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54 Colour formers for recording sheets.

57 Novel bis-(indolyl)ethylenes, process for their production when novel and generally, and record systems utilizing bis-(indolyl)ethylene chromogens; novel di-[bis-(indolyl)ethyleneyl] tetrahalophthalides.

EP 0 386 992 A2

INDOLYL ETHYLENE COMPOUNDS, THEIR PRODUCTION, AND RECORD SYSTEMS USING THEM.

FIELD OF THE INVENTION

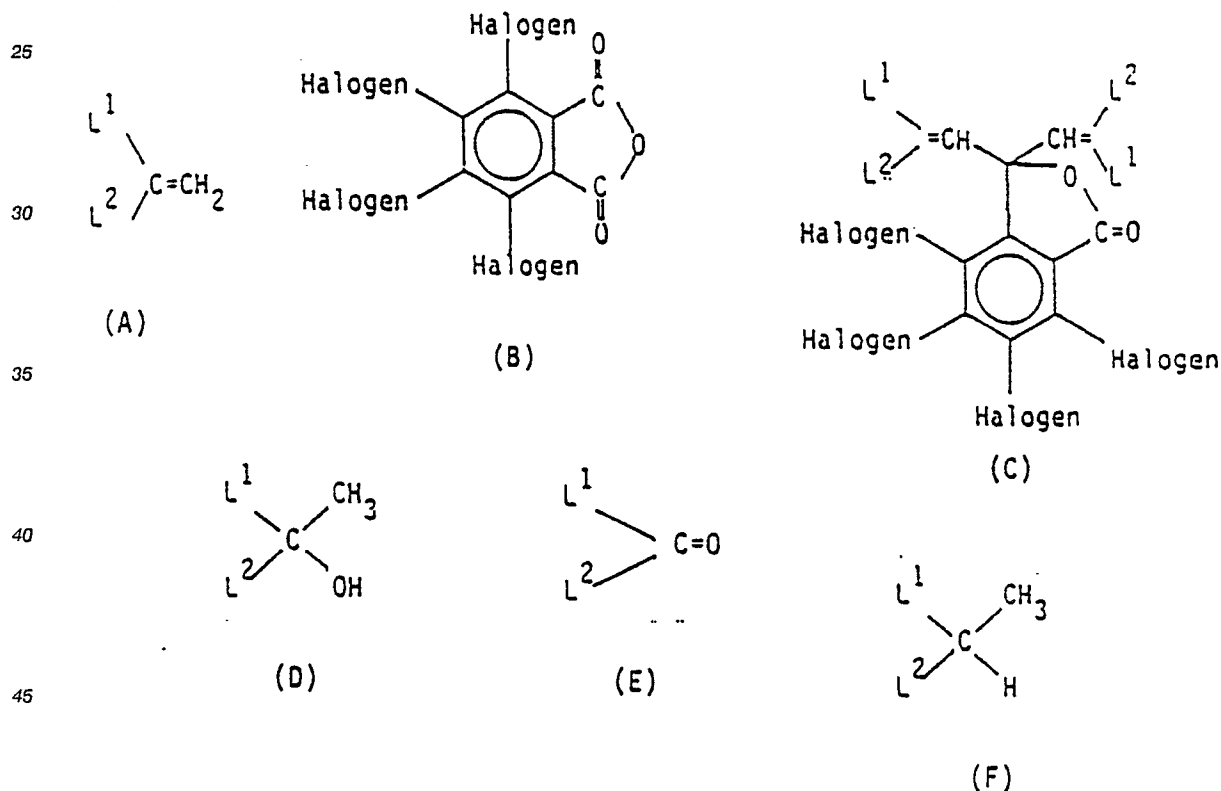
The invention relates to indolyl ethylene compounds, their production, and record systems using them.

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FIRST ASPECT OF INVENTION

More particularly in one aspect this invention relates to bis-indolyl ethylenes, methods for their production and their use to give intense colors when reacted with an electron accepting coreactant material. More specifically, this aspect relates to methods for the production of such chromogenic compounds and novel pressure-sensitive or heat-sensitive mark-forming record systems incorporating such compounds. As used in mark-forming systems, marking in desired areas on support webs or sheets may be accomplished by effecting selective localized reactive contact between the chromogenic material and the electron-accepting material on or in such web or sheet, such material being brought thereto by transfer or originally there in situ. The selective reactive contact forms colored images in the intended image marking areas.

