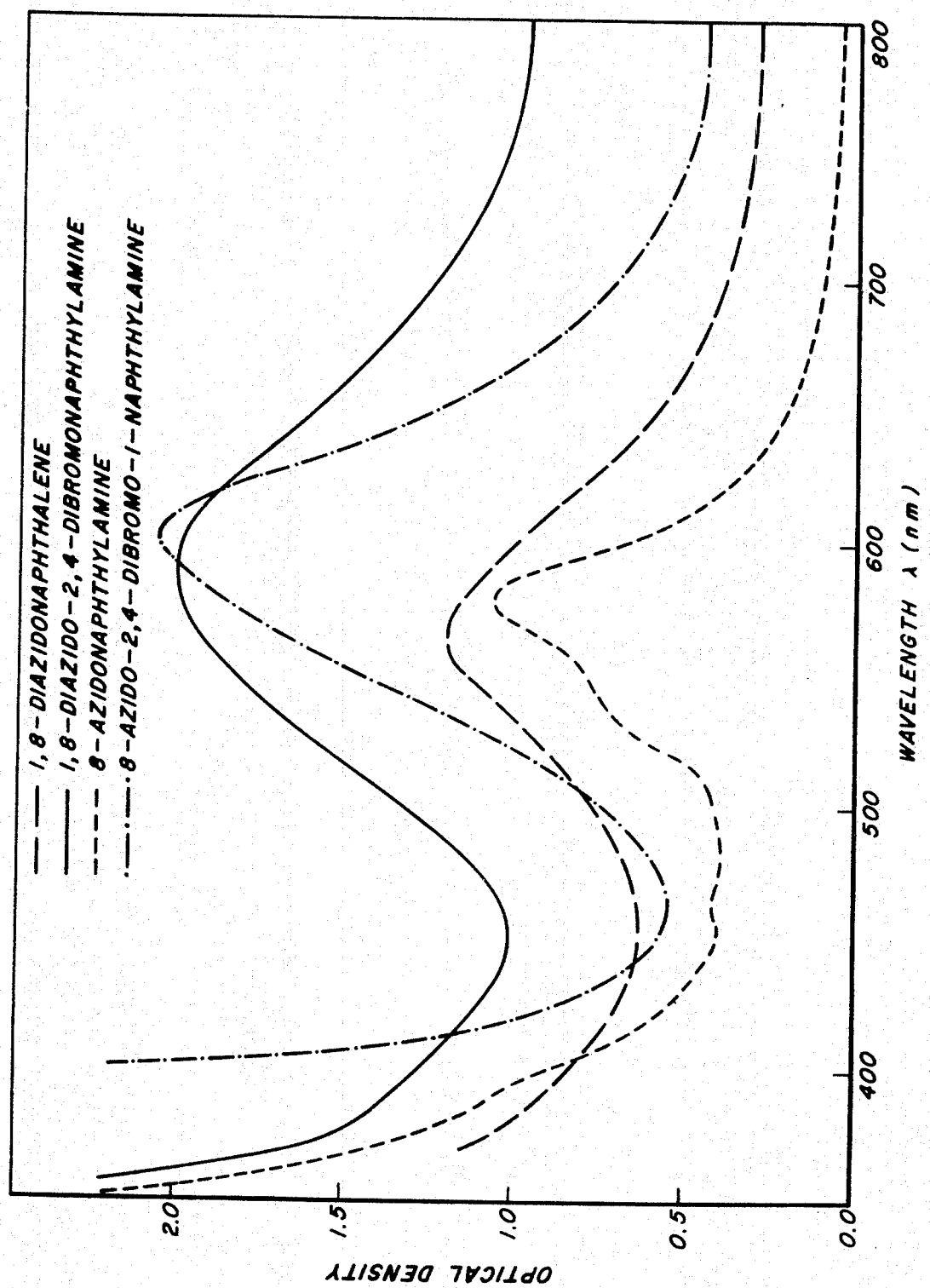
MATERIAL CONTAINING PHOTOSENSITIVE HALO AZIDO NAPHTHALENES

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MATERIAL CONTAINING PHOTOSENSITIVE HALO AZIDO NAPHTHALENES

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U.S. Cl. 96—91 N 5 Claims

ABSTRACT OF THE DISCLOSURE

Novel halo azido naphthalenes and dry photoimaging processes and compositions employing said naphthalenes are disclosed.

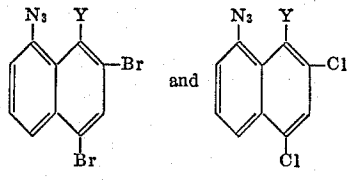
This application is a division of application Ser. No. 147,117, filed May 26, 1971, now Pat. No. 3,699,130.

