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[54] N-VINYL AMINE/HALOGEN LIBERATING COMPOSITION SENSITIZED WITH 9-VINYL CARBAZOLES OR POLYACENES, OR TRANSANNULAR PEROXIDES OF POLYACENES
7 Claims, No Drawings

[52]	U.S. Cl.....	96/48, 96/90
[51]	Int. Cl.....	G03c 5/24, G03c 1/72
[50]	Field of Search.....	96/48, 88, 90, 115 P

[56] **References Cited**

UNITED STATES PATENTS

3,476,562	11/1969	Yamoda et al.	96/90
3,042,516	7/1962	Wainer.....	96/90
3,042,519	7/1962	Wainer.....	96/90
3,102,810	9/1963	Sprague.....	96/90
3,147,117	9/1964	Wainer et al.	96/90

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Assistant Examiner—Richard E. Fichter

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ABSTRACT: The photographic response of compositions comprising mixtures of (1) N-vinyl carbazole (or other N-vinyl amine) and (2) CBr_4 (or other organic halogen compound) to radiant energy having wavelengths longer than 4,500 Å. is enhanced so as to include a response to radiant energy having wavelengths of up to about 7,000 Å. by adding a slightly colored visible light sensitizer to the mixture.

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**N-VINYL AMINE/HALOGEN LIBERATING
COMPOSITION SENSITIZED WITH 9-VINYL
CARBAZOLES OR POLYACENES, OR TRANSANNULAR
PEROXIDES OF POLYACENES**

This invention relates to the polymerization of N-vinyl compounds as a result of exposure to suitable dosages of visible light. More particularly, it relates to the visible light-induced photopolymerization of N-vinyl compounds, such as N-vinyl carbazole in the presence of certain types of sensitizing agents.

Numerous United States Patents issued to Eugene Wainer and others describe photosensitive compositions comprising at least the following constituents:

1. An N-vinyl amine
2. An organic halogen containing compound
3. Various optional ingredients, such as a synthetic resin or other film-forming material in which the two essential constituents are dispersed or supported.

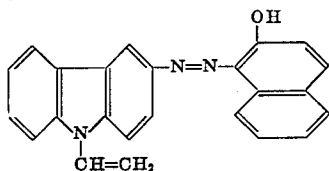
These patents include the following: U.S. Patent 3,042,517, issued July 3, 1962, U.S. Patent 3,042,518, issued July 3, 1962, U.S. Pat. 3,042,519, issued July 3, 1962, U.S. Pat. 3,046,125, issued July 24, 1962, U.S. Pat. 3,056,673, issued Oct. 2, 1962, and U.S. Pat. 3,147,117, issued Sept. 1, 1964.

Various improvements thereover are described in copending U.S. Pat. applications Ser. No. 445,273, filed Apr. 2, 1965, now U.S. Pat. No. 3,377,167 claiming the addition of Group V aryl compounds such as triphenylstibine, triphenylarsine, triphenylphosphine or triphenylbismuthine to such compositions, and Ser. No. 398,097, filed Sept. 21, 1964, now U.S. Pat. No. 3,342,602, claiming the use of mercaptobenzothiazole in such compositions. The disclosures in these applications are incorporated herein by reference.

The patents of Eugene Wainer noted above describe extensively the use of N-vinyl compounds for preparing polymeric images by photolysis with halogen containing hydrocarbons as the activating source of free radicals. These patents describe the use of compounds such as N-vinyl carbazole and carbon tetrabromide coated in plastic binders, dissolved in suitable organic solvents and coated on appropriate supports such as paper, glass or plastic film. The photographic systems described in the foregoing paragraphs are essentially sensitive only to ultraviolet irradiation with a tail of very low sensitivity extending in to the very early visible portion of the electromagnetic spectrum. If a means could be found for extending the spectral sensitivity of these photographic systems to longer wavelengths on the electromagnetic spectrum their usefulness as practical photographic medium would be greatly enhanced. This invention describes a means for extending the sensitivity of these systems into the visible portion of the spectrum. Certain colored sensitizers have been found which effectively increase the visible light sensitivity of N-vinyl carbazole to photopolymerization. These colored sensitizers are taken from the class of compounds such as carbocyanine dyes, styryl dyes and their colorless bases, polyacene compounds and the transannular peroxides of polyacene compounds. Some colored derivatives of vinyl carbazole made by the introduction of other aromatic moieties into the vinyl carbazole molecule by substitution or by means of azo linkages to form azo dyes were also found to sensitize these photopolymer systems to visible light. These colored sensitizers include the following compounds:

1a. Azovinylcarbazoles

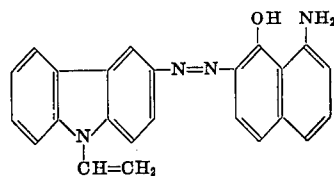
A. 3-(2-Hydroxy-1-Naphthyl-azo)-9-vinyl carbazole



sensitizes to 5500 Å.

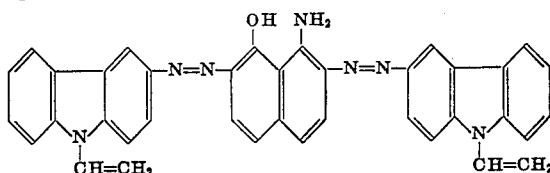
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B. 3-(1-amino-8-hydroxy-7-naphthylazo)-9-vinyl carbazole



sensitizes to 5800 Å.

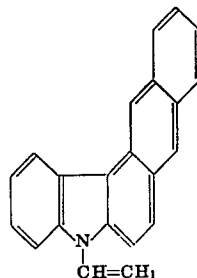
C. 2,7(3-bis-6-9 vinyl carbazoyl-azo)-8-hydroxy-1 naphthyl-amine



sensitizes to 6500 Å.

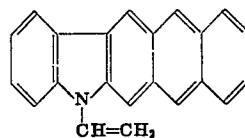
1b. Naphthovinylcarbazoles

A. 9-vinyl(2',3':3,4)-naphthocarbazole



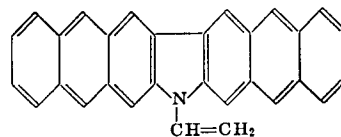
sensitizes to 5500 Å.

B. 9-vinyl(2',3':2,3)-naphthocarbazole



sensitizes to 6000 Å.

C. 9-vinyl(2',3':2,3,2'',3'',6,7)dinaphthocarbazole



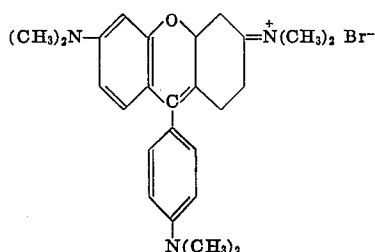
sensitizes to 6500 Å

2. Polyacene compounds and the transannular peroxides of polyacene compounds: (For structures see Review of "Transannular Peroxides" Bergmann and McLean, Chemical Reviews 28 (1941))

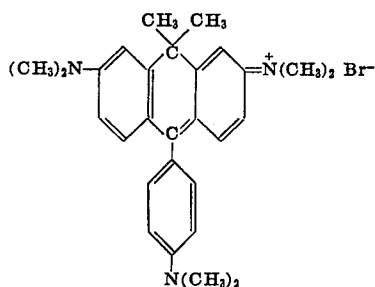
- Ascaradole
- Anthracene
- Naphthacene or Tetracene
- Pentacene
- Naphthalene
- Acenaphthylene
- Azulene
- Fluorene
- Pyrene
- Perylene
- Benzperylene
- Coronene
- Rubrene

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3. Xanthene dyes and their leuco bases
3,6-(Tetramethyldiamino-9-p-dimethylaminophenyl)
xanthylium bromide