In related art several divinyl phthalide chromogenic compounds (C1) [(C) L¹, L² = substituted phenyl] (read as Compound C1 arrived at by referring to formula C wherein L¹ and L² are as stated) have been prepared by the condensation of ethylenes (A1) [(A) L¹, L² = substituted phenyl] with phthalic anhydrides (B1) [(B) Each Halogen is independently Cl or Br] in acetic anhydride (Sheldon Farber, U.S. Patent Nos. 4,020,056, 4,022,771, 4,107,428, 4,119,776;)



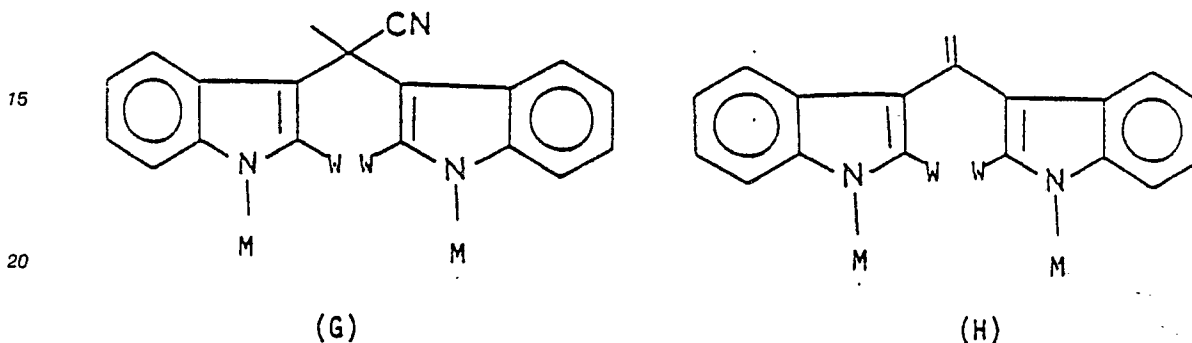
Substituted ethylenes (A1) or their precursors (D1) [(D) L¹, L² = substituted phenyl] were prepared by the reaction of methylmagnesium bromide (also known as methyl Grignard reagent) with ketones (E1) [(E) L¹, L² substituted phenyl]. The use of a Grignard reaction to prepare (A1) imposes severe restrictions on the scaleup synthesis of (A1) and consequently on the manufacture of divinyl phthalides (C1).

In another synthetic approach, the alcohol (D1) was obtained by reacting the ethane (F1) [(F)

L¹, L² = substituted phenyl] with lead peroxide in either nitric acid or formic acid; and the substituted ethylene (A) was obtained from (D1) by dehydration [Yamada Kagaku, Japan Kokai 1988-8360, filed June 30, 1986].

When indole was heated with acetic anhydride containing 10% acetic acid a bis-(indolyl)ethylene (A2) [(A) L¹, L² = acetylindole-3-yl] Apparently was obtained as a by-product in 5-10% yield (J. E. Saxton, J. Chem. Soc., 3592 (1952)).

Substituted (2- and 1,2-) indoles when reacted with acetyl cyanide in the presence of hydrogen chloride yielded 1-cyano-1,1-di(3-indolyl)ethanes (G) and apparently some of these products may be converted to bis-(indolyl)ethylenes (H) by heating them under vacuum either alone or with soda lime. In some cases, dependent on certain select substituents M and W, (G) may yield some (H) type compounds on refluxing with aqueous-ethanolic 10% potassium hydroxide [A. K. Kiang and F. G. Mann, J. Chem., Soc., 594 (1953)].