This invention relates to certain novel halo azido naphthalenes and to dry photoimaging processes and compositions employing said compounds.

Photosensitive compounds, compositions and processes play an essential role in photography and the related arts dealing with the formation of images with the aid of some activating influence, such as light, heat, etc. For many applications, as in the case of printing on white paper, it is desirable to maximize the neutrality of the image, in addition to achieving good color stability, speed, acuity, resolution and tonal range as well as to achieve the convenience of a dry imaging process employing relatively inexpensive materials.

Accordingly, it is an object of the present invention to provide photosensitive compositions which are suitable for the formation of images having broad spectral characteristics as well as a good image stability, acuity, resolution and tonal range. It is a further object to provide a convenient, dry photoimaging process for the formation of such images. These and other objects of the present invention will become apparent from the description and examples which follow.

In copending application Ser. No. 82,129, filed Oct. 19, 1970, the use of 1,8-diazidonaphthalene and 8-azido-1-naphthylamine in photoimaging was disclosed. It has been unexpectedly found that images of enhanced neutrality and optical density can be achieved by employing the novel halo azido naphthalenes selected from the group consisting of:

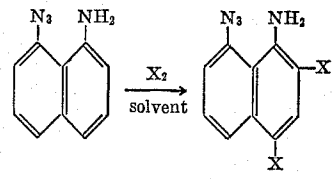


wherein Y is a member selected from the group consisting of $-N_3$ and $-NH_2$.

While applicant does not wish to be limited to a specific theory, it is believed that the halo substituents function as internal heavy atoms to produce internal spin orbital coupling in the image forming process.

The photosensitive compounds can be readily prepared by chlorination or bromination of the known compound, 8-azido-1-naphthylamine. This can be accomplished by conventional halogenation procedures such as those set forth in the text entitled, Reactions of Organic Compounds by W. J. Hickenbottom, Longmans, Green and Co., London, New York, 1936, pages 291–293.

Introduction of the halo substituents may be graphically illustrated as follows:



wherein X is Cl or Br.

The corresponding dihalo 1,8-diazidonaphthalenes can be readily formed by converting the amine function to an azide function by conventional procedures such as those disclosed, for example, in U.S. Pat. No. 3,123,621.

The novel, photosensitive compounds of the present invention are 8-azido-2,4-dibromo-1-naphthylamine, 8-azido-2,4-dichloro-1-naphthylamine, 1,8-diazido-2,4-dibromonaphthylamine and 1,8-diazido-2,4-dichloronaphthylamine.

The photosensitive material of the present invention comprise a suitable photographic substrate having a photosensitive film or coating deposited thereon. The coating is composed of conventional film-forming plastics having one or more of the above photosensitive compounds uniformly incorporated (preferably dissolved) therein.

Suitable substrates include, for example, such materials as paper, plastic, wood, metal and glass.

Among the suitable conventional polymeric binders, one may mention, for example, polyvinyl chloride, polyethylene, polymethylmethacrylate, polyvinyl acetate, cellulose acetate, copolymers of the corresponding monomers, copolymers of vinylidene chloride and acrylonitrile and mixtures of the above polymers.

Incorporation of the photosensitive compounds within the film-forming polymer can be conveniently achieved by selecting an organic solvent in which both the polymer and photosensitive compound are soluble. Suitable solvents include for example toluene, tetrahydrofuran, benzene, methyl ethyl ketone, mixtures of the above and the like. The resulting solution can be applied to the substrate of choice by a variety of standard coating techniques.

Of the suitable methods of applying the sensitized dope to the structure, the Fixed Blade Method, the Imbibing Method and the Meyer Rod Method are among the preferred techniques.

In the Fixed Blade Method, the base material is positioned under a fixed blade and an excess of the coating material is placed on the base. The base is then passed under the blade to produce a uniform coating having a thickness determined by the distance between the mounted blade and the base material.

In the Imbibing Method, a base stock having a plastic surface is coated with the active compound by passing it under a roller, touching a solution of the azido compound. The excess coating is removed from the surface by an air knife. By way of illustration, one may mention passing paper coated with polyvinyl chloride, polyvinyl acetate, or polymethylmethacrylate through a solution of 1,8-diazido-2,4-dibromonaphthalene in a solvent such as tetrahydrofuran, methyl ethyl ketone, acetone or toluene or mixtures thereof.

In the Meyer Rod Method, the coating composition is placed at one end of the base material and a metal rod wound with fine wire is passed through the liquid causing it to be spread over the surface of the base material. The thickness of the coating produced by this method is determined by the size of the wire usd in the winding.

