United States Patent [19]

Tiers et al.

[11] **3,916,069**

[45] **Oct. 28, 1975**

[54] **REDUCED STYRYL/CYANINE DYE**

[75] Inventors: **George V. D. Tiers; Joseph A. Wiese, Jr.**, both of St. Paul, Minn.

[73] Assignee: **Minnesota Mining and Manufacturing Company**, St. Paul, Minn.

[22] Filed: **Apr. 2, 1973**

[21] Appl. No.: **347,193**

[52] **U.S. Cl.** **428/411**; 96/1.6; 96/129; 250/475; 260/240.9

[51] **Int. Cl.²** **B41M 5/00**; B41M 5/20

[58] **Field of Search** 96/1.6, 129; 260/240.9; 117/36.7; 250/475

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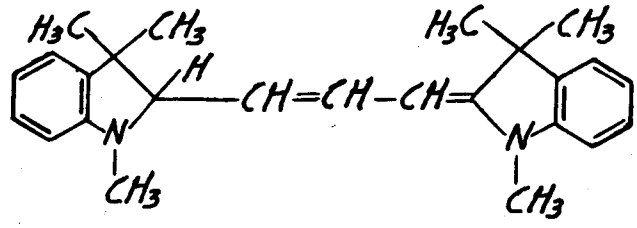
Chemical Berichte, Vol. 65, pages 1737–1742 (1932).

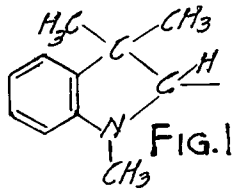
Primary Examiner—Thomas J. Herbert, Jr.
Attorney, Agent, or Firm—Alexander, Sell, Steldt & DeLaHunt

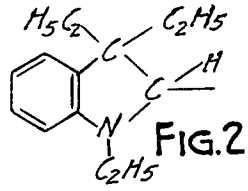
[57] **ABSTRACT**

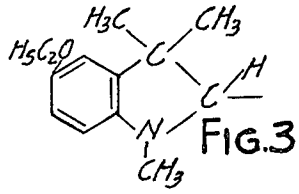
Dihydroheterocyclic amines having a N-hydrocarbyl substitution and a 2-(or 4-) (omega-(nuclearly substituted cyclic)) vinylenyl substitution are described. These compounds are oxidized in an acidic environment to produce styryl and cyanine dyes.

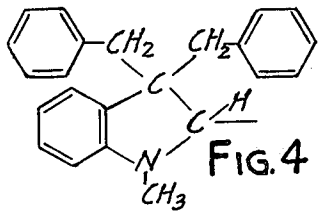
7 Claims, 150 Drawing Figures

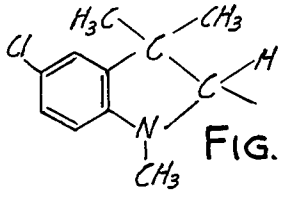


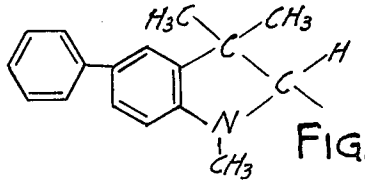

FIG. 1

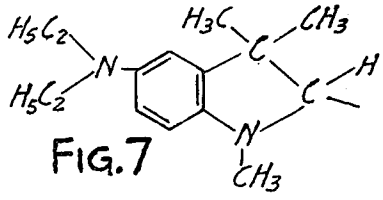

FIG. 2

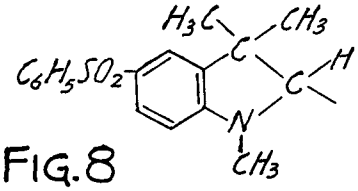

FIG. 3

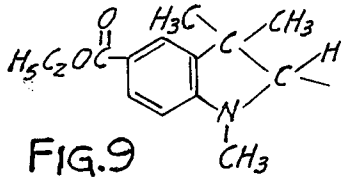

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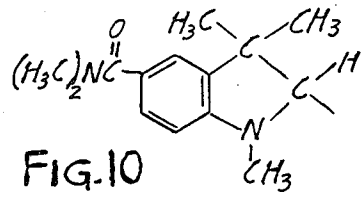

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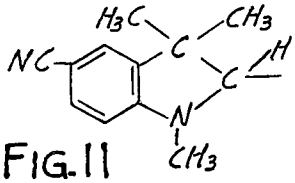

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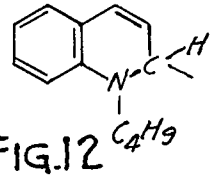

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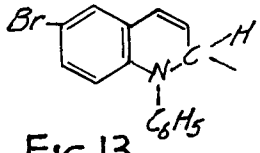

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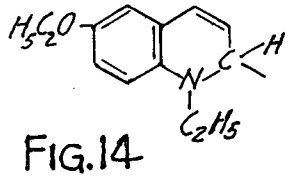

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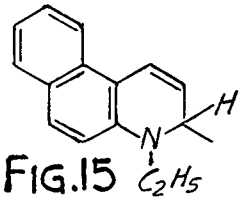

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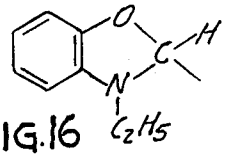

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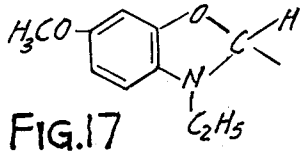

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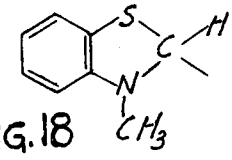

FIG. 13

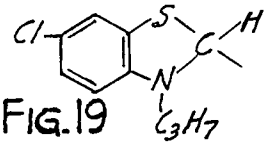

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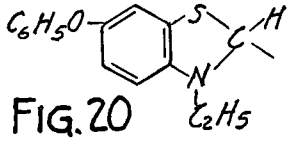

FIG. 15

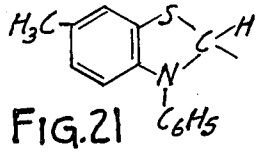

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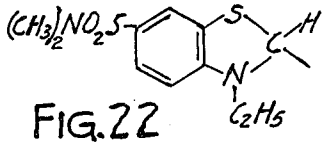

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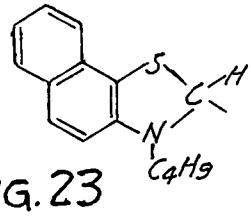

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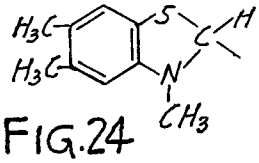

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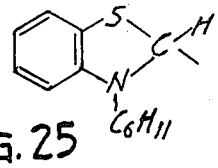

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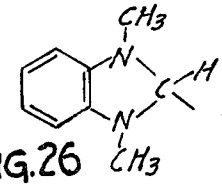

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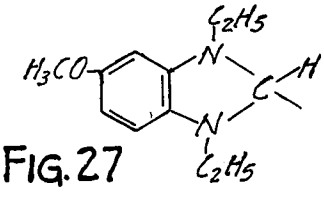

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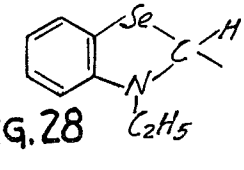

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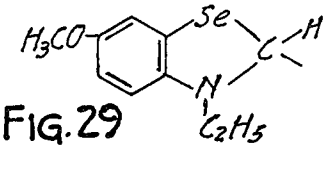

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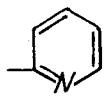


FIG. 30

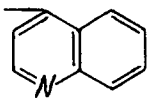


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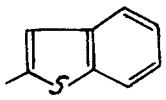


FIG. 32

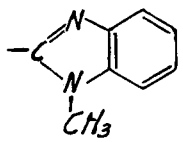


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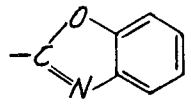


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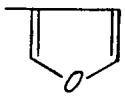


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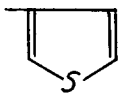


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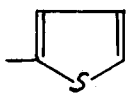


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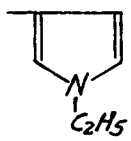


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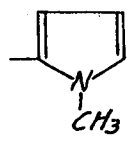


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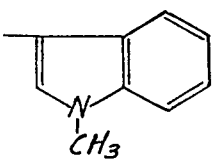


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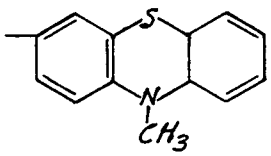