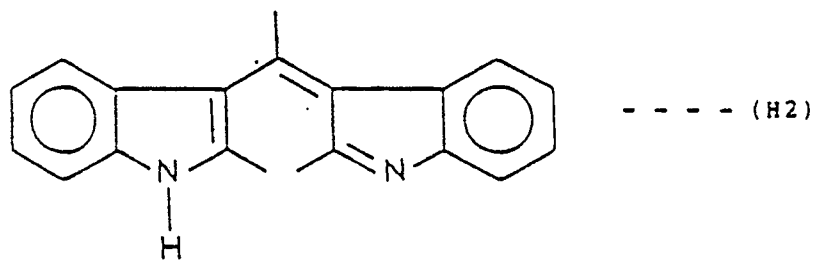


M = H, Ph

W = Me, Ph

Bis-(indolyl)ethylene (H1) [(H) M=H and W=Me] was speculated to be a product (m.p. 203 °C) from the reaction of 2-methylindole with ethyl acetate and sodium ethoxide. No other data were given to substantiate the structure [A. Angeli and G. Marchetti, Atti. Accad. Lincei, 16 (II), 179 (1970)].

In another report (W. Borsche and H. Groth, Annalen, 549, 238 (1941)), 2-methylindole when boiled with acetyl chloride formed a product that on treatment with alkali gave a pseudobase, (C₂₀H₁₈N₂, pale rose, m.p. 208 °C). The pseudobase was suggested to be 1-(2-methylindole-3-yl)-1-(2-methyl-3-indolidene)ethane (H2). Again, insufficient data precludes the substantiation of this structure. Furthermore, similar structure was proposed for the pseudobase obtained by substituting 2-phenylindole for 2-methylindole.



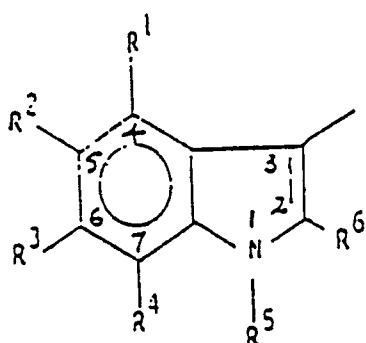
SUMMARY OF PRESENT ASPECT

A novel method for producing bis-(indolyl)ethylenes and novel bis-(indolyl)ethylene compounds are described along with record systems incorporating such compounds.

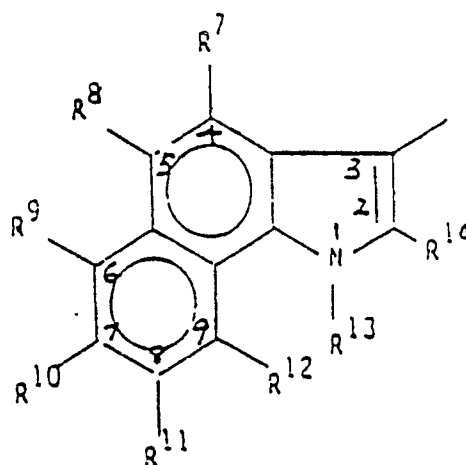
In the process bis-(indolyl)ethylenes of the following general formula are prepared:



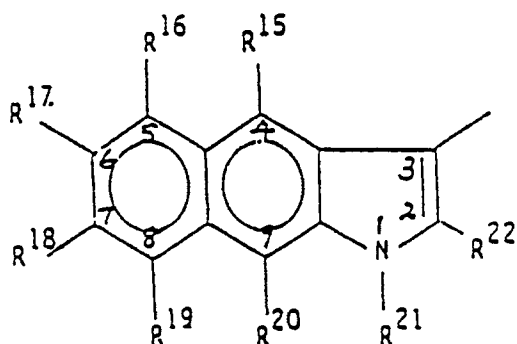
wherein each L^1 and L^2 is the same or different and is each independently selected from indole moieties (J1) through (J4) (L^1 need not be the same as L^2), wherein Z is hydrogen, alkyl (C_1-C_8), substituted or unsubstituted aryl, aralkyl, aroxyalkyl, alkoxyalkyl and halogen,