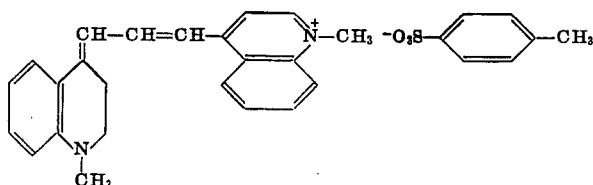


4. Anthracene dyes and their leuco bases
2,7-Bis(dimethylamino)-10-p-dimethylaminophenyl-9,9-
dimethylantracene bromide

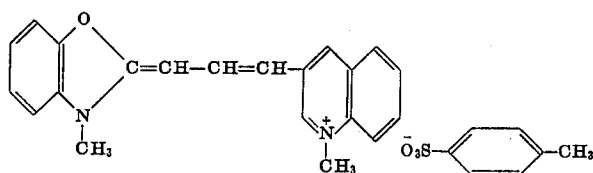


5. Carbocyanine Dyes and their bases

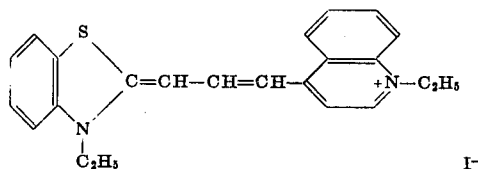
A. 1,1'-Dimethyl-4,4'-carbocyanine-p-toluene sulfonate
(The ethyl iodide of this dye is Kryptocyanine)



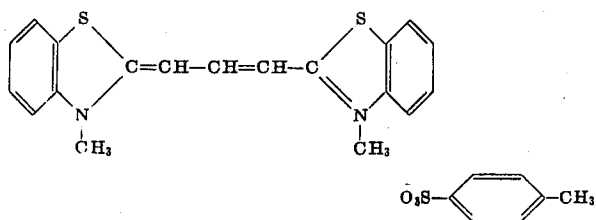
B. 1',3-dimethyloxa-2'-carbocyanine-p-toluene sulfonate



C. 1',3-diethylthia-4'-carbocyanine iodide

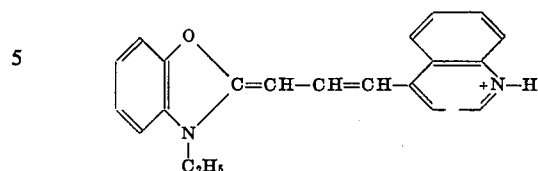


D. 3,3'-dimethylthiocarbocyanine-p-toluene sulfonate

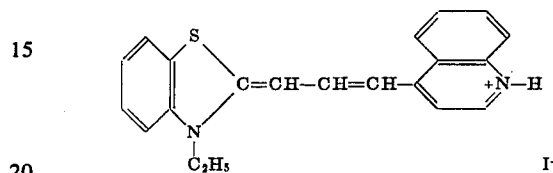


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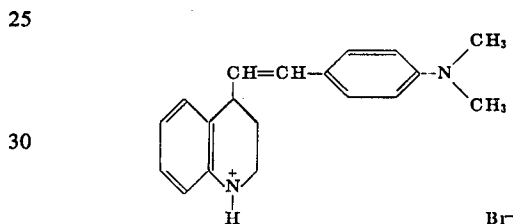
E. 4-[3-(3-ethyl-2(3H)benzoxazolylidene)propenyl]-
quinoline hydroiodide



F. 4-[3-(3-ethyl-2(3H)benzothiazolylidene)propenyl]-
quinoline iodide



6. Styryl dyes and their bases
4-(p-Dimethylamino styryl)quinoline bromide



Each of these compounds has been found to extend the sensitivity of N-vinyl carbazole well into the visible portion of the electromagnetic spectrum. Without a colored sensitizer present, the simplest photographic system, namely one containing only N-vinyl carbazole, carbon tetrabromide coated in a film-forming binder, shows sensitivity only to 4,500 Å. When exposed to light of longer wavelengths than 4,500 Å. no response is observed, that is, no imaging takes place. If, however, a very small quantity of one of the above colored compounds is added to this simple system photographic response is observed with light of wavelengths of 6,000, 6,500 and sometimes 7,000 Å. These exposures were made with a monochromator and the exposed film was heated with infrared to make the latent image visible or to intensify any printout image which occurs on exposure.