FIG. 41

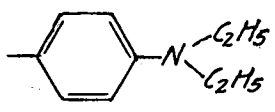


FIG. 42

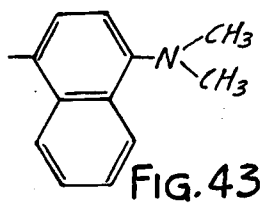


FIG. 43

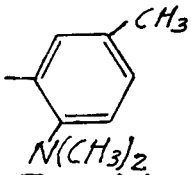


FIG. 44

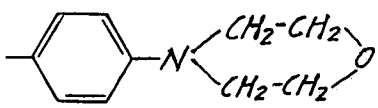


FIG. 45

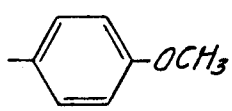


FIG. 46

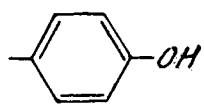


FIG. 47

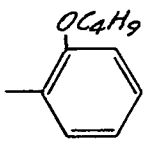


FIG. 46

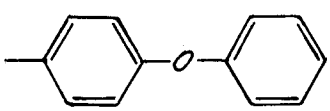


FIG. 49

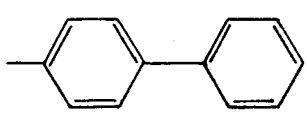


FIG. 50

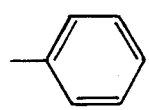


FIG. 51

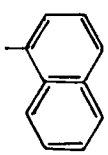


FIG. 52

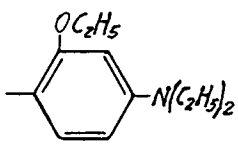


FIG. 53

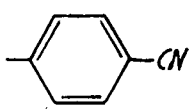


FIG. 54

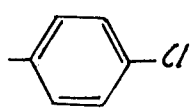


FIG. 55

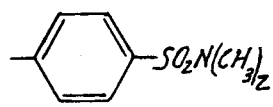


FIG. 56

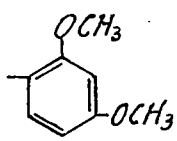


FIG. 57

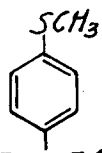


FIG. 58

-CH=

FIG. 59

-CH=CH-CH=

FIG. 60

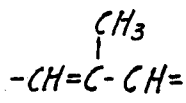


FIG. 61

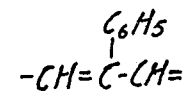


FIG. 62

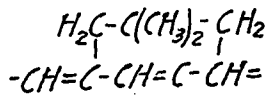


FIG. 63

-CH=CH-CH=CH-CH=

FIG. 64

-CH=CH-CH=CH-CH=CH-CH=

FIG. 65

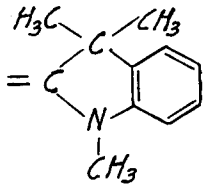


FIG. 66

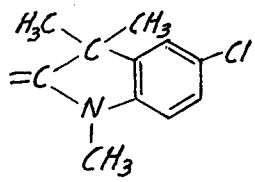


FIG. 67

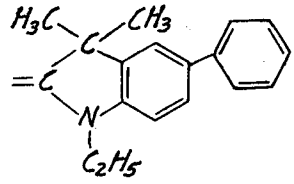


FIG. 68

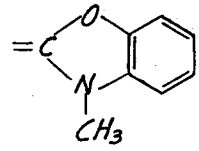


FIG. 69

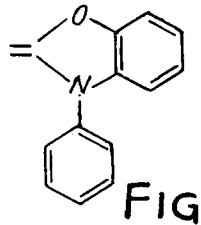


FIG. 70

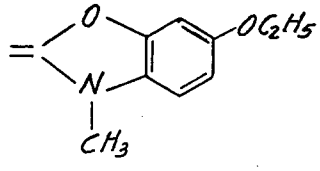


FIG. 71

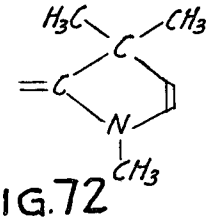


FIG. 72

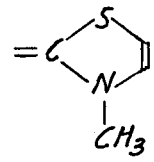


FIG. 73

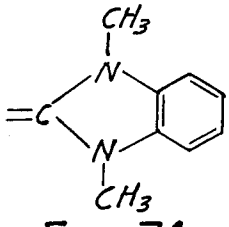


FIG. 74

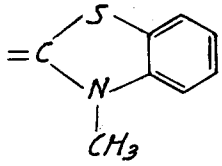


FIG. 75

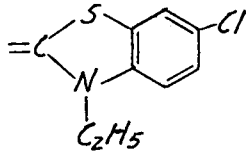


FIG. 76

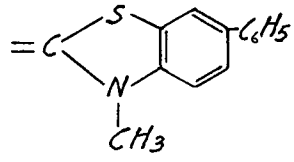


FIG. 77

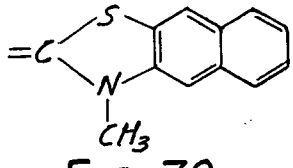


FIG. 78

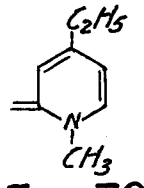


FIG. 79

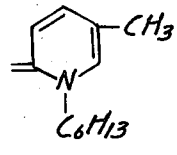


FIG. 80

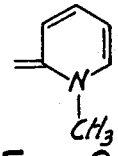


FIG. 81

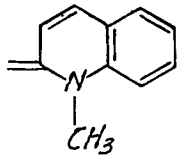


FIG. 82

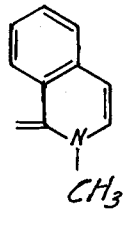


FIG. 83

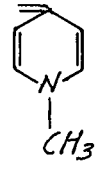


FIG. 84

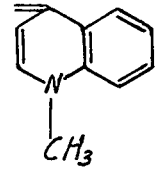


FIG. 85

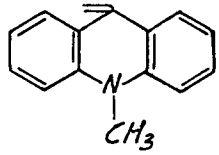


FIG. 86

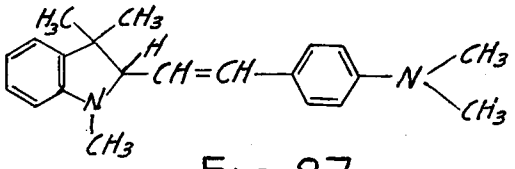


FIG. 87

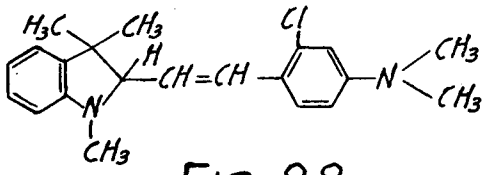


FIG. 88

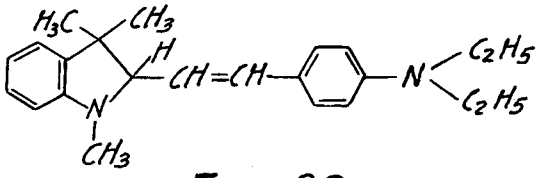


FIG. 89

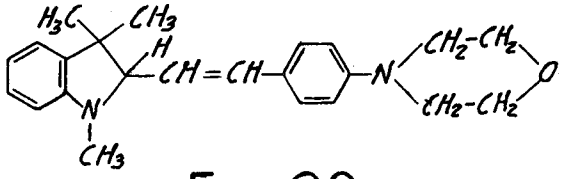


FIG. 90

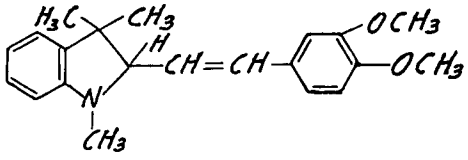


FIG. 91

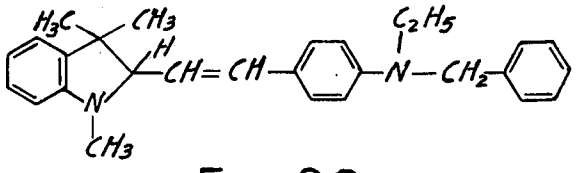


FIG. 92

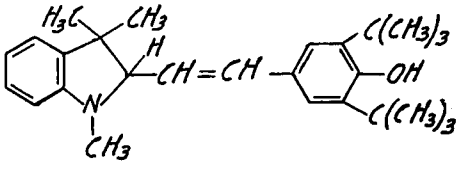


FIG. 93

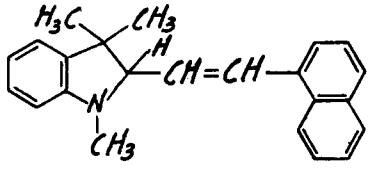


FIG. 94