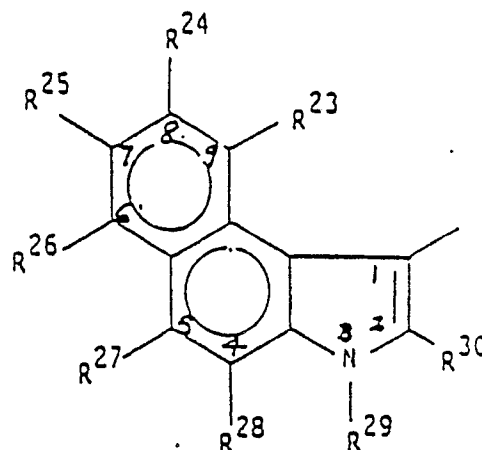
(J1)



(J2)



(J3)

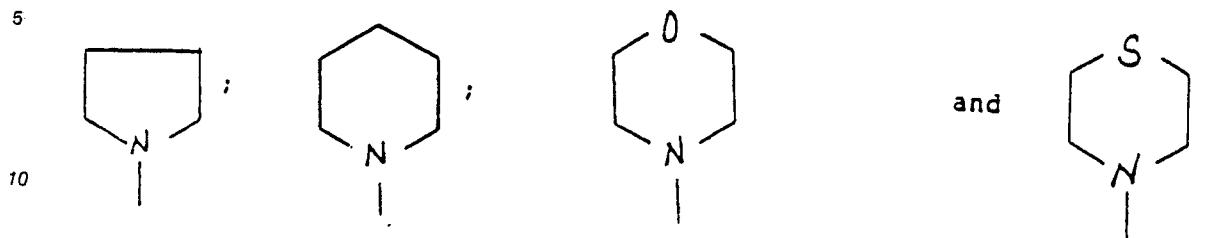


(J4)

wherein in (J1) through (J4) above, each of R^5 , R^6 , R^{13} , R^{14} , R^{21} , R^{22} , R^{29} and R^{30} need not be the same and is each independently selected from hydrogen, alkyl (C_1-C_8), cycloalkyl, aroxyalkyl, alkoxyalkyl and substituted or unsubstituted aryl, such as phenyl, naphthyl, or heterocyclyl.

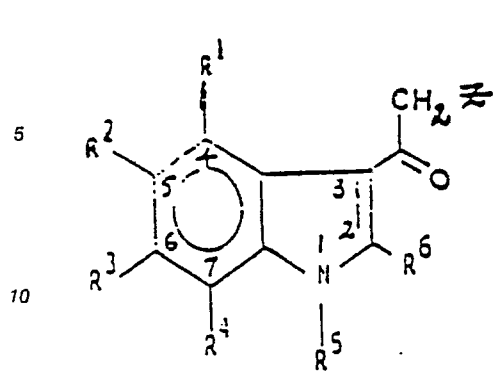
Each of R^1 , R^2 , R^3 , R^4 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} and R^{28} need not be the same and is each independently selected from hydrogen, alkyl (C_1-C_8), cycloalkyl,

substituted or unsubstituted aryl, halogen, alkoxy (C_1-C_8), aroxy, cycloalkoxy, dialkylamino including symmetrical and unsymmetrical alkyl groups with one to eight carbon, alkylcycloalkylamino, dicycloalkylamino,

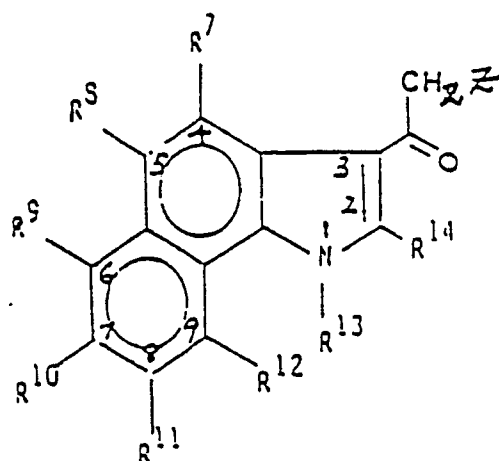


15 The bis(indolyl)ethylenes (I) are formed by three major routes. The first route uses the corresponding indoles, acid anhydride (such as $(ZCH_2CO)_2O$, Z as defined elsewhere) and Lewis Acid such as zinc chloride or other electron acceptor preferably in approximately 1:1:0.5 molar ratios respectively in a suitable solvent. The second route uses the corresponding indoles with acid chloride (such as ZCH_2COCl , Z as defined earlier) preferably in approximately 1:(0.15-2.0) molar amounts at temperatures (15-75°C) with or without solvent. The third route involves a condensation of a component selected from (K1) through (K4)