While not wishing to be bound by any set theory, it is proposed that the mechanism operating to produce this sensitizing effect is one in which the added color sensitizer or its oxidation product absorbs light of longer wavelength than either the N-vinyl compound, the carbon tetrabromide or any product of their combination. Whatever the mechanism it is the presence of the colored species which absorbs the longer wavelength of electromagnetic energy and transfers it to the polymer-forming reaction.

Briefly the present process comprises applying a composition comprising an N-vinyl amine monomer, an organic halogen containing compound, and a colored sensitizer of one of the types described above as a coating to a suitable base or support, exposing the composition to a dose of visible light and then heat developing the polymeric image e.g., when the exposure has been made to a pattern of light, such as is normally termed a photographic exposure) by means of infrared at 130°-150° C.

The range of quantities for preparing compositions of this invention is widespread. The maximum amount of N-vinyl amine which can be present in the composition is limited only to the extent of its solubility in the coating mixture. The amount of the activating halogen-containing compound is also dependent to some extent upon the degree of its activity and its solubility in the coating mixture. The resinous binder can

be present in any amount which will form a continuous film and adequately protect the active ingredients of the photographic reaction. The amount necessary to fulfill this requirement will be determined by the type of resin chosen, the solvent from which it is cast, the solubility of the resin in the chosen solvent and the inherent viscosity of the resin in its ultimate viscosity in solution. If assisting addenda are used, such as the triaryl Group V compounds described in U.S. Pat. application Ser. No. 445,273, filed Apr. 2, 1965, now U.S. Pat. No. 3,377,167 for background cleanliness and for allowing longer and more intense heating to develop and/or intensify the image, these should be present in amounts ranging from 25 milligrams to 200 milligrams per gram of monomer depending on the particular compound and again its solubility. Other additives such as sodium iodide to give blacker images and heterocyclic compounds such as mercaptobenzothiazole to give increases in speed are frequently added in ranges described in patents and applications referenced above. Compounds such as straight chain hydrocarbons are frequently added to these coating compositions as a part of the resinous film former. These compounds are believed to lessen the rigidity of the film formed on evaporation of solvent and to allow greater mobility for the reacting radicals.

The range of addition of colored sensitizing compounds which make up the subject of this invention and make it novel over the previously described systems of limited sensitivity is much more critical than the range of the monomer and its activator described above. It is the presence of very small quantities of these sensitizing dyes that are responsible for giving the added sensitivity, and their amounts are more rigidly limited. If the added quantity is too great the sensitizers tend to color the background and some detail of the resulting image is lost in this colored background. It has been found that if the sensitizers are used in the range of 0.1 milligram to 2.0 milligrams of sensitizer per gram of monomer the maximum degree of sensitizing effect can be realized with the minimum amount of color in the background. The following examples will serve to illustrate the practice of this invention but the invention is not to be considered limited by these examples.

EXAMPLE 1

1 cc. Elvax Grade 220 (Copolymer, polyethylene and vinyl acetate) 10 percent solution in benzene
 1 cc. Eicosane (Straight chain paraffin hydrocarbon C₂₀) 25 percent in benzene
 5 cc. Carbon tetrabromide solution 25 percent in benzene
 3 cc. N-vinyl carbazole solution 25 percent in benzene
 2 mg. 3(2-Hydroxy-1-naphthyl-azo)-9-vinyl carbazole

The above mixture was coated at 0.003 wet thickness on standard baryta coated photographic paper then dried and the resulting coating exposed for 120 seconds to a monochromator at each of the following wavelength settings: 3,900 A., 4,000 A., 4,200 A., 4,500 A., 5,000 A., 5,500 A. After exposure the paper was developed for 60 seconds under an IR lamp after which images appear in the exposed area. Exposures at 5,000 A. and 5,500 A. of this composition showed definite images after heat development while a control coating which contained none of the colored vinyl carbazole compound showed no images beyond 4,500 A.