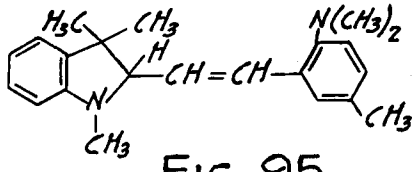


FIG. 95

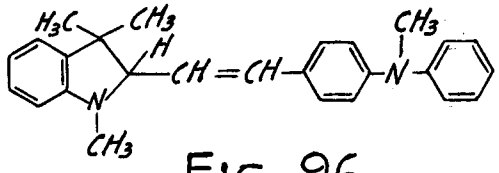


FIG. 96

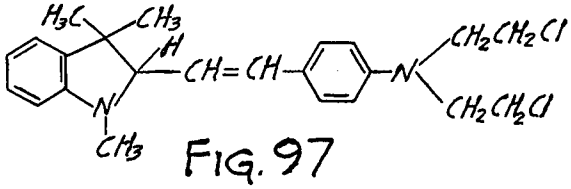


FIG. 97

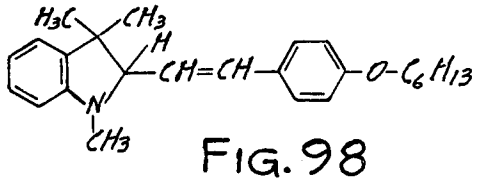


FIG. 98

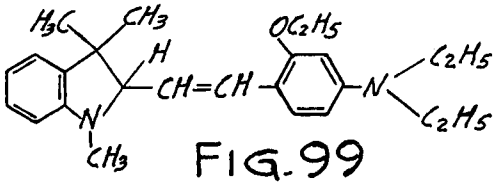


FIG. 99

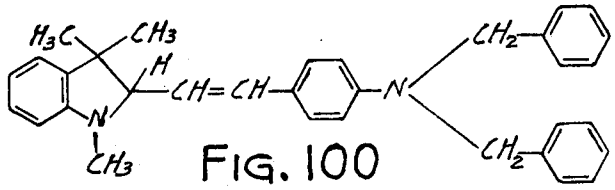


FIG. 100

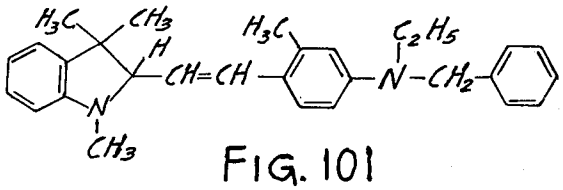


FIG. 101

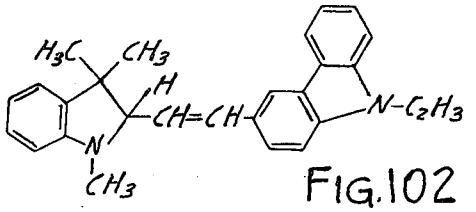


FIG. 102

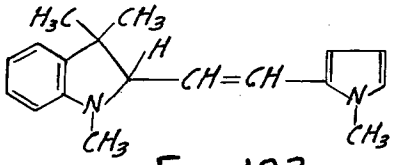


FIG. 103

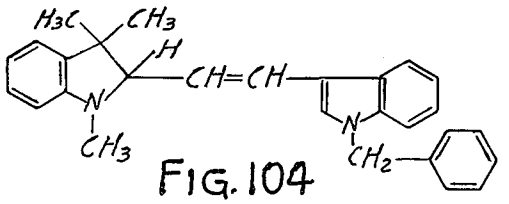


FIG. 104

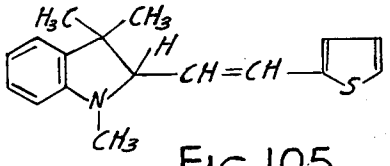


FIG. 105

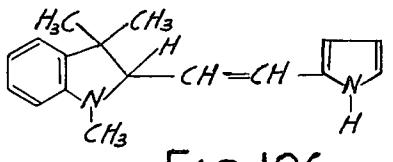


FIG. 106

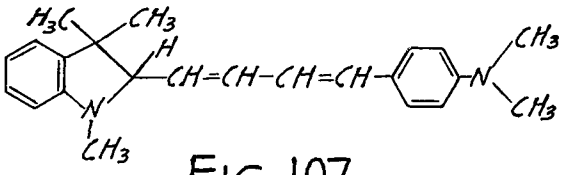


FIG. 107

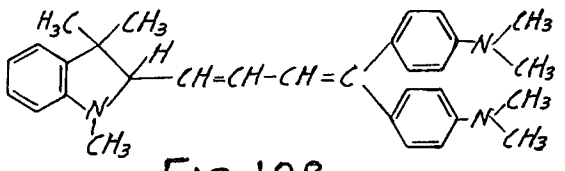


FIG. 108

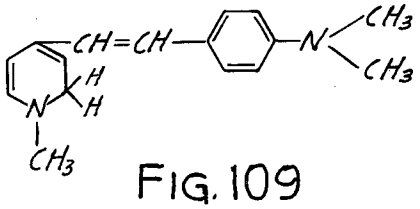


FIG. 109

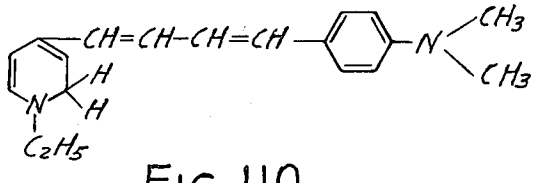


FIG. 110

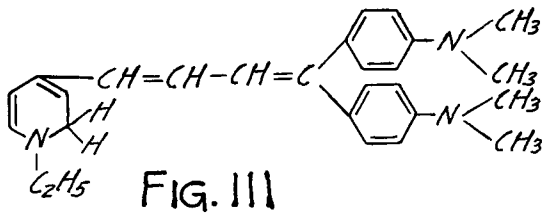


FIG. 111

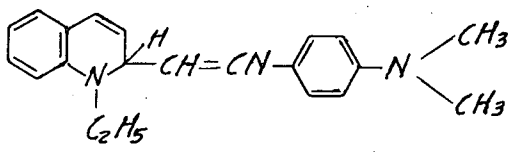


FIG. 112

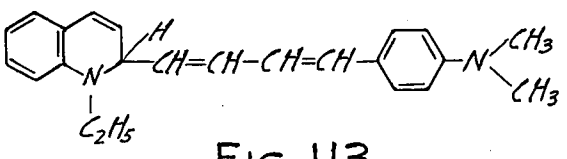


FIG. 113

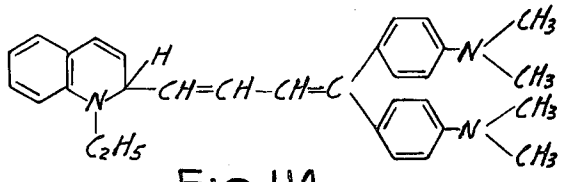


FIG. 114

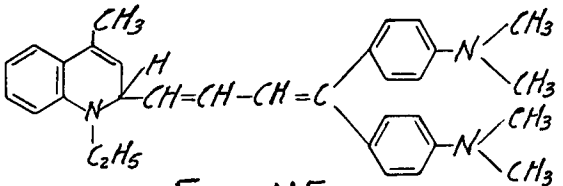


FIG. 115

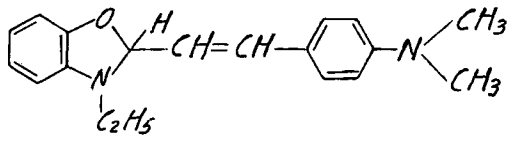


FIG. 116

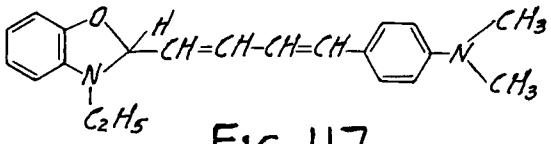


FIG. 117

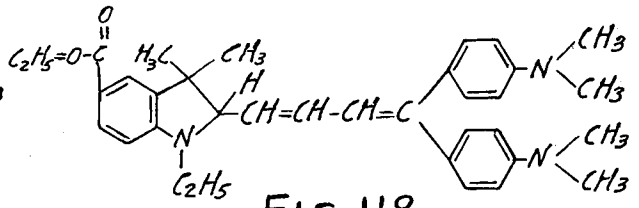


FIG. 118

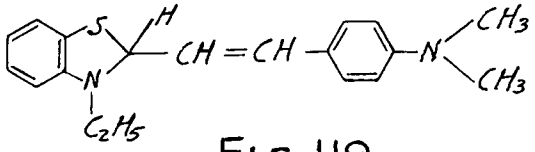


FIG. 119

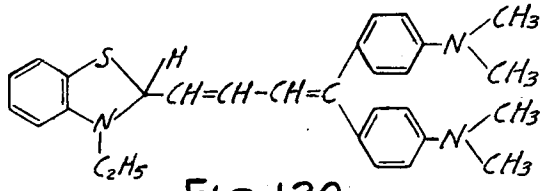


FIG. 120

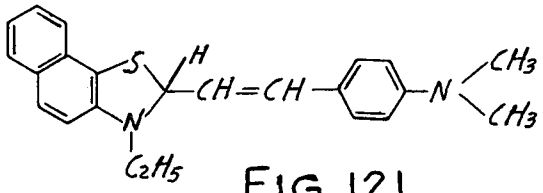


FIG. 121

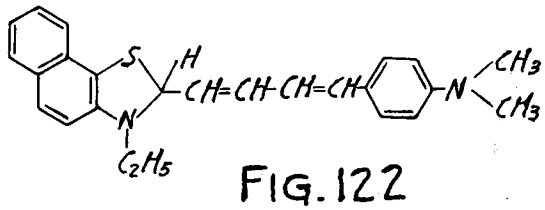


FIG. 122

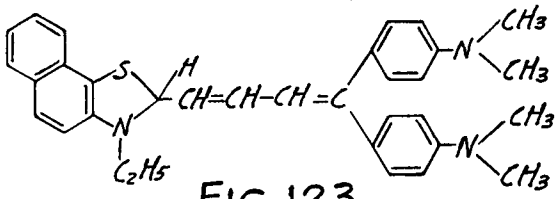


FIG. 123

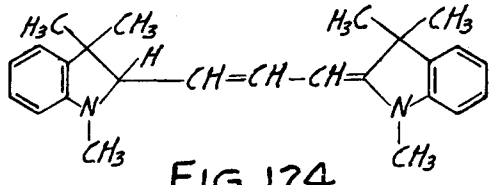


FIG. 124

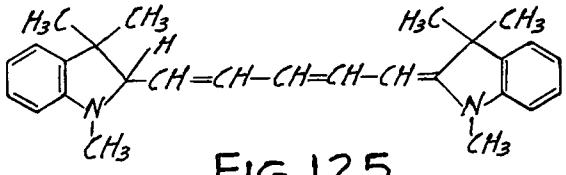


FIG. 125

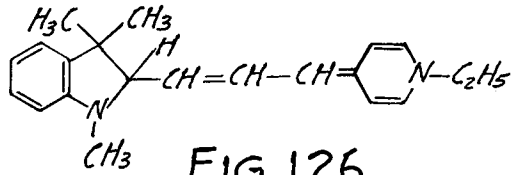


FIG. 126

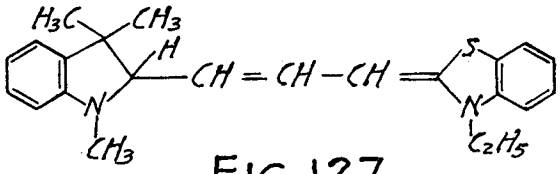


FIG. 127

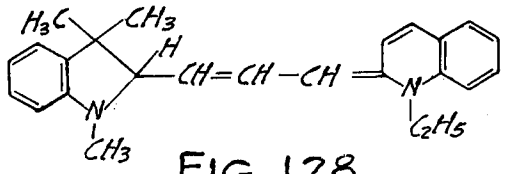


FIG. 128

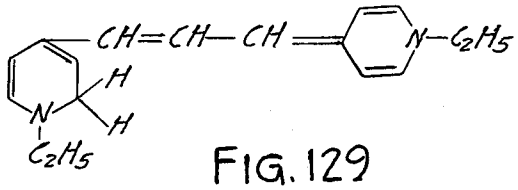


FIG. 129

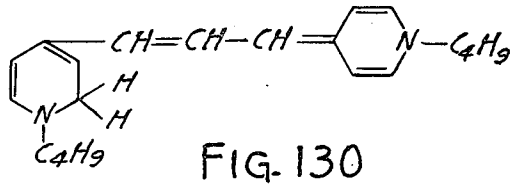


FIG. 130

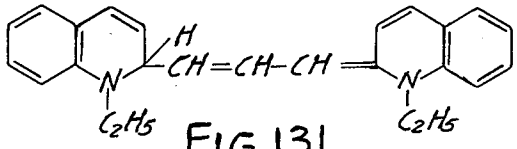


FIG. 131

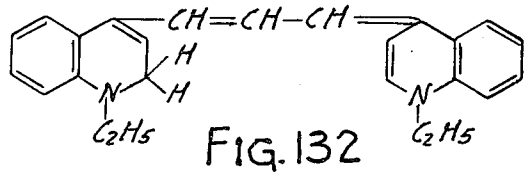


FIG. 132

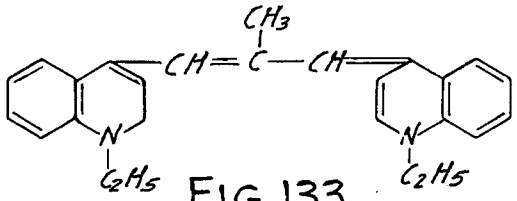


FIG. 133

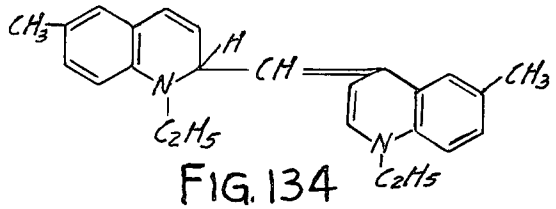


FIG. 134

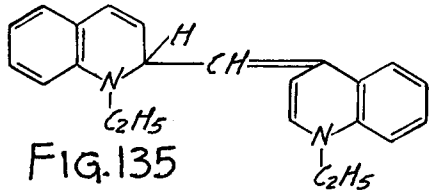


FIG. 135

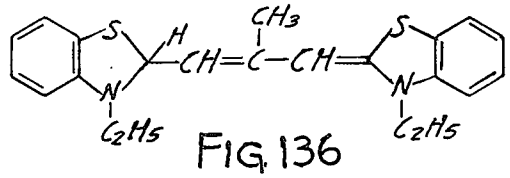


FIG. 136

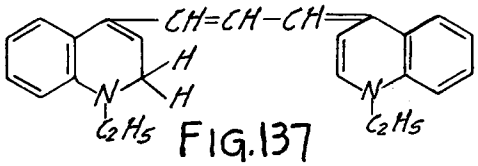


FIG. 137

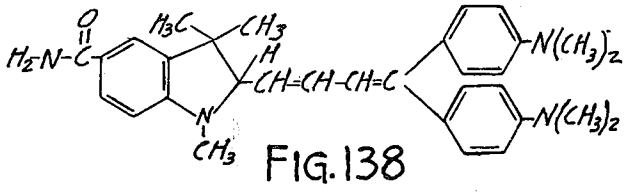


FIG. 138

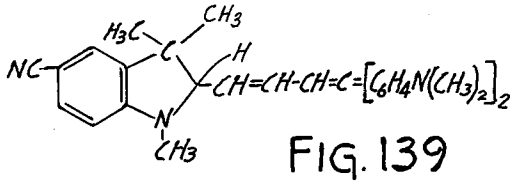


FIG. 139

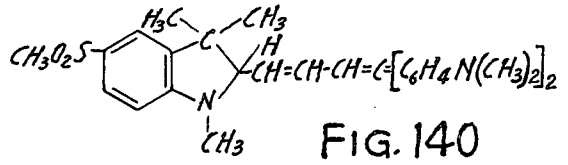


FIG. 140

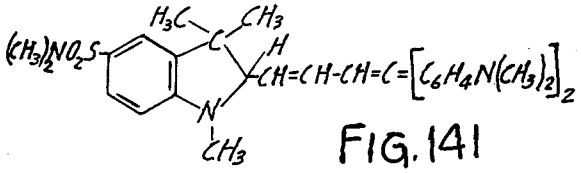


FIG. 141

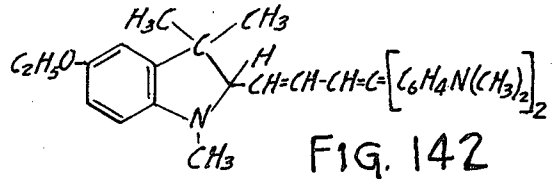


FIG. 142

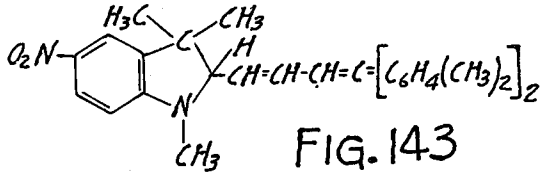


FIG. 143

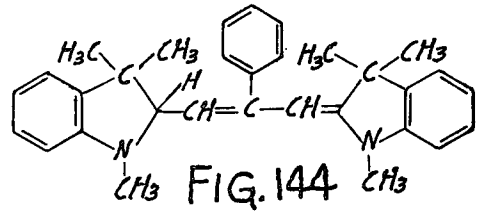
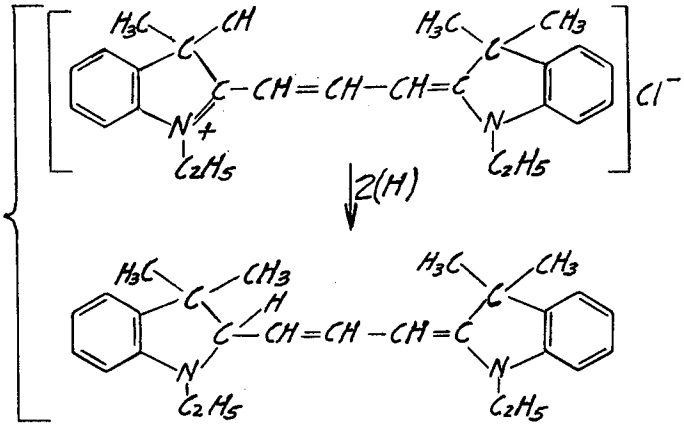


