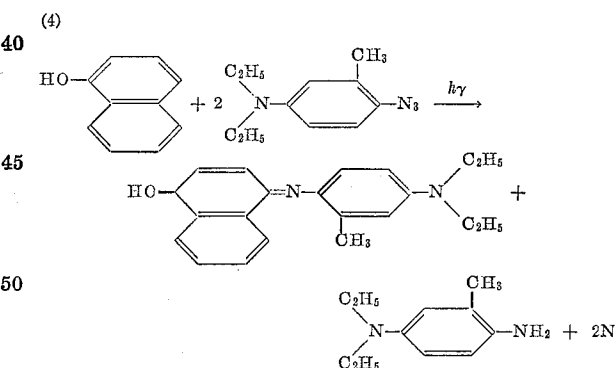
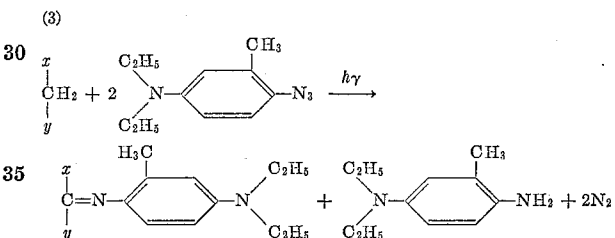
The present invention is based upon the discovery that certain organic azido compounds on exposure to light are capable of effecting oxidative condensation of p-phenylenediamine color developing agents with color-forming couplers containing reactive methylene or methine groups to form indoaniline or azomethine dyes. The dye forming reactions are illustrated by Equations 1 and 2 below where-

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in X and Y are groups which activate the methylene group and Ar represents an aryl group.

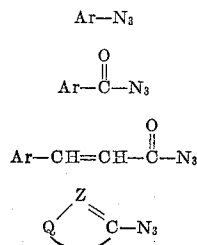


In a preferred embodiment of the invention the required azido group replaces the primary amino group of the p-phenylenediamine color developer. Equations 3 and 4 below illustrate dye forming reactions between compounds of this type and couplers having reactive methylene groups.



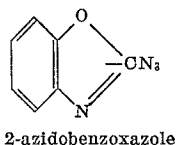
Reactions between azido compounds and p-phenylenediamine developing agents, or compounds combining the functions of these two, with couplers containing reactive methine groups proceed in the same manner as the reactions with couplers containing methylene groups which are illustrated above.

The organic azido compounds useful in the present invention have the general formula:

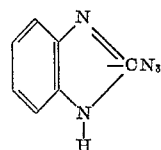


in which Ar— represents an aryl group, Z represents a hetero atom having an unbonded pair of electrons, examples of which are the nitrogen, oxygen or sulfur atoms, and Q stands for an organic residue which when taken together with the carbon atom and the atom represented by Z in the general formula, forms a five or six membered ring. The organic residue represented by Q may be either a hydrocarbon or a heterocyclic residue, either aromatic or non-aromatic, and may include one or more single or condensed ring systems. The aryl groups represented by Ar— and the organic groups represented by Q may be substituted or unsubstituted. Substituted azido compounds of the above general formulae containing alkyl (e.g., methyl, ethyl, propyl, butyl, etc.), alkoxy (e.g., methoxy, ethoxy, propoxy, butoxy, etc.), nitro and halo (e.g., chlorine, bromine, etc.), groups among others have been found useful. The lower alkyl and alkoxy groups, especially those having from one to about four carbon atoms are generally desirable substituents. For example, useful azido aniline compounds of the type shown in Equations 3 and 4 above include alkyl substituted azido anilines such as 2-methyl-4-diethylaminophenyl azide, 2-methyl-4-dipropylaminophenyl azides and 2-methyl-4-dibutylaminophenyl azides as well as the corresponding compounds in which one or more of the lower alkyl groups is replaced by an alkoxy group. The aryl nucleus represented by Ar— may also be substituted with one or more heterocyclic or carbocyclic rings; rings having not more than eight atoms and particularly rings containing six atoms usually being most desirable. In general, the heterocyclic azides are particularly useful, especially those in which the azido group is conjugated with a hetero atom having an unbonded pair of electrons. The azido compounds of the four general formulae may also have azide substituents on the rings represented by Ar— and Q although in general such polyazides are no more effective than monoazides.

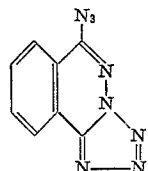
Specific heterocyclic azides useful in the invention include:



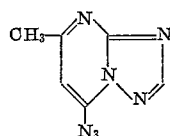
2-azidobenzoxazole



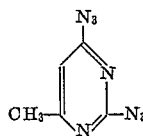
2-azidobenzimidazole



5-azidotetrazole[a]phthalazine



4-azido-6-methyl-1,3,3a,7-tetrazaindene



2,4-diazido-6-methylpyrimidine

Any of the well known phenylenediamine color developing agents may be employed in the present invention although the p-phenylenediamine agents are preferred. Suitable developing agents include the alkyl phenylenediamines, alkyl toluene diamines and the N-alkyl sulfonamido alkyl-p-phenylenediamines of Weissberger U.S. Patent No. 2,193,015, issued March 12, 1940.