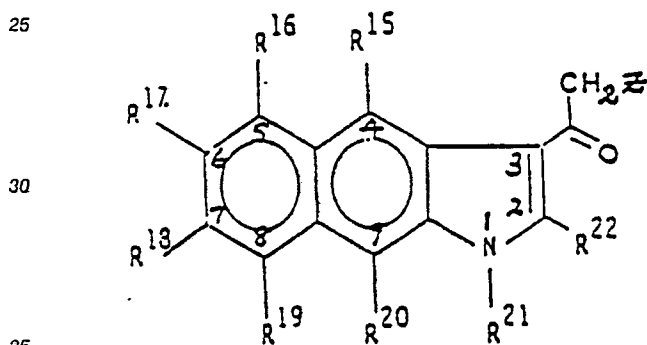
20 with an indole selected from (J1) through (J4) in the presence of a Vilsmeier reagent (such as phosphoryl chloride, phosgene, oxalyl chloride, benzoyl chloride, alkanesulfonyl chloride, arenesulfonyl chloride, alkyl chloroformate and arylchloroformate) with or without solvent. Moreover, the third route can be used to prepare unsymmetrical indolyl ethylenes (i.e. (I) with different L^1 and L^2).



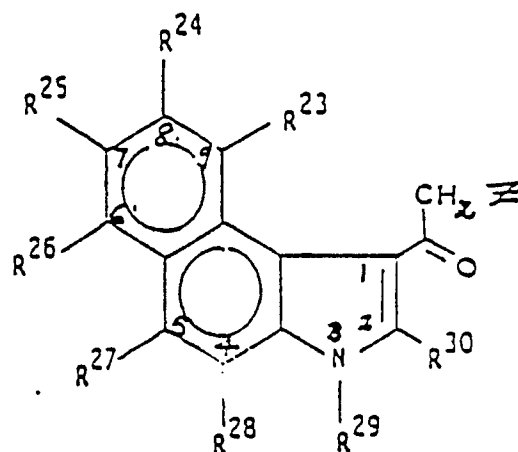
(K1)



(K2)



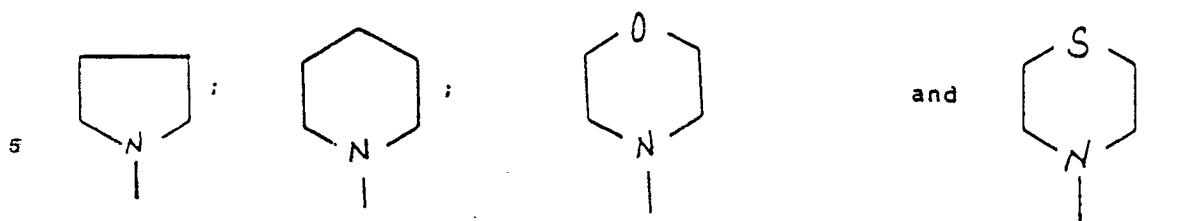
(K3)



(K4)

In (K1) through (K4) above, each of R^5 , R^6 , R^{13} , R^{14} , R^{21} , R^{22} , R^{29} and R^{30} need not be the same and is each independently selected from hydrogen, alkyl (C_1 - C_8), cycloalkyl, aroxyalkyl, alkoxyalkyl, and substituted or unsubstituted aryl, such as phenyl, naphthyl, or heterocyclyl.

Each of R^1 , R^2 , R^3 , R^4 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} and R^{28} need not be the same and is each independently selected from hydrogen, alkyl (C_1 - C_8), cycloalkyl, substituted or unsubstituted aryl, halogen, alkoxy (C_1 - C_8), aroxy, cycloalkoxy, dialkylamino including symmetrical and unsymmetrical alkyl groups with one to eight carbon, alkylcycloalkylamino, dicycloalkylamino,



Z is hydrogen, alkyl (C₁-C₈), substituted or unsubstituted aryl, aralkyl, aroxyalkyl, alkoxyalkyl and halogen.