FIG. 144

FIG. 145



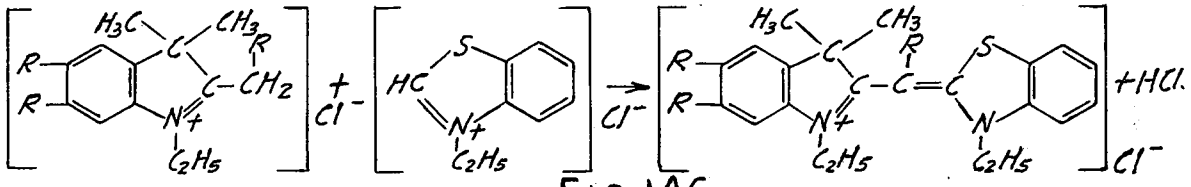


FIG. 146

FIG. 147

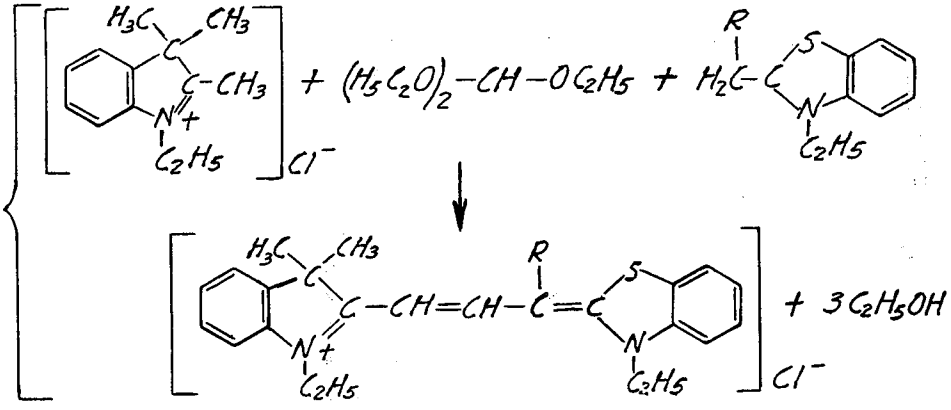
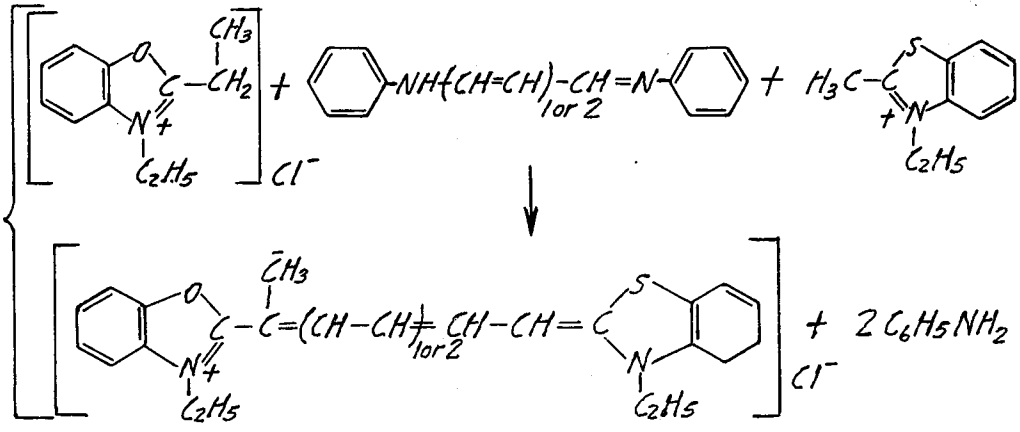


FIG. 148



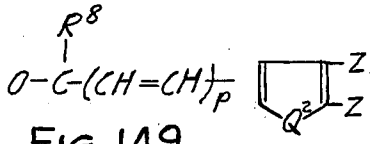


FIG. 149

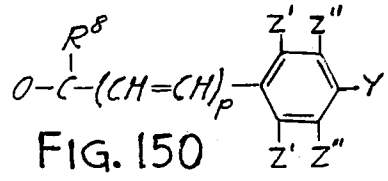


FIG. 150

REDUCED STYRYL/CYANINE DYE

The present invention relates to derivatives of dihydroheterocyclic amines which are N-heterocycles in which the nitrogen and one other member are in a reduced state. More particularly, it relates to N-hydrocarbylsubstituted dihydroheterocyclic amines having a 2-(or 4-) (omega(-nuclearly substituted cyclic)) -vinylenyl substituent and to processes for the preparation of such amines.

The N-hydrocarbyl-substituted dihydroheterocyclic amines of the invention are substantially colorless but when oxidized in an acidic environment yield compounds exhibiting practically any desired color of the visible spectrum depending on the choice of substituents in the molecule. The N-hydrocarbyl-substituted dihydroheterocyclic amines of the invention find utility in radiation-sensitive elements.

Non-silver radiation-sensitive elements in which colored images are produced on exposure of the element to various kinds of radiation have been described. Such elements generally contain one or more color progenitors, which form color on protonation, in combination with an acid progenitor. Thus, in U.S. Pat. Nos. 2,474,084; 2,505,470, and 2,983,756 there are described light-sensitive elements containing as the color progenitor leuco or carbinol bases of tri-phenylmethane or diphenylmethane dyes. These elements produce colorations limited mainly to the blue to green range of the visible spectrum. In U.S. Pat. No. 3,102,810, there are described light-sensitive elements containing as the color progenitor one or more styryl or leuco dye bases. These latter elements produce colorations generally limited to the yellow to red range of the visible spectrum.

Elements containing the above described color progenitors, although providing colors that are generally dense and relatively stable, tend to develop color on storage even in the absence of radiation. Furthermore, the backgrounds of elements that have been imaged tend to deteriorate and to develop color on storage. This is disadvantageous as to the stability of the image.

It has now been found that N-hydrocarbyl dihydroheterocyclic amines having a vinylenyl substituent in the 2-(or 4-) position which has a nuclearly substituted cyclic group in the omega (distal) positions are color progenitors which when oxidized in an acidic or anionogenic environment yield colored products exhibiting practically any desired color of the visible spectrum depending on the choice of additional substituents.

The term "hydrocarbyl" will be understood herein as a monovalent radical of 1 to 10 carbon atoms and hydrogen, including alkyl, cycloalkyl, phenyl and benzyl and including not more than about 60 atomic weight units of the atom elements, O, N, F, Cl or S.

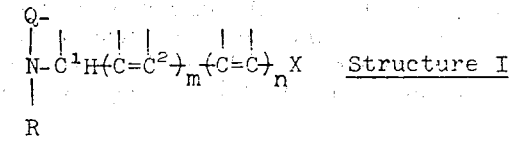
O, N and S may be in chains as hydroxyethyl, ethoxyethyl, dimethyaminoethyl, 3-thia pentyl, or the like or in cyclic structures as morpholino, piperidino, thiazino or the like. Hydrogen atoms are usually simple substituents.

The term dihydroheterocyclic amine refers to a nitrogen heterocycle in which the nitrogen and one other atom (usually adjacent) are in a reduced state as indolenine is related to indole. The term cyclic itself will be understood to refer particularly to fully unsaturated cyclic structures as phenyl, pyridine, pyrrole, furan,

thiophene and that reduced forms will in general be named appropriately.

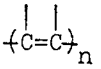
In radiation sensitive elements containing anionogens, these color progenitors are storage stable for all practical purposes indefinitely (i.e., the element does not develop color in areas that have not been exposed to suitable radiation). More specifically, the amines of the invention are essentially colorless N-hydrocarbyl-substituted-2-(or 4-) (omega-(nuclearly substituted cyclic)vinylenyl) dihydroheterocyclic amines. These many frequently be referred to herein as substituted heterocyclic amines or as vinylenyl-substituted heterocyclic amines. They may also be called 2-(or 4-) (omega-(nuclearly substituted cyclic)) vinylenyl N-hydrocarbyl dihydronitrogen heterocycles. On oxidation in an acidic environment, these heterocyclic amines produce styryl or cyanine dyes. A compound mentioned under Beilstein System No. 3493 which is an isomer of a compound of the invention (see FIG. 144) but in which there are no vinylenyl group is found not to give clean colors when subjected to radiation.

The structure of amines of the invention may be represented by Structure I:



Structure I

wherein Q is a divalent radical of 1 to 4 atoms which joins N to C^1 when $m = 1$ or 1, or joins N to C^2 when $m = 1$ and, except for auxochromic substituents and hydrogen, consisting essentially of the nonmetallic atoms necessary to complete a 5 or 6 member dihydroheterocyclic nucleus including at least 1 hydrocarbyl-substituted nitrogen atom; R is hydrocarbyl and preferably is primary alkyl having 1 to 6 carbon stoms;



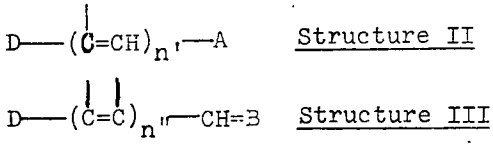
is n vinylenyl groups each composed of two methinyl



groups and providing a conjugated chain of carbon atoms joined by alternating double and single bonds; m is 0 or 1; n is an integer from 1 to 3; and X is a member, unsubstituted or substituted by an auxochromic substituent, of the group consisting of phenyl, 5 to 6 member heterocyclic nuclei, or a chian of 2 to 4 atoms including 1 to 2 hetero atoms as no more than one half the total atoms of said chain, which chain taken together with one or the other of the two closest methinyl groups forms a 5 to 6 member heterocyclic nucleus and otherwise unused valences of C, C^1 or C^2 are attached to H except that not more than one may be attached to phenyl or not more than two may be attached to alkyl of 1–6 carbon atoms. The auxochromic substituents on phenyl or heterocyclic nuclei include aryl, alkyl, dialkylamino, dialkylsulfonamido, alkylsulfonyl, arylsulfonamido, alkoxy, aryloxy, nitro, cyano, alkoxycarbonyl and halogen as well as divalent benzo or naphthaleno groups, but any group which is compatible with synthetic methods employed and influences the absorption spectrum of the oxidized compound may be em-

ployed. It is convenient to designate the two methinyl groups nearest the X group which form a vinylenyl group as the proximal and anteproximal methinyl groups. With respect to the dihydroheterocyclic nucleus they are respectively distal and antedistal or ultimate and penultimate.