The color-forming couplers useful in the present invention are also well known in the art of color development. Although many types of couplers are known in the art those useful in the present invention are those which contain a reactive methylene or methine group. Suitable couplers are disclosed in many U.S. patents including: Mannes and Godowsky 2,304,939 and 2,304,940, issued December 15, 1942; Jelley et al. 2,322,027, issued June 15, 1943; Fierke et al. 2,801,171, issued July 30, 1957; Porter et al. 2,369,489, issued February 13, 1945; Mannes and Godowsky 2,039,730, issued May 5, 1936; and Mannes and Godowsky 2,108,602, issued February 15, 1938, among many others. Suitable couplers are also disclosed in Tables I, II, and III of P. W. Vittum and A. Weissberger, J. Photo. Sci., 2, 81 (1954). The term, reactive methylene or methine group, encompasses coupler compounds in which the hydrogen or hydrogens of the methylene and methine groups can be replaced with certain other substituents such as halogen or azo substituents.

The light sensitive photographic elements of the present invention may be prepared by conventional coating procedures. In general, the azides, developing agents and couplers are dissolved or dispersed in a natural or synthetic polymer in a suitable solvent and coated on a suitable photographic support by means of a plate whirler or other device capable of producing a thin, uniform coating of the light sensitive composition. The vehicle in which the light sensitive composition is coated may be any of the natural or synthetic high polymers ordinarily used for photographic layers, such as gelatin, casein, polystyrene, vinyl resins including poly(vinyl alcohol), poly(vinyl butal), etc., cellulose derivatives, or mixtures of these polymers. The support for the light sensitive layer may be a plate, sheet or strip of any of the commonly used materials, such as paper, cellulose derivatives, glass, synthetic high polymers and the like. Any of the solvents commonly employed in the art for coating high polymer layers may be used with advantage, an excellent solvent for this purpose being 2-butanone.

In addition to the more conventional procedure of coating the described light sensitive compositions in a colloid layer on an inert photographic support, the invention also includes, in another embodiment, the provision of light sensitive elements in which the light sensitive composition is incorporated in the base layer, thus eliminating one of the two coating operations usually required. This may be accomplished by dissolving the azide, developing agent and coupler, and a high polymer such as cellulose triacetate in a suitable organic solvent such as a mixture of methylene chloride and methanol and coating the resulting composition on a glass plate or other suitable surface. When the coating has dried sufficiently it is stripped from the glass plate to produce a self-supporting film containing the light sensitive azide-developing agent-coupler composition.

The light sensitive elements of the invention, whether of the type in which the azide-developing agent-coupler composition is coated in a colloid layer on a separate support or of the type in which the base itself contains the light sensitive composition, produce a colored print-out image on an uncolored or contrasting background when exposed through a pattern to a suitable source of actinic light. The light sensitive layer becomes colored where it is exposed to light and thus a positive print-out image will be obtained when the exposure is made through a negative, or a negative image when the exposure is made through a positive. Any suitable source of actinic light

may be employed for the exposure including arc lamps, mercury lamps, photoflood lamps and sun lamps.

In general, in the practice of the present invention a coating solution is made up of a natural or synthetic high polymer dissolved in a suitable solvent containing the azido compound and the developing agent, or a compound combining these two functions, and a coupler. The solution is then coated on a suitable photographic base by means of a plate whirler and whirled until dry. The coated material is then exposed through a pattern, for example, under a sun lamp at a distance of ten inches for about 30 seconds to one minute to obtain a colored print-out image.

Example 1

A solution of 0.027 gram of 2-methyl-4-[(methylsulfonamidoethyl)ethylamino]aniline color developing agent, 0.032 gram of 2-azidobenzoxazole and 0.017 gram of 3-methyl-1-phenyl-5-pyrazolone coupler in 30 ml. of a 5% solution of poly(vinyl butal) in 3A alcohol is whirl-coated onto a sheet of photographic paper base. The coated plate thus formed is whirled until dry. The coated side of the photographic element is then exposed through a negative pattern to a sun lamp at ten inches for one minute to obtain a magenta-on-white positive image.

Example 2

A solution of 0.027 gram of 2-methyl-4-[(methylsulfonamidoethyl)ethylamino]aniline developer, 0.032 gram of 2-azidobenzoxazole and 0.014 gram of 1-naphthol in 30 ml. of a 5% solution of poly(vinyl butal) and 3A alcohol is coated on paper and whirled until dry as in the previous example. The photographic element thus obtained is exposed through a negative pattern to a sun lamp at ten inches for one minute to obtain a cyan-on-white positive image.

Example 3

A mixture of 2-methyl-4-diethylaminophenyl azide hydrochloride (2 moles), a compound combining the required azido and p-phenylenediamine functions, and 1 mole of 1-naphthol in methanol is treated with a slight excess of triethylamine to effect solution of the azide as the free base. An equal volume of 10% poly(vinyl butal) in 3A alcohol is added and the resulting dope is coated on paper by means of a plate whirler. The dry, coated material is then exposed for one minute through a negative pattern to a sun lamp at ten inches as previously to obtain a cyan positive image.