DETAILED DESCRIPTION OF PRESENT ASPECT

15 Teaches three processes for the preparation of chromogenic compounds which in color form have absorbance in the visible region of the spectrum at approximately 400-700 nm and thus are eligible for use in pressure-sensitive and thermal recording systems. Compounds which are chromogenic and absorptive in the visible region of the spectrum have commercial utility by being capable, when imaged, of being detected by optical reading machines.

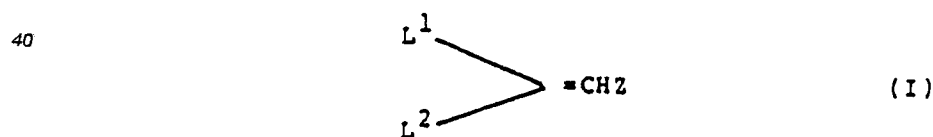
20 More particularly, describes novel pressure-sensitive and thermal record systems and a method for the preparation of substantially colorless but colorable chromogenic compounds eligible for use in pressure-sensitive recording and thermal recording systems. Advantageously recording systems utilizing these compounds can be read by optical reading machines, particularly those capable of reading for the wavelength range of 400-700 nm.

25 The colorable chromogenic compounds can be combined with other chromogenic materials covering other or wider spectral ranges and can be used in pressure-sensitive and thermal recording systems to provide images which absorb over wider ranges of the electromagnetic spectrum. The commercial significance is that a larger assortment of available optical readers can thus be effectively useful with such imaged record systems.

30 The chromogenic compounds also find use in photosensitive printing material, typewriter ribbons, inks and the like.

Specifically the process relates to the preparation of bis-(indolyl)ethylenes. These compounds are substantially colorless or slightly colored solids but can be converted to colored forms upon reactive contact with an electron accepting material. The compounds in imaged or colored form are typically visibly colored and can be detected by conventional optical readers capable of detecting in the wavelength range of 400-700 nm.

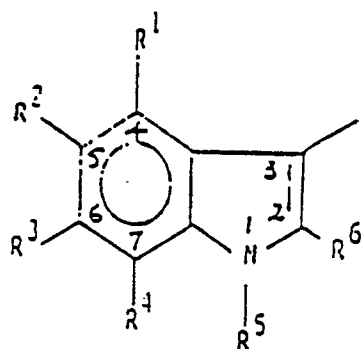
In the process bis(indolyl)ethylenes of the following general formula are prepared:



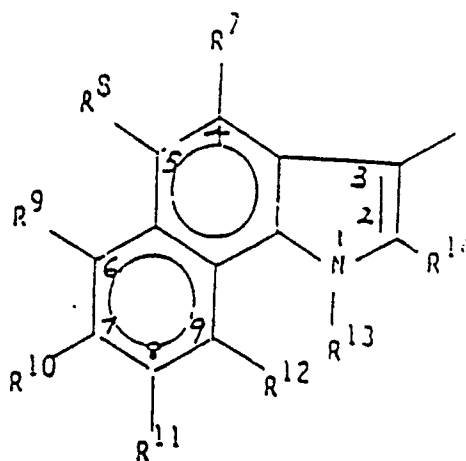
45 wherein each L¹ and L² is the same or different and each is independently selected from indole moieties (J1) through (J4) (L¹ need not be the same as L²), wherein Z is hydrogen, alkyl [(C₁-C₈), substituted or unsubstituted aryl, aralkyl, aroxyalkyl, alkoxyalkyl and halogen,