The substituted dihydroheterocyclic amines of the invention have a dihydroheterocyclic nucleus joined at its 2- or 4- position to an auxochromically substituted cyclic nucleus either directly or through divalent linking chain of 1 to 5 methinyl groups. These amines may be represented by two general structures depending on whether there is an odd or even number of methinyl groups in the linking chain;

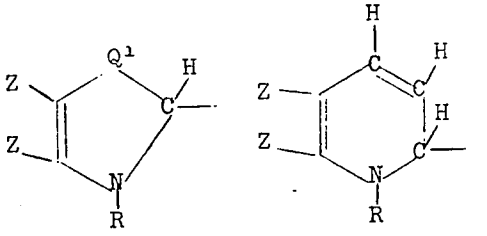


Structure II

or

Structure III

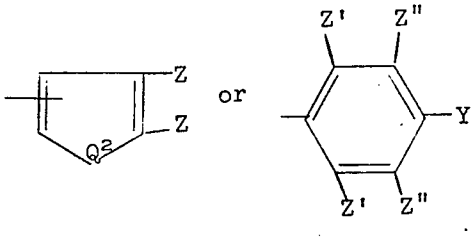
In Structures II and III, n' is an integer from 1 – 3 and n'' is 0 to 3 and D is a dihydroheterocyclic nucleus, represented by one or the other of the structural variations shown as Structure IV. The free valences in the vinylenyl groups are usually attached to H but one may be attached to hydrocarbyl, preferably methyl, ethyl or phenyl.



Structure IV

In Structure IV, R is hydrocarbyl and preferably primary alkyl of 1 – 6 carbon atoms, Q^1 is CR^1R^1, S, O, Se, or NR in which each R^1 is H or hydrocarbyl selected from the group consisting of alkyl or 1 to 6 carbon atoms, phenyl and benzyl and preferably is methyl and the two Z groups may be individually hydrogen atoms or together may be either a benzo- or naphtho- substituent with or without auxochromic substituents as described above.

In Structure II, A is a monovalent cyclic nucleus having one of the structural variations designated as Structure V.



Structure V

In structure V, R and the two Z's are as defined above, Q^2 is O, S, Se, NH or NR; Y is H, Cl, F, alkyl of 1 – 6 carbon atoms OH, OR^2, or NR^3R^4;

Z' is H, Cl, F, alkyl of 1 – 6 carbon atoms, OR^5 or NR_2^5;

Z'' is H, Cl, F, alkyl of 1 – 6 carbon atoms or OR^5;

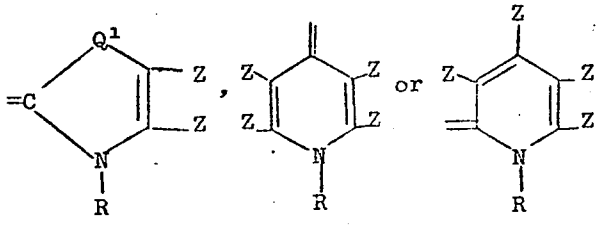
Z' and adjacent Z'' taken together can be benzo or naphtho with or without auxochromic substituents;

R^2 is alkyl of 1 – 6 carbon atoms;

R^5 is methyl or ethyl;

R^3 and R^4 are independently hydrocarbyl or taken together with an adjacent Z'' each can be independently 1,2-ethylene, 1,3-propylene or 1,2-phenylene or in conjunction with each other can form a 5 to 6 membered ring including not more than one oxygen or one additional nitrogen.

In Structure III, B is a divalent heterocyclic nucleus having the structure:



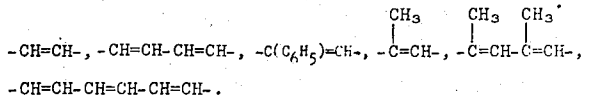
Structure VI

wherein R, Q^1 and the two Z's are as defined above.

Examples of suitable dihydroheterocyclic nuclei or radicals (Structures IV) that may be present in the substituted dihydroheterocyclic amine of the invention include those shown in FIGS. 1 to 29 inclusive, wherein the names of the respective structures are:

FIG.	Name
1	1,3,3-trimethyl-2,3-dihydro-2-indolyl
2	1,3,3-triethyl-2,3-dihydro-2-indolyl
3	5-ethoxy-1,3,3-trimethyl-2,3-dihydro-2-indolyl
4	1-methyl-3,3-dibenzyl-2,3-dihydro-2-indolyl
5	5-chloro-1,3,3-trimethyl-2,3-dihydro-2-indolyl
6	5-phenyl-1,3,3-trimethyl-2,3-dihydro-2-indolyl
7	5-diethylamino-1,3,3-trimethyl-2,3-dihydro-2-indolyl
8	5-benzene sulfonyl-1,3,3-trimethyl-2,3-dihydro-2-indolyl
9	5-ethoxycarbonyl-1,3,3-trimethyl-2,3-dihydro-2-indolyl
10	5-dimethylamino carbonyl-1,3,3-trimethyl-2,3-dihydro-2-indolyl
11	5-cyano-1,3,3-trimethyl-2,3-dihydro-2-indolyl
12	N-butyl-1,2-dihydro-2-quinolyl
13	6-bromo-1-phenyl-1,2-dihydro-2-quinolyl
14	6-ethoxy-1-ethyl-1,2-dihydro-2-quinolyl
15	1-ethyl-1,2-dihydro-2-(5,6-benzo)-quinolyl
16	3-ethyl-2,3-dihydro-2-benzoxazolyl
17	6-methoxy-3-ethyl-2,3-dihydro-2-benzoxazolyl
18	3-methyl-2,3-dihydro-2-benzothiazolyl
19	6-chloro-3-n-propyl-2,3-dihydro-2-benzothiazolyl
20	6-phenoxy-3-ethyl-2,3-dihydro-2-benzothiazolyl
21	6-methyl-3-phenyl-2,3-dihydro-2-benzothiazolyl
22	6-dimethylaminosulfonyl-3-ethyl-2,3-dihydro-2-benzothiazolyl
23	3-butyl-2,3-dihydro-2[2,1,d]-naphththothiazolyl
24	3,5,6-trimethyl-2,3-dihydro-2-benzothiazolyl
25	3-cyclohexyl-2,3-dihydro-2-benzothiazolyl
26	1,3-dimethyl-1,2-dihydro-2-benzimidazolyl
27	5-methoxy-1,3-diethyl-1,2-dihydro-2-benzimidazolyl
28	3-ethyl-2,3-dihydro-2-benzoselenazolyl
29	6-methoxy-3-ethyl-2,3-dihydro-2-benzoselenazolyl

The substituted dihydroheterocyclic nuclei D, of Structures IV, exemplified in FIGS. **1 – 29,** are attached to cyclic nucleus A (cf. Structure II) by a divalent bond or a divalent chain having 2, 4, or 6 methinyl or substituted groups, including as examples:



$-CH=CH-$, $-CH=CH-CH=CH-$, $-C(C_6H_5)=CH-$, $-\overset{CH_3}{\underset{|}{C}}=CH-$, $-\overset{CH_3}{\underset{|}{C}}=CH-\overset{CH_3}{\underset{|}{C}}=CH-$,

$-CH=CH-CH=CH-CH=CH-$.

Examples of suitable nuclei A, Structure V heterocyclic radicals include those shown in FIGS. **30** to **58** inclusive wherein the names associated with the respective structures are:

FIG.	Name
30	2-pyridyl
31	4-quinolyl
32	2-benzothienyl
33	1-methyl-2-benzimidazolyl
34	2-benzoxazolyl
35	3-furyl
36	3-thienyl
37	2-thienyl
38	1-ethyl-3-pyrryl
39	1-methyl-2-pyrryl
40	1-methyl-3-indolyl
41	10-methyl-7-phenothiazinyl
42	4-diethylamino-phenyl
43	4-dimethylamino-α-naphthyl
44	2-dimethylamino-5-methyl-phenyl
45	4-morpholinyl-phenyl
46	p-anisyl
47	p-hydroxyphenyl
48	o-butoxyphenyl
49	p-phenoxy-phenyl
50	biphenylyl
51	phenyl
52	α-naphthyl
53	2-ethoxy-3-(diethylamino)-phenyl
54	p-cyanophenyl
55	p-chlorophenyl
56	p-dimethylamino-sulfonyl
57	2,4-dimethoxyphenyl
58	p-thioanisyl

The substituted dihydroheterocyclic nuclei of Structures IV, exemplified in FIGS. **1 – 29,** are attached to Structures VI heterocycles by a trivalent chain with two points for attachment having 1, 3, 5, or 7 methinyl groups, i.e., have a monovalent and divalent end; as shown in FIGS. **59** through **65** inclusive wherein the names associated with the structures of the respective figures are:

FIG.	Name
59	methinyl
60	prop-1-en-1-yl-3-ylidene
61	2-methylprop-1-en-1-yl-3-ylidene
62	2-phenylprop-1-en-1-yl-3-ylidene
63	1,3-(2′,2′-dimethylpropano)-penta-1,3-dien-1-yl-5-ylidene
64	penta-1,3-dien-1-yl-5-ylidene
65	hepta-1,3,5-trien-1-yl-7-ylidene

Examples of suitable Structures VI heterocycles include those shown in FIGS. **66** to **86** which will be seen to be similar in structure to those of FIGS. **1 – 29** except that they have two valences to a single carbon atom. This is reflected in the names which for the structures of the FIGS. **66 – 86** are given below.

FIG.	Name
66	1,3,3-trimethyl-1,2-dihydro-2-indolylidene
67	5-chloro-1,3,3-trimethyl-1,2-dihydro-2-indolylidene
68	5-phenyl-1-ethyl-3,3-dimethyl-2,2-dihydro-2-indolylidene
69	3-methyl-2,3-dihydro-2-oxazolylidene
70	3-phenyl-2,3-dihydro-2-oxazolylidene
71	6-ethoxy-3-methyl-2,3-dihydro-2-oxazolylidene
72	1,3,3-trimethyl-2,3-dihydro-2-pyrrylidene
73	3-methyl-2,3-dihydro-2-thiazylidene
74	1,3-dimethyl-1,2-dihydro-2-benzimidazolylidene
75	3-methyl-2,3-dihydro-2-benzothiazolylidene
76	6-chloro-3-ethyl-2,3-dihydro-2-benzothiazolylidene
77	6-phenyl-3-methyl-2,3-dihydro-2-benzothiazolylidene
78	3-methyl-2,3-dihydro-2-naphthothiazolylidene
79	1-methyl-4-ethyl-1,2-dihydro-2-pyridylidene
80	1-n-hexyl-5-methyl-1,2-dihydro-2-pyridylidene
81	1-methyl-1,2-dihydro-2-pyridylidene
82	1-methyl-1,2-dihydro-2-quinolylidene
83	2-methyl-1,2-dihydro-1-isoquinolylidene
84	1-methyl-1,4-dihydro-4-pyridylidene
85	1-methyl-1,2-dihydro-4-quinolylidene
86	10-methyl-9,10-dihydro-9-acridinylidene

As described by the general structures of the vinylenyl-substituted heterocyclic amines of the invention have two or three structural parts illustrated in part in FIGS. **1 – 86.** Illustrations of these structures are provided in FIGS. **87** through **144** the names of the respective compounds of which are given below.