Preparation of the photosensitive composition is completed by merely removing the solvent from the photosensitive film by evaporation.

The concentrations of the photosensitive compound and thickness of the coating applied to the substrate may be varied to tailor the photosensitive system so as to achieve the desired degree of image intensity, speed, etc. Optimum concentrations and thicknesses will, of course, vary depending upon the particular photosensitive compound, binder material, coating thickness, temperature, time, and other factors. In general, satisfactory photoimages can be produced by employing binder compositions having from about 10 %to about 20% by weight of the photosensitive compound and coatings having thicknesses in the range of from about 0.05 to about 1.50 mils. Preferred concentrations and thicknesses are about 15% by weight and about 0.3 mils, respectively.

The aromatic azido compounds are themselves generally sensitive to radiation containing wavelengths within the ultraviolet region. By means of the addition of a sensitizing agent to the polymer binder, the sensitivity can be extended into the range of from 360 mμ to 470 mμ or greater. The energy transfer of such systems is surprisingly efficient in view of the typically high viscosity of the binder polymer systems being sensitized.

Several advantages are provided by the use of sensitized systems. They permit the use of apparatus equipped with inexpensive and convenient light sources, such as incandescent lamps, and allow projection printing through various optical systems with normal optical glass. They also permit the simultaneous use of both direct and indirect exicitation of azido compounds through simultaneous exposure of the photosensitive compounds to both visible and ultraviolet light. Alternatively, enhanced absorption can be achieved by using an ultraviolet absorbing sensitizer in combination with the azido composition.

Suitable sensitizers include, for example, fluoranthene, thioxanthone, fluorenone, perylene, benzanthrone, benzophenone, phenazine and thioacridone.

Sensitizers which absorb light in the visible spectrum are of necessity colored compounds. Where the colors caused thereby are found to be objectionable, one may employ a colorless, ultraviolet absorbing sensitizer or a volatile sensitizer, such as, fluorenone, in a gas permeable binder, such as, polyvinyl chloride. The period and degree of heat treatment is adjusted to be sufficient to effect volatilization of the fluoreone without producing excessive background colorup.

Optimum relative concentrations of the sensitizer and azido compound will, of course, vary with the particular system being employed. Generally, energy transfer is favored by high concentrations of the photosensitive compound. It is preferred to employ the sensitizer in a sufficient concentration to absorb the incident light. However, excessively high concentrations of the sensitizer will cause complete absorption of the incident light at the surface of the plastic matrix and may thereby reduce the efficiency of the system.

Imaging is achieved by exposing the photosensitive compositions to patterned activating radiation, namely, an information containing beam of visible or ultraviolet light.

A convenient source of ultraviolet radiation is provided by lamps which emit a wide range of ultraviolet frequencies. A light table equipped with a film transparency (positive or negative) and a bank of ultraviolet-rich fluorescent lamps, such as, 15 watt black light, No. F15T8–BL by General Electric and Rayonet photochemical reactor lamps, No. RPR 3000A by The Southern New England Ultraviolet Company provides a convenient source of activating radiation. Conventional azo printing machines, equipped with high pressure mercury vapor lamps may also be employed. Since they emit both visible and ultraviolet light, they are especially well adapted for use with those compositions having sensitizers to visible light.

Absorption of incident light can be maximized by matching the frequencies of the incident light with the absorption frequencies of the photosensitive compound or the sensitizer if one is employed.

Patterning of the activating radiation can generally be achieved by any of the conventional methods. Suitable methods include passing the light through a film transparency or a template, use of a cathode ray tube containing an ultraviolet phosphor, such as, a Litton Industries, Inc. cathode ray tube, Serial No. 4,188, which contains a P16 phosphor; and using an ultraviolet pen light, such as Ultraviolet Products, Inc. pen light, or ultraviolet laser, such as might be used in spatial frequency modulation and halographic information storage, etc.

Optimum periods of irradiation will vary widely, depending upon the particular photosensitive composition, opacity of transparency, and light source employed. Exposure for a few seconds in a conventional azo printer is generally adequate while periods of two minutes or more may be required for a source such as the abovementioned light table.

The enhancement of image neutrality and optical density produced by the presence of the halo substituent is shown in the figure. These characteristics were observed by irradiating polyester film substrates (Mylar® by E. I. du Pont de Nemours) uniformly coated with a layer of polyvinyl chloride (Geon 101, d=1.4, by The B. F. Goodrich Chemical Company) having a thickness of from about 0.2 to about 0.3 mil which was 1.0 N in one of the following photosensitive compounds: 8-azido-2,4-dibromo - 1 - naphthylamine, 1,8 - diazido-2,4 - dibromonaphthylamine, 8 - azido - 1 - naphthylamine and 1,8-diazidonaphthylamine. Imaging was achieved by exposure through a film transparency to a bank of black light fluorescent lamps transmitting light in the 300–380 nm. (peaking at 350 nm.) region for a period of from about 10 to about 30 seconds. The result was a gray-black image of excellent tonal range, resolution and acuity in each case. However, the image neutrality and optical density were in each case substantially enhanced by the presence of the halo substituent.