Example 4

A mixture of 2-methyl-4-diethylaminophenyl azide hydrochloride (2 moles) and 1 mole of 3-methyl-1-phenyl-5-pyrazolone in methanol is treated with a slight excess of triethylamine to effect solution of the azide as the free base. An equal volume of 10% poly(vinyl butal) in 3A alcohol is added and the resulting dope is coated on paper by means of a plate whirler and dried. The resulting photographic element is exposed as in the previous examples to obtain a magenta positive image.

Example 5

A mixture of 2-methyl-4-diethylaminophenyl azide hydrochloride (2 moles) and o-acetoacetanilide (1 mole) in methanol is treated with slight excess of triethylamine to effect solution of the azide as the free base. An equal volume of 10% poly(vinyl butal) in 3A alcohol is added and the resulting dope is coated on a suitable photographic base as previously. The dry coated material is then exposed for one minute through a negative pattern to a sun lamp at ten inches to obtain a yellow positive image.

The print-out images of the present invention when formed in a water permeable material such as gelatin

may be stabilized with a dilute acid such as aqueous ascorbic acid.

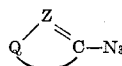
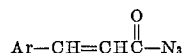
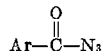
The azides and heterocyclic couplers employed in the present invention and methods by which these compounds may be prepared are described in the literature. The azido compounds, for example, may be prepared by the methods described in Chem. Revs., 54, No. 1 (February 1954). See also J. Am. Chem. Soc., 76, 1859 (1954).

It will be apparent from the foregoing description that the present invention provides an advantageous method and materials for photographic reproduction of graphic material and that due to the highly colored indoaniline and azomethine dyes formed, print-out images of good contrast can be achieved. The new system and materials are particularly advantageous and convenient to use inasmuch as they eliminate the wet processing required by previous photographic systems employing indoaniline and azomethine dyes. This results in substantial savings in both time and labor and provides the art with a completely new method of obtaining colored reproductions. A considerable economic advantage is also provided by the new materials in which the light sensitive compositions are incorporated directly in the support material due to the elimination of one of the usual coating operations.

It should be understood that the specific embodiments of the invention described above are merely illustrative and are not intended to limit the scope of the claims.

What is claimed is:

1. A light-sensitive photographic element having therein at least one organic azide selected from the class consisting of those having the formulae



in which Ar is an aryl group selected from the class consisting of an unsubstituted aryl group, an alkaryl group, an alkoxyaryl group, a nitroaryl group, a haloaryl group, an aminoaryl group, an alkaminoaryl group, a dialkylaminoaryl group, an azidoaryl group, an aryl group substituted with a heterocyclic ring having not more than 8 atoms in the ring and an aryl group substituted with a carbocyclic ring having not more than 8 atoms in the ring, Z is selected from the group consisting of the nitrogen, oxygen and sulfur atoms, and Q is an organic residue which includes the atoms required to complete a 5- to 6-membered ring with the carbon atom and atom represented by Z to which Q is bonded in the formula, said ring selected from the class consisting of a benzoxazole group, a benzimidazole group, a tetrazole[a]phthalazine group, a 6-methyl-1,3,3a-7-tetrazaindene group, and a 6-methylpyrimidine group, at least one p-phenylenediamine color developing agent such that when Ar in the said organic azide represents a p-aminoaryl group, the said organic azide is the said color developing agent and a color-forming coupling agent containing a reactive group selected from the class consisting of the methylene and methine groups, said coupling agent being capable of reacting with the oxidized form of said color developing agent to produce a dye.

2. A light-sensitive photographic element according to claim 1 in which the organic azide is 2-azidobenzoxazole, the p-phenylenediamine color developing agent is 2-methyl-4-[(methylsulfonamidoethyl)ethylamino]aniline and the color-forming coupling agent is 3-methyl-1-phenyl-5-pyrazolone.

3. A light-sensitive photographic element according to claim 1 in which the organic azide is 2-azidobenzoxazole,

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the p-phenylenediamine color developing agent is 2-methyl - 4 - [(methylsulfonamidoethyl)ethylamino]aniline and the color-forming coupling agent is 1-naphthol.

4. A light-sensitive photographic element according to claim 1 which contains the compound 2-methyl-4-diethylaminophenyl azide and the color-forming coupling agent is 1-naphthol.

5. A light-sensitive photographic element according to claim 1 which contains the compound 2-methyl-4-diethylaminophenyl azide and the color-forming coupling agent is 3-methyl-1-phenyl-5-pyrazolone.

6. A light-sensitive photographic element according to claim 1 which contains the compound 2-methyl-4-diethylaminophenyl azide and the color-forming coupling agent is o-acetoacetanisidide.

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7. A light-sensitive photographic element having therein at least one p-aminoarylazide and a color-forming coupling agent containing a reactive group selected from the class consisting of the methylene and methine groups, said coupling agent being capable of reacting with the oxidized form of said color developing agent to produce a dye.

References Cited in the file of this patent

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822,125	Great Britain	Oct. 21, 1959
901,048	France	July 16, 1945