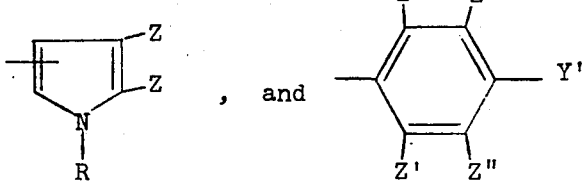
FIG.	Name
87	2-(4-(dimethylamino)styryl)-1,3,3-trimethylindoline
88	2-(2-chloro-4-dimethylaminostyryl)-1,3,3-trimethyl-indoline
89	2-(4-diethylaminostyryl)-1,3,3-trimethylindoline
90	2-(4-morpholinostyryl)-1,3,3-trimethylindoline
91	2-(3,4-dimethoxy styryl)-1,3,3-trimethylindoline
92	(2-(4-(ethylbenzylamino)styryl)-1,3,3-trimethylindoline
93	2-(3,5-di-t-butyl-4-hydroxystyryl)-1,3,3-trimethyl-indoline
94	2-(2,3-benzostyryl)-1,3,3-trimethylindoline
95	2-(2-dimethylamino-5-methyl-styryl)-1,3,3-trimethylindoline
96	2-(4-(phenylmethylamino)styryl)-1,3,3-trimethyl-indoline
97	2-(4-bis(2-chloroethyl)amino styryl)-1,3,3-trimethylindoline
98	2-(4-hexyloxystyryl)-1,3,3-trimethylindoline
99	2-(2-ethoxy-4-diethylaminostyryl)-1,3,3-trimethyl-indoline
100	2-(4-dibenzylaminostyryl)-1,3,3-trimethylindoline
101	2-(2-methyl-4-(benzylethylamino)styryl)-1,3,3-trimethylindoline
102	2-(2-(9-ethyl-3-carbazolyl)ethenyl)-1,3,3-trimethyl-indoline

-continued

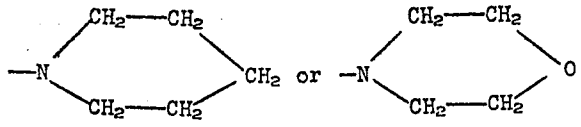
FIG.	Name
103	2-(2-(N-methyl-2-pyrryl)ethenyl)-1,3,3-trimethyl-indoline
104	2-(2-(N-benzyl-3-indolyl)ethenyl)-1,3,3-trimethyl-indoline
105	2-(2-thienyl-ethenyl)-1,3,3-trimethylindoline
106	2-(2-pyrryl-ethenyl)-1,3,3-trimethylindoline
107	2-(4-(4-dimethylaminophenyl)butadienyl-1,3,3-trimethylindoline
108	2-(4,4-bis(4-dimethylaminophenyl) butadienyl)-1,3,3-trimethylindoline
109	4-(4-dimethylaminophenyl-styryl)-N-ethyl-1,2-dihydro-pyridine
110	4-(4-(4-dimethylaminophenyl)butadienyl)-N-ethyl-1,2-dihydropyridine
111	4-(4,4-bis(4-dimethylaminophenyl)butadienyl)-N-ethyl-1,2-dihydropyridine
112	2-(4-dimethylaminostyryl)-N-ethyl-1,2-dihydro-quinoline
113	2-(4-(4-dimethylaminophenyl)butadienyl)-N-ethyl-1,2-dihydroquinoline
114	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-N-ethyl-1,2-dihydroquinoline
115	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-4-methyl-N-ethyl-1,2-dihydroquinoline
116	2-(4-dimethylaminophenyl)styryl-N-ethyl-2,3-dihydro-benzoxazole
117	2-(4-(4-dimethylaminophenyl)butadienyl)-N-ethyl-2,3-dihydro-benzoxazole
118	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-N-ethyl-5-carbethoxy-3,3-dimethyl-indoline
119	2-(4-dimethylaminophenyl)-styryl-N-ethyl-2,3-dihydro-benzothiazole
120	2(4-bis(4-dimethylaminophenyl)butadienyl)-N-ethyl-2,3-dihydrobenzothiazole
121	2-(4-dimethylamino styryl)-N-ethyl-2,3-dihydro-naphthothiazole
122	2-(4-(4-dimethylaminophenyl)butadienyl-N-ethyl-2,3-dihydronaphthothiazole
123	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-N-ethyl-2,3-dihydronaphthothiazole
124	2-(3(1,3,3-trimethylindolylidene-2)prop-1-enyl-1)-1,3,3-trimethylindoline
125	2-(5-(1,3,3-trimethylindolylidene-2)penta-1,3-dienyl-1)-1,3,3-trimethylindoline
126	2-(3-(N-ethyl-1,4-dihydropyridylidene-4)prop-1-enyl-1)-1,3,3-trimethylindoline
127	2-(3-(N-ethyl-2,3-dihydrobenzothiazoylidene-2)-prop-1-enyl-1)-1,3,3-trimethylindoline
128	2-(3-(N-ethyl-2,3-dihydroquinolylidene-2)prop-1-enyl-1)-1,3,3-trimethylindoline
129	4-(3(N-ethyl-1,4-dihydropyridylidene-4)prop-1-enyl-1)-N-ethyl-1,2-dihydropyridine
130	4-(3(N-butyl-1,4-dihydropyridylidene-4)prop-1-enyl-1)-N-butyl-1,2-dihydropyridine
131	2-(3-(N-ethyl-1,2-dihydroquinolylidene-2)prop-1-enyl-1)-N-ethyl-1,2-dihydroquinoline
132	4-(3-(N-ethyl-1,4-dihydroquinolylidene-4)prop-1-enyl-1)N-ethyl-1,2-dihydroquinoline
133	4-(3-(N-ethyl-1,4-dihydroquinolydidene-4)2-methyl prop-1-enyl-1)-N-ethyl-1,2-dihydroquinoline
134	2-(6-methyl-N-ethyl-1,4-dihydroquinolylidene)-4)-methinyl)-6-methyl-N-ethyl-1,2-dihydroquinoline
135	2-(N-ethyl-1,4-dihydroquinolyidene-4) methinyl-N-ethyl-1,2-dihydroquinoline
136	2-(3-(N-ethyl-2,3-dihydrobenzothiazolylidene-2)-2-methyl-prop-1-enyl-1)-N-ethyl-2,3-dihydrobenzo-thiazole
137	4-(3-(N-ethyl-1,4-quinolylidene-4)-prop-1-enyl-1)-N-ethyl-1,2-dihydroquinoline
138	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-1,3,3-trimethyl-5-carbonamidoindoline
139	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-1,3,3-trimethyl-5-cyanoindoline
140	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-1,3,3-trimethyl-5-methylsulfonylindoline
141	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-1,3,3-trimethyl-5-dimethylsulfonamidoindoline
142	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-1,3,3-trimethyl-5-ethoxyindoline
143	2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-1,3,3-trimethyl-5-nitroindoline
144	2-(3- 1,3,3-trimethylindolinylidene)-2-phenyl prop-1-enyl-1)-1,3,3-trimethylindoline

The preferred substituted dihydroheterocyclic amines are those amines which are defined as N-(lower alkyl)-substituted-2-(or 4-) [(omega-dihydrocarbyl-aminocyclic)-vinylenyl]dihydroheterocyclic amines. These substituted dihydroheterocyclic amines are preferred because on acid oxidation they yield dyes having deep tinctorial strength, i.e., a 1 mil (25 micron) thick resin coating containing 1 part by weight of dye per 10

parts by weight of colorless resin has an optical density of at least 1. Because of their stability toward adventitious discoloration, the preferred dihydroheterocyclic amines of the invention are those of Structure III above with 5 membered rings and particularly where Q^1 is $-C(CH_3)_2$ and the dyes of Structure II above wherein cyclid nucleus A has the Structures V as follows:



wherein Q^1, R, Z, Z', Z'' are as defined above and Y' is NR^6R^7,



wherein R^6 and R^7 are hydrocarbyl.

The substituted dihydro-heterocyclic amines of the invention are conveniently prepared by the reduction of a corresponding dye. Thus, the substituted dihydroheterocyclic amines of Structure II are obtained by the reduction of styryl dyes and the amines of Structure III by the reduction of cyanine dyes as is illustrated for the reduction of a cyanine dye in FIG. **145** which shows the formation of 2-(3-(1-ethyl-3,3-dimethylindolylidene-2)prop-1-enyl-1)-1-ethyl-3,3-dimethylindoline from the indolinium chloride.

The cyanine dyes which are precursors to the substituted heterocyclic amines (Structures III) of the invention are readily available. Some can be purchased commercially and all are readily prepared by procedures that are well known in the art (see, for example, *Cyanine Dyes and Related Compounds*, Hamer, Interscience Publishers (1964)). Those cyanine dyes having a single methine group joining the quaternized heterocycle and a heterocyclic nucleus, the methincyanines are prepared, among other ways, by the condensation of an N-heterocyclic quaternary salt having a reactive methylene group in the 2-position with a quaternary salt of N-heterocyclic compound as shown in Equation 2 in FIG. 146.

The carbocyanine or trimethincyanine dyes are prepared by the condensation of a methine group former such as ethylorthoformate with two equivalents of a single N-heterocyclic quaternary salt having a reactive group in the 2-position to obtain a symmetrical carbocyanine dye or first with one equivalent of one such salt and then one equivalent of another such salt to obtain unsymmetrical carbocyanine dyes such as is shown in Equation 3, in FIG. **147.**

Pentamethincyanine and higher methinecyanine dyes are prepared in a manner similar to the carbocyanine dyes by substituting the methine group-former i.e., ethyl orthoformate, with a polymethine group former such as 1-anilino-3-aniloprop-1ene-or 1-anilino-5-anilopenta-1,3-dine, as Equation 4 illustrated in FIG. **148.**

The styryl dyes are also readily avialble. They may be prepared by procedures well known in the art. Thus, styryl dyes which are precursors for the substituted heterocyclic amines of Structure II may be prepared in one procedure by condensation of an N-heterocyclic quaternary salt having a reactive group in the 2-position with aldehydes or ketones having the structures of FIGS. **149** and **150** wherein Z,Z', Z'', Y', and Q^2 are as defined before; *p* is 0 to 3; and R^8 represents substituents such as hydrogen, methyl or phenyl that may be on the vinylene chain.

The reduction of polymethine dyes to the substituted heterocyclic amines of the invention as is illustrated in FIG. **145** is accomplished using any reducing agent having sufficient reducing power. A reducing agent has sufficient reducing power if, when added to a solution of the dye, it will discharge the dye color from the solution. One generally useful reducing agent is sodium borohydride. The reduction of the polymethine dyes is carried out by the addition of the selected reducing agent in small portions to a solution of the dye in a solvent at a temperature of from about 0° to 50° C. allowing sufficient time between additions for the reducing agent to react before the next portion is added. No additional reducing agent is added after color is completely discharged from the dye solution. Preferably, the temperature is maintained at from about 15° to 30° C. in which range the reaction usually proceeds rapidly but with minimization of any tendency for the reduction of unsaturation in the dye molecule other than at the quaternized nitrogen. In producing the amine of the invention, sufficient reducing agent is required to provide 2 atoms of hydrogen per molecule of dye. Lesser amounts may be used where the dye is not pure and greater amounts may be required in some instances in a range of from about 1.8 to about 4 atoms of hydrogen per molecule of dye. It is desirable that the dye be of sufficient purity that the color is discharged after the addition of sufficient reducing agent to provide 1.9 to 2.1 atoms of hydrogen per molecule of dye.

Solvents in which the reaction may be carried out are those solvents in which the dyes are soluble and which are not reduced by the reducing agent at a rate appreciably faster than are the dyes. Examples of such solvents include water, aqueous alcohol, methanol, ethanol, acetone (the dyes reduce faster than does acetone) isopropanol, and the like. Generally, from 10 to 100 parts by volume of solvent per part by weight of dye is used depending on the solubility of the particular dye. It is often advantageous to carry out the reduction in a mixture of water and a water-immiscible solvent such as, for example, benzene, toluene, methylene chloride or chloroform because the amine is generally more soluble in the water-immiscible solvent.