The processes and compositions of the present invention are further illustrated by the following examples which are not to be taken as limitative thereof. All parts and percentages herein are by weight unless otherwise indicated.

EXAMPLE 1

1-amino-8-azido-2,4-dibromonaphthylamine

A solution of 1-amino-8-azidonaphthylamine (2.3 g., 0.0125 mole) in 125 ml. of glacial acetic acid was treated with a solution of bromine (4.0 g., 0.025 mole) in 50 ml. of glacial acetic acid. The precipitated hydrobromide was removed by filtration and washed with ether. The nearly white precipitate was digested with aqueous $NaHCO_3$. The dibromoamioazide was extracted with ether, washed, dried and filtered through charcoal. Removal of ether left a residue which was recrystallized from ether to yield 3.1 g., 82% of the desired product having an M.P. of 127°–130° C. Identification was made by infrared and elemental analysis:

Calcd. for $C_{10}H_6N_4Br_2$ (percent): C, 35.10; H, 1.75; N, 16.40; Br, 46.95. Found (percent): C, 35.38; H, 1.46; N, 16.33; Br, 47.19.

EXAMPLE 2

1,8-diazdio-2,4-dibromonaphthylamine

A solution of 1-amino-8-azido-2,4-dibromonaphthylamine (500 mg., 1.46 moles) in 50 ml. of acetic acid was mixed with 10 ml. of concentrated hydrochloric acid and cooled to 5° C. in an ice bath. A solution of $NaNO_2$ (280 mg., 0.4 mole) in water (1 ml.) was added dropwise with stirring. After ½ hour, the mixture was poured into an excess of NaN_3 (2 g., in 100 ml. of ice-water mixture). The precipitate of the diazide was removed by filtration,

dissolved in ethyl ether, dried over anhydrous $MgSO_4$ and filtered through charcoal. Removal of the ether left the desired product as a residue. It was recrystallized from n-hexane to yield 334 mg. (63%), M.P. 130° C.–132° C. Identification was made by infrared and elemental analysis:

Calcd. for $C_{10}H_6N_4Br_2$ (percent): C, 32.60; H, 0.90; N, 22.80; Br, 43.50: Found (percent): C, 32.85; H, 0.84; N, 23.00, Br, 43.75.

EXAMPLE 3

The enhancement of optical density produced by the halo substituents is demonstrated by the following tests.

Photosensitive compositions were prepared by uniformly coating polyester film substrates (Mylar®) with layers of polyvinyl chloride (Geon 101) which were 0.7 N in the photosensitive compound. The films were imaged by exposing them through a film transparency to a bank of black light fluorescent lamps transmitting light in the 300–380 nm. (peaking at 350 nm.) region for various equal intervals of time. The films were thereafter heated in an oven at 135° C. for sixty seconds and the optical density of each film was thereafter measured. In each case, as shown by the data presented in Table I below, the bromo substituents produce about 50% increases in efficiency.

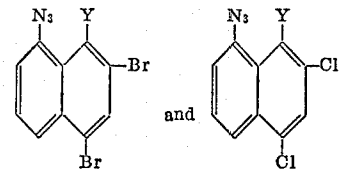
TABLE I

Exposure time (min.)	1,8-diazidonaphthalene [a] (OD)	1,8-diazido-2,4-dibromonaphthalene [a]
1	0.56	0.92
2	0.70	1.18
3	0.80	1.32
4	0.84	1.42
5	0.90	1.50
6	0.94	1.54
7	1.02	1.56
8	1.04	1.60

[a] Thickness of coating=0.2 mil.

I claim:

1. A photosensitive material suitable for the formation of images comprising a photographic substrate having a photosensitive coating thereon, said coating comprises a film-forming plastic having incorporated therein a photosensitive compound selected from the group consisting of:



wherein Y is a member selected from the group consisting of $—N_3$ and $—NH_2$.

2. A material according to claim **1** wherein said compound is 8-azido-2,4-dibromo-1-naphthylamine.

3. A material according to claim **1** wherein said compound is 1,8-diazido-2,4-dibromonaphthalene.

4. A material according to claim **1** wherein said coating contains a visible or ultraviolet light spectral sensitizer.

5. A material according to claim **4** wherein the sensitizer is fluorenone or benzanthrone.

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