EXAMPLE 2

Example 2 is identical to example 1 except that the colored compound 3(2-Hydroxy-1-naphthyl-azo)-9-vinyl carbazole is replaced by 9-vinyl-(2', 3', 3,4)naphtho carbazole. The results are exactly the same as those observed in example 1. Response was observed at 5,500 A. after the heat development step while no response was observed beyond 4,500 A. in the control coating which contained no colored sensitizer.

EXAMPLE 3

1 cc. Elvax 220 10 percent in benzene
 1 cc. n-Octacosane 10 percent solution in benzene
 5 cc. Carbon tetrabromide 25 percent in benzene

3 cc. N-vinyl carbazole 25 percent in benzene
 5 mg. Rubrene

When the above mixture was coated on baryta photographic paper and exposed for 60 and 120 seconds to various wavelengths on a monochromator then infrared developed for 60 seconds following the monochromatic exposure photographic response was observed as shown in the following table which lists the optical densities read on a reflection densitometer that resulted after exposure and infrared treatment. A control coating which contained no rubrene showed no measurable densities at wavelengths longer than 4,500 A.

TABLE FOR EXAMPLE 3 (RUBRENE)

Wavelength	Monochromator exposures		
	Test		Control, 60 sec.
	60 sec.	120 sec.	
3,900 A.	0.56	0.98	0.36
4,000 A.	0.69	0.62	0.31
4,200 A.	0.24	0.38	0.22
4,600 A.	0.185	0.29	0.175
5,000 A.	0.50	0.65	-----
5,500 A.	0.80	0.46	-----
6,000 A.	0.12	0.14	-----
Base plus fog	0.10	0.10	0.10

EXAMPLE 4

One-half mg. of the magenta dye 1'-dimethyloxa-2'-carbocyanine-p-toluene sulfonate which is a member of the carbocyanine class of dyestuffs was added in place of the substituted vinyl carbazole compound of example 1, strong photographic response was observed with monochromatic exposures at 6,000 A. after infrared heating for intensification of the image. A control coating which contained none of the aforementioned carbocyanine dye showed sharp cutoff in photographic response at 4,500 A. after monochromatic exposures.

EXAMPLE 5

One mg. of the cyan colored carbocyanine dye 1',3-Diethylthia-4-carbocyanine iodide was added to the coating composition of example 1 in place of the substituted vinyl carbazole compound. Strong photographic response was observed as far out in the visible spectrum as 6,500 A. at both 60 seconds and 120 seconds exposures to the monochromator followed by infrared heating for image intensification. Control coatings without the carbocyanine dye and similarly exposed showed no response beyond 4,500 A. on similar exposure and heat intensification.

EXAMPLE 6

One mg. of the magenta colored symmetrical carbocyanine dye 3,3'-Dimethylthiocarbocyanine-p-toluene sulfonate was added to the coating mixture of example 1 in place of the colored substituted vinyl carbazole compound and this mixture coated on baryta photographic paper. Photographic response was observed at 6,000 A. after monochromatic exposures and infrared heating for image intensification. A similar control coating made without the carbocyanine dye showed response only to 4,500 A. after exposing and heat intensifying in a similar manner.

EXAMPLE 7

When 4 mg. of the polyacene compound, naphthacene, were added to the coating mixture of example 1 in place of the colored substituted vinyl carbazole compound and the mixture coated on baryta photographic paper, photographic response was observed at 5,000 A. after monochromatic exposure and heat intensification with an infrared lamp. A control coating of similar composition but without naphthacene showed no response beyond 4,500 A.