The reduction is complete when color has been discharged from the dye solution. This generally required from a minute or so to 3 or more hours depending on the amount and solubility of dye being reduced as well as on the solubility of the reducing agent and whether it is liquid or solid. Although quantities of several grams of dye in water may be reduced in a few minutes by aqueous solutions of sodium borohydride, quantities of 10 kg or more of dye may require 3 or more hours with the same reducing agent. Because the reaction is exothermic, it is advantageous to cool the reaction.

In addition to sodium borohydride, mentioned above as a reducing agnet, suitable reducing agents include tetramethyl ammonium borohydride, sodium hydride,

sodium amalgam, aluminum hydride, lithium aluminum hydride, sodium in alcohol, stannous chloride in alcohol, zinc and alcoholic hydrochloric acid, amalgamated tin and hydrochloric acid (care must be taken to exclude oxygen during the reaction and then to neutralize the acid with base immediately following the reaction). Some of these must be used under anhydrous conditions. Electrochemical reduction is also a suitable procedure.

Following the reduction reaction, the solution of crude substituted heterocyclic amine, if in a nonaqueous solvent, is conveniently diluted with water and extracted with several portions of a water insoluble solvent such as benzene, toluene, dipropylether, chloroform, methylene chloride, or the like. Methylene chloride is found to be especially convenient. The crude amine is recovered from the combined extracts and purified by recrystallization or by liquid chromatography.

The substituted heterocyclic amines of the invention find use in nonsilver photosensitive compositions and in elements or constructions utilizing these compositions which print out an image directly on exposure to suitable radiation. Such compositions generally comprise at least one amine of the invention, an acid progenitor or anionogen in a suitable binder. An anionogen is a compound which is stable when exposed to normal room light, is soluble in the binder system, and provides an anion when exposed to a source of energy such as an electron beam. In a preferred composition, the binder is also the anionogen such as a polymer containing halogen. The composition may also contain additional components such as, for example, sensitizing compounds or dyes, fillers, plasticizers, or other modifiers all coated on a supporting film such as polyethylene terephthatate, or in a self-supporting film.

In the absence of sensitizing compound or dye, the compositions, including the heterocyclic amines of the invention, are insensitive to visible radiation, i.e., those radiations having a wavelength greater than about 4000A. Such compositions, contrary to prior art compositions are stable to storage, even in normal light, essentially indefinitely. However, they are somewhat sensitive to, and hence exposed by ultraviolet light, i.e., light having a wavelength substantially less than about 4000A as a result of formation of acid or much more readily by harder radiations such as are afforded by electron beams, X-rays, and other high energy radiation in the presence of anionogens. Many of the compositions are also sensitive to heat.

The dye progenitor compounds herein described by which will be understood the dihydroheterocyclic amines of the invention find particular utility in the preparation of normally stable image recording sheets on which images may be recorded directly by exposure to a suitably modulated electron beam; and in one aspect the invention therefore relates to the preparation and use of such sheet materials.

Sheet materials capable of being directly imaged by exposure to the electron beam have been previously described. The sheets of U.S. Pat. No. 3,370,981 are initially colored, being converted to a different color by the action of the beam. They do not provide a colorless background and accordingly cannot be combined in multiple-color packs to provide true color reproduction. U.S. Pat. No. 3,425,867 uses colorless materials but the colored product obtained on treatment is unstable and the color soon fades.

In forming and using the recording sheets of the present invention, a transparent, translucent, or opaque substrate is coated with a polymeric binder containing an electron beam sensitive colorless dye progenitor. An electron beam impinging on such a sheet produces a permanent image immediately and does not require fixing. Positive or negative images of a copy and full color copies can be made. Color correction is easy and enhancement of any given color is possible. Additional images may be added to a previously imaged sheet.

The electrical characteristics of the substrate are of considerable importance in the preparation of the recording sheets. If the dielectric constant is high enough (e.g. above about 5.0), no conductive coating is required. If the dielectric constant is lower (e.g. below about 5.0), then a conductive coating is required. If the substrate has a dielectric constant below about 5.0, then a conductive coating must be laid down on the substrate so that the resistivity will be less than 10^8 ohm-cm.

By interaction with an electron beam, the progenitors yield cationic dyes which are intensely colored and transparent. A source of anion, which is referred to as an anionogen, must be available in order to allow formation of the colored form. The anionogenic function can come from the dye molecule, from the binder or from an additive in the binder-dye progenitor system.

The anionogen is a required component, and may come from the dye progenitor or precursor molecule, the binder, or an additive.

For example, the dye progenitor of FIG. **88** itself serves as an anionogen by virtue of the ring-substituted halogen atom. The compound is colorless and may be incorporated into a neutral binder (e.g. ethylcellulose, polyvinyl acetate, styrene-acrylonitrile copolymer). Upon exposure to an electron beam, a magenta image is produced immediately in the areas struck by the electron beam at about 10^{13} to 10^{14} electrons/cm^2.

The anionogen must be a compound which is stable to normal room light, soluble in the binder system, and able to provide an anion upon interaction with the electron beam. Halogen-containing compounds which provide a halide ion by interaction with the electron beam are useful. They include

polyvinyl chloride
p-diiodobenzene
4,4′-dibromobiphenyl
1,2,4,5-tetrabromobenzene
4,4′-dibromodiphenyl ether
1,3,6,8-tetrachloropyrene
hexachloro diphenyl oxide
bromotrifluoroethylene fluid
chlorinated biphenyl
tetrabromomethyl methane
p-phenoxybenzenesulfonylfluoride

Full color positive or negative copies of colored transparencies or hard copy can be prepared using the sheet material of this invention. The material to be copied is mounted in a convenient position and a video camera is focused on the material. The image viewed by the video camera may be monitored by a color TV monitor and the signal from the camera is fed into the electron beam recorder. For full color copies, color filters are sequentially placed before the video camera to provide color separation and the sheet material containing appropriate dye progenitor is used sequentially in the electron beam recorder. Finally, the three ex-

posed sheets are laminated in register to form the full color transparency.

The invention is further illustrated by the following non-limiting examples in which all parts are by weight and temperatures in degrees centigrade unless otherwise indicated.

EXAMPLE 1

The substituted heterocyclic amine of FIG. **87**, 2(4-dimethylaminostyryl)-1,3,3-trimethylindolenine, is prepared by the dropwise addition of a solution of 1 part of sodium borohydride in 10 parts of water to a stirring mixture of 30 parts of methylene chloride and 40 parts of an aqueous solution containing 2 parts of the styryl dye, 2(4-dimethylamino-styryl)-1,3,3-trimethylindolinium chloride. The addition of borohydride solution is continued until the color is fully discharged from the dye solution. The stirring is stopped, the phases separated, and the lower nonaqueous phase washed several times with several parts of water. The washed phase is then dried over anhydrous sodium sulfate (about 2 parts) and the methylene chloride distilled off. The residue obtained is recrystallized from methanol and yields the desired amine having a melting point of 124.5° – 126° C. Data from high resolution mass spectrography establishing the molecular formula of the purified substituted heterocyclic amine as $C_{21}H_{26}N_2$.

EXAMPLE 2 (FIG. 88)

The substituted heterocyclic amine of FIG. **88** 2(2-chloro-4-dimethylaminostyryl)-1,3,3-trimethylindolenine is prepared by following the procedure of Example 1 with the substitution of the styryl dye 2(2-chloro-4-dimethylaminostyryl)-1,3,3-trimethylindolinium chloride for that used above. The desired amine is obtained with a melting point of 153.5° – 155.5° C., molecular formula by high resolution mass spectrography: $C_{21}H_{25}N_2Cl$.

EXAMPLE 3 (FIG. 90)

The heterocyclic amine of FIG. **90** (2-(4-morpholinostyryl)-1,3,3-trimethylindoline) is obtained by replacing the styryl dye used in the procedure of Example 1 with the styryl dye, 2(4-morpholinostyryl)-1,3,3-trimethylindolinium chloride. The desired amine is obtained as a partially purified material having a melting point of 121°–131° C. and an empirical formual of $C_{23}H_{26}ON_2$.

EXAMPLE 4 (FIG. 108)

The substituted heterocyclic amine of FIG. **108** (2-(4,4-bis(4-dimethylaminophenyl)butadienyl)-1,3,3-trimethylindoline is prepared by dropwise addition of a solution of 1.1 parts of sodium borohydride in 13 parts of water to a stirring mixture of 4.86 parts (0.01 moles) of the styryl dye, 2(4,4-bis(4-dimethylaminophenyl)-butadienyl)-1,3,3-trimethylindolinium chloride in 100 parts of water and 37 parts of methylene chloride. After 4.6 parts of the sodium borohydride solution has been added the blue color of the styryl dye is fully discharged. The methylene chloride layer is separated, dried over sodium sulfate and the methylene chloride distilled off in a rotory evaporator. The dark brown residue is milled in 95 percent ethanol containing about 0.1 parts of sodium borohydride and then filtered. After vacuum drying, the tan colored insoluble portion weighs 3.25, sinters at 172° C. and melts at 182° – 183° C. The molecular formula of the purified substituted heterocyclic amine is found to be $C_{31}H_{37}N_3$.

EXAMPLE 5

In a suitable container equipped with an air condenser and a drying tube to exclude atmospheric moisture and heated by a steam bath are replaced 50 part glacial acetic acid, 2 parts of concentrated hydrochloric acid, 7.07 parts of 3,3-bis(4-dimethylaminophenyl-)acrolein (0.024 moles) and 4.16 parts of 1,3,3-trimethyl-2-methylene-indoline (0.024 moles). The mixture is heated for 18 hours during which time it takes on a deep blue coloration. The solution is concentrated to about one-half its initial volume, diluted to 600 parts by volume with water and salted out with a mixture of sodium chloride and sodium acetate. After filtering and drying, the solid is extracted with chloroform in a Soxhlet extractor to remove salt and the chloroform concentrate evaporated to yield 11.7 parts of green-grey microcrystals of 2-(4,4-bis-(4-dimethylaminophenyl)butadienyl)-1,3,3-trimethylindolinium chloride.

The above indolinium chloride is used in place of the styryl dye of Example 1 to give the heterocyclic amine of FIG. **107.**

EXAMPLE 6

By replacing the styryl dye used in the procedure of Example 1 with 2(5(1,3,3-trimethylindol ylidene)-penta-1,3-dienyl-1)-1,3,3-trimethylindolinium chloride, the dihydroheterocyclic amine of FIG. **125** (2[5(1,3,3-trimethylindol ylidene)penta-1,3-dienyl-1]-**1,3,3-**trimethylindoline) is prepared. The molecular formula is established as $C_{27}H_{32}N_2$ by high resolution mass spectroscopy.

EXAMPLE 7

The substituted heterocyclic amines shown in FIGS. **87 – 137** are prepared by the dropwise addition of a solution of 1 part of sodium borohydride in 20 parts of ethanol to a solution of 1 part of the corresponding methine dye in 100 parts of methanol. The addition of borohydride solution is continued until the color is discharged from the dye solution. The methanol is evaporated from the reaction mixture and the residue taken up in about 20 parts methylene chloride. The supernatant solution is decanted from the insoluble residue formed on standing and is evaporated. The essentially colorless substituted heterocyclic amine obtained as a residue by evaporation of the methylene chloride is added to 100 parts of a 10 percent weight per weight solution of a copolymer of 87 percent vinyl chloride-13 percent vinyl acetate (Bakelite VYHH) in 75/25 methyl ethyl ketone/toluene by weight to form a coating composition. The coating composition is coated at a wet thickness of 3 mils (75 microns) onto a transparent electrically conductive polyester film and dried. Samples of the coated sheet are exposed to a conventional electron beam at 20 kilovolts and 3 microamperes. Color of the developed image, and sensitivity, are given in Table 1.

Table 1

Compound of FIG.	Color	Sensitivity[a]
87	Magenta	A
88	Magenta	A
89	Magenta	A
90	Red-magenta	A

Table 1-continued

Compound of FIG.	Color	Sensitivity[a]
91	Yellow	C
92	Magenta	A
93	Orange	B
94	Amber	C
95	Yellow	D
96	Magenta	A
97	Scarlet	A
98	Yellow	C
99	Magenta	A
100	Magenta	A
101	Magenta	A
102	Red-orange	A
103	Orange	A
104	Orange	A
105	Yellow	B
106	Yellow	A
107	Blue	B
108	Blue	A
109	Orange-yellow	A
110	Purple	A
111	Blue	A
112	Magenta	A
113	Blue	A
114	Blue	A
115	Blue	A
116	Yellow	D
117	Magenta	B
118	Blue	B
119	Magenta	C
120	Blue	B
121	Magenta	C
122	Magenta	C
123	Blue	B
124	Red	A
125	Cyan	A
126	Blue-cyan	A
127	Magenta	C
128	Blue	C
129	Blue	B
130	Blue	B
131	Pink	B
132	Blue	D
133	Blue	B
134	Magenta	C
135	Magenta	B
136	Magenta	A
137	Blue	C

[a]Sensitivity
A = Good
B = Medium
C = Low
D = Insensitive

Those skilled in the art will readily perceive that numerous other dihydroheterocyclic amines of the invention can be obtained by the procedures herein disclosed and that they can be used similarly in radiation-sensitive compositions.

EXAMPLE 8

Transparent polyester film (2.5 mil or 0.0625 mm) was vapor coated with chromium to yield a sheet material with a resistivity of 10^4 ohms per square and a visible light transmission of 50 percent. The conductive surface of the sheet was knife coated at a wet thickness of 3 mils or 0.075 mm. with a solution of 50 mgm. of the dihydroheterocyclic amine compound of FIG. 108 and 0.5 gm. copolymer of 87 percent vinyl chloride — 13 percent vinyl acetate ("Vinylite VYHH") dissolved in 3.4 gm. methylethylketone and 1.1 gm. toluene.

The dihydroheterocyclic amine was dissolved in the polymer solution to form a clear colorless solution. After coating, the sheet was dried at room temperature to form a colorless transparent sheet which was stable in room light.

The sheet was exposed to a conventional electron beam using 20kV, 3μA. The film, upon exposure to the electron beam, immediately developed a transparent blue color. After removing the film from the electron beam assembly, the exposed portion of the film maintained its blue transparent color and the background remained clear, colorless, and transparent. Unexposed film was stored in room light for an extended period of time without deleterious effect. The exposed film was also uniformly stable. Another portion of the prepared film was tested using an electron beam of 20kV, one square inch raster at from 10^{11} to 10^{14} electrons/cm^2. Variations in the optical density were achieved from visible marking at 10^{11} electrons/cm^2 to dense blue transparent image at 10^{14} electrons/cm^2. The unexposed film was stored in the laboratory under normal light conditions for about one-half year. This film was then exposed in the electron beam arrangement and the color developed immediately. A comparison with film which had been exposed to the electron beam one year before and allowed to remain in the laboratory under normal lighting showed no discernible difference.

Other color progenitor dihydroheterocyclic amines were substituted for that of FIG. 108 used above to produce equally effective electron beam recording sheets which produced images of other colors. Typical examples are as tabulated, the exposure in electrons/cm^2 required to produce an optical density of 1 being indicated for convenience.

Compound (FIG.)	Color	Exposure
91	Yellow	10^{14}
105	Yellow	10^{14}
111	Blue	10^{14}
125	Cyan	10^{14}

EXAMPLE 9

In order to provide increased surface conductivity, a polyester film carrier was first coated with a dilute solution of polydimethyl dialkyl ammonium chloride ("Calgon 261"), and dried. The film was then further coated with the solution of binder and color precursor as in Example 8. The sheet had a resistivity of 10^4 ohms/-square and a light transmissivity approximately 97 percent of that of the uncoated polyester film. Under an electron beam exposure of 10^{14} electrons/cm^2 the sheet produced a blue transparent image.

EXAMPLE 10

The film base of Example 8 was coated with a solution of 0.5 g of styrene-acrylonitrile copolymer ("Tyril 880") and 50 mgm. of the dihydroheterocyclic amine of FIG. 88 in 4.5 g. of methyl isobutyl ketone. Exposure of the dried colorless sheet to the electron beam at 20kV and 3μA produced a transparent magenta image.

After removing the film from the electron beam assembly, the exposed portion maintained its magenta transparent color and the background remained clear, colorless, and transparent even though it was left on an intensely lighted (600 watt) overhead projector for over 4 hours.

Similar results were obtained when the binder was replaced with:

A. VYHH applied as 10% solution in 3/1 mixture of methylethylketone and toluene.

B. 10 percent solution of polyvinyl acetate (Gelva V-100 from Shawinigan Products) in methylethylketone.

C. 3 percent solution of ethylcellulose in toluene (Ethocel N-200 from Dow Chemical Co.).

D. 10 percent solution of a chlorinated polyethylene containing 48 percent chlorine (QX 2243.25 from Dow Chemical) in methylethylketone.

Other materials which liberate anions on exposure to an electron beam and which serve as anionogens suitable for the purposes of the invention, such as those listed above, are also employed in making useful electron beam recording sheets.

EXAMPLE 11

A clear colorless solution of 50.0 mgm. of the dihydroheterocyclic amine of FIG. **88** and 5.0 gm. VYHH solution (10 percent by weight VYHH in methylethylketone-toluene solvent; 3 parts methylethylketone, 1 part toluene) was knife coated on a sheet of polyvinylidene fluoride (3 mil or 0.075 mm) to a wet thickness of three mils (0.075 mm) and then dried at room temperature to form a light-stable colorless transparent sheet.

Exposure of the sheet material to a conventional electron beam yields a transparent, sharp magenta image. The magenta image is clearly visible at 10^{12} electrons/cm^2 and at 10^{14} electrons/cm^2 the optical density equals one.

EXAMPLE 12

Polyester (2.5 mil or 0.0625 mm) was vapor coated with chromium to yield a sheet material with a resistivity of 10 ohms-cm and a visible light transmission of 50 percent. A clear colorless solution of 50 mgm each of the dihydroheterocyclic amines of FIGS. **87** and **108** and 5.0 g. of a solution of 10 percent VYHH in 3:1 methylethylketone-toluene solvent was knife coated on the conductive surface of the substrate at a wet thickness of 3 mils (0.075 mm) and dried at room temperature to form a colorless transparent sheet which was stable to room light.

The resulting sheet was exposed to a conventional electron beam using 20kV, 3μA. The film, upon exposure to the electron beam, immediately developed a sharp transparent purple image. The image was easily defined at 10^{11} electrons/cm^2. An optical density of one was obtained by an exposure of 5×10^{13} electrons/cm^2. The imaged sheet was stored under normal room light for one week and then re-exposed to the electron beam on an area of the film which previously has not been struck by the beam. The transparent purple image developed and the optical density of image was essentially the same as the originally developed areas.

EXAMPLE 13

Bond paper (No. 10) was knife coated with a solution of Calgon 261 (4 parts Calgon 261 to 6 parts H_2O) to a wet thickness of 3 mils (0.075 mm). The resulting sheet was allowed to dry, but while it was still tacky it was knife coated with the dye progenitor-binder formulation of Example 11 above. The coated sheet was dried at room temperature to form a light-stable colorless sheet.

Exposure of the sheet to conventional electron beam yields a sharp magenta image at 10^{12} electrons/cm^2.

EXAMPLE 14

Three separate transparent recording sheets (A, B and C) are prepared in accordance with the procedures described in Example 8, but using the specific dihydroheterocyclic amines of FIGS. **125, 88** and **98** respectively.

A full color picture was mounted horizontally in a rigid frame and a television camera (Concord Separate Mesh Vidicon- Model CTC-30) was focused on the picture. Focusing and centering is observed on a TV monitor. A red filter (peak transmission at 630 mμ) is placed in front of the camera lens and the resulting signal is fed into a 3M Electron Beam Recorder Model 100. Sheet A is used to record the resulting red separation and gives a cyan image. The process is repeated using a green filter which peaks at 525 mμ and the green separation is recorded on Sheet B to give a magenta image. The process is again repeated using a blue filter which peaks at 450 mμ and the blue separation is recorded on Sheet C to give a yellow image. The resulting three images are laminated in register, with the yellow image on the bottom, then the cyan and finally the magenta image on the top. The composite is then a full color 16 mm positive transparency of the original 8½ × 11 inches color picture. The transparency was projected to about a 4 × 5 foot size to give a sharp, clear, faithful color reproduction of the original picture.

EXAMPLE 15

Three sheets of polyester were coated with Calgon 261 as described in Example 9. The resulting conductive sheets were coated with dye progenitor-binder systems and exposed to the modulated electron beam as described in Example 13. The three exposed color separations were laminated in register and the resulting positive transparency was projected to give a superior, sharp, brightly colored copy of the original.

EXAMPLE 16

Three sheets of polyester were coated with Calgon 261 as described in Example 9. The first sheet was coated with a mixture of 50.0 mgm of the dihydroheterocyclic amine of FIG. **88** in 5.0 gms of a 10 percent solution of VYHH in methylethylketone to a wet thickness of 3.0 mils. The resulting sheet yields a magenta image upon exposure to an electron beam.

The second sheet was coated with a mixture of 50.0 mgm of Michler's Hydrol, bis(p-dimethylaminophenyl)-carbinol, in 5.0 gms of a 10 percent solution of VYHH in methylethylketone to a wet thickness of 3.0 mils. The resulting sheet yields a cyan image upon exposure to an electron beam.

The third sheet was coated with 50.0 mgm of 2-(2-(4-carbamidoxyphenyl)ethenyl)-3,3-dimethylindolenine (described in U.S. Pat. No. 3,542,775) in 5.0 gms of a 10 percent solution of VYHH in methylethylketone. The resulting sheet yields a yellow image upon exposure to an electron beam.

The three sheets are exposed as described in Example 13 and the resulting positive transparency yields a very sharp, faithful projection of the original.

What is claimed is:

1. A normally stable electron beam recording sheet having an electron beam-sensitive layer comprising a polymeric binder and substantially colorless oxidizable dye-progenitor consisting of N-hydrocarbyl substituted dihydroheterocyclic amine having an omega-(nuclearly

substituted cyclic) vinylenyl substituent in the 2 or 4 position; said layer comprising anionogen yielding halide anion on exposure to the radiation of an electron beam.

2. Sheet of claim **1** wherein said N-hydrocarbyl-substituted dihydroheterocyclic amine having an omega-(nuclearly substituted cyclic) vinylenyl substituent on the 2 or 4 position contains a halogen atom which is removable upon bombardment with an electron beam as said anionogen.

3. Sheet of claim **1** wherein said binder contains a halogen atom removable by electron bombardment as said anionogen.

4. Sheet of claim **1** wherein said layer includes anionogen component in addition to said binder and said N-hydrocarbyl-substituted dihydroheterocyclic amine having an omega-(nuclearly-substituted cyclic) vinylenyl substituent in the 2 or 4 position.

5. Sheet of claim **1** wherein the N-hydrocarbyl group is alkyl of 1–6 carbon atoms.

6. Sheet of claim **1** wherein dihydroheterocyclic amine is 1,3,3-trimethyl indoline having its substituent in the 2 position.

7. The normally stable electron beam recording sheet of claim **1** wherein the N-hydrocarbyl substituted dihydroheterocyclic amine is 2-(4-(dimethylamino)styryl)-1,3,3-trimethylindoline.

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