EXAMPLE 8

When 1 mg. of the magenta dye of the xanthene class, 3,6-(Tetramethyldiamino)-9-p-(dimethylaminophenyl)-xanthylium bromide, was added to the coating mixture of example 1 in place of the colored substituted vinyl carbazole compound and coated on baryta photographic paper, strong photographic response was observed at 5,500 A. and a trace of photographic response was observed at 6,000 A. after monochromatic exposures and infrared intensification. A control coating of similar composition but without the colored sensitizers gave no photographic response beyond 4,500 A. when exposed and heated in the same fashion.

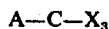
EXAMPLE 9

When 1 mg. of the cyan colored carbocyanine dye, 4-[3-(3-Ethyl-2(3H)benzoxazolyldene)propenyl]quinoline hydroiodide, was added to the coating mixture of example 1 in place of the colored substituted vinyl carbazole compound and coated on baryta photographic paper, strong photographic response was observed at 6,000 A. of monochromatic exposure and infrared intensification. When the monochromatic exposure was raised from 60 seconds to 120 seconds images appeared at 6,500 A. after heat intensification. A control coating of similar composition without the colored sensitizer added showed no response after 4,500 A. with the same exposure and heat intensification.

EXAMPLE 10

When 5 mg. of the magenta dye of the styryl class known as 4(p-Dimethylamino styryl)quinoline bromide was added to the coating mixture of example 1 in place of the colored substituted vinyl carbazole compound and coated on baryta photographic paper, photographic response at 6,000 A. was observed after monochromatic exposures and heat intensification with an infrared lamp. A control heating of similar composition but without the color sensitizer showed response only to 4,500 A. after similar exposure and infrared intensification.

Other suitable organic halogen compounds may be used instead of carbon tetrabromide, exemplified in the preceding specific examples, such compounds being compounds in which at least three halogen atoms are attached to a terminal carbon atom. e.g., compounds represented by the general formula



wherein each X represents a chlorine, bromine or iodine atom and not all of the x's need be the same; and A represents either

another halogen atom as in CBr_4 , or an alkyl, aryl, aralkyl, aroyl or other aliphatic or aromatic nucleus which may be substituted or unsubstituted. Preferred compounds are the halogen substituted alkanes, such as CBr_4 , $CHBr_3$, CHI_3 , C_2Br_6 , C_2HBr_5 , and aroyl compounds such as $\alpha\alpha$ -tribromoacetophenone.

PROPORTIONS

For each 1,000 parts by weight of N-vinyl monomer the preferred proportions of organic halogen compound are between 500 and 5,000 parts by weight or organic halogen compound and between 0.1 and 2.0 parts by weight of sensitizer.

Having described the invention in accordance with the Patent Statutes it is not intended that it be limited except as may be required by the appended claims.

I claim:

1. A photosensitive composition comprising an intimate mixture consisting essentially of

a. an N-vinyl amine;

b. an organic halogen compound in which at least three halogen atoms are attached to a single carbon atom;

c. a sensitizing amount of at least one visible light sensitizer for said mixture selected from the group consisting of colored 9-vinyl carbazoles, polyacenes, and transannular peroxides of polyacenes; and

d. a synthetic resin film-forming binder in which said constituents are dissolved.

2. The composition of claim 1 in which for each 1,000 parts by weight of N-vinyl amine monomer there are between 500 and 5,000 parts by weight of organic halogen compound and between 0.1 and 2.0 parts by weight of sensitizer.

3. The composition of claim 1 in which the organic halogen compound is one in which at least three bromine atoms are attached to a single carbon atom.

4. The composition of claim 3 in which the organic halogen compound is CBr_4 .

5. The composition of claim 1 in which the N-vinyl amine monomer compound is N-vinyl carbazole.

6. In the process of photopolymerization of N-vinyl amine monomers which comprises exposing an N-vinyl amine monomer to a suitable dose of visible radiation, the improvement which comprises exposing a composition according to claim 1 to said dosage of visible light.

7. The process of claim 8 including in addition the step of heat developing the polymeric image resulting from exposure to visible light by exposing said image to infrared at 130°-150° C.

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