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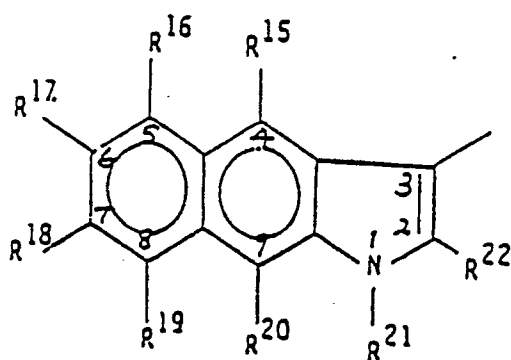
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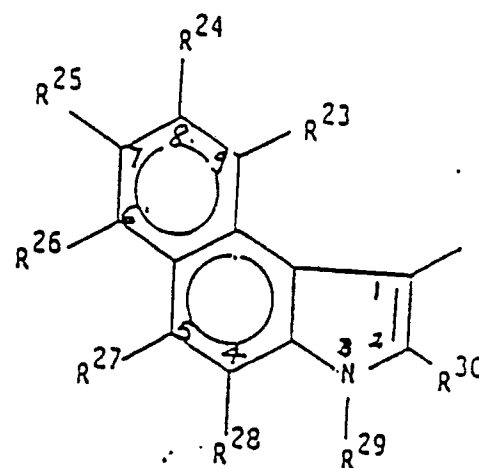
(J1)



(J2)



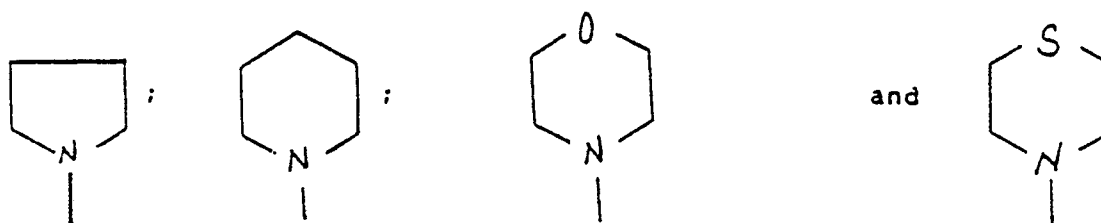
(J3)



(J4)

wherein in (J1) through (J4) above, each of R^5 , R^6 , R^{13} , R^{14} , R^{21} , R^{22} , R^{29} and R^{30} need not be the same and is independently selected from hydrogen, alkyl (C_1 - C_8), cycloalkyl, alkoxyalkyl, alkoxyalkyl, and substituted or unsubstituted aryl, such as phenyl, naphthyl, or heterocyclyl.

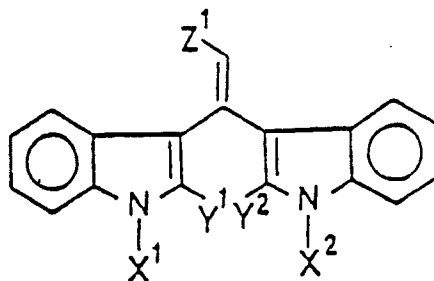
Each of R^1 , R^2 , R^3 , R^4 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} and R^{28} need not be the same and is each independently selected from hydrogen, alkyl (C_1 - C_8), cycloalkyl, substituted or unsubstituted aryl, halogen, alkoxy (C_1 - C_8), alkoxy, cycloalkoxy, dialkylamino including symmetrical and unsymmetrical alkyl groups with one to eight carbon, alkylcycloalkylamino, dicycloalkylamino,



It is advantageous for clarity of discussion to also establish the following subgroup of formula I compound for the special case when L_1 and L_2 are simultaneously (J1). Higher precision is then

advantageous to draw clear demarcation between the invention and the art. Thus, for L_1 and L_2 being simultaneously (J1) the following subgroup is established. (For clarity note that "simultaneously (J1)" contemplates allowing each (J1) the full panoply of variables available for J1, thus L_1 and L_2 when both are (J1) however need not be precisely identical in that the R^1 through R^6 variables can differ.)

The above-referenced subgroup is as follows:
Chromogenic bis(indolyl)ethylene of the formula



wherein Z^1 is hydrogen, alkyl (C_1 - C_8) substituted or unsubstituted aryl, aralkyl, aroxyalkyl, alkoxyalkyl and halogen;

wherein X^1 and X^2 need not be the same and is each independently selected from alkyl (C_1 - C_8), cycloalkyl, aroxyalkyl, alkoxyalkyl substituted aryl and unsubstituted aryl;

wherein Y^1 and Y^2 need not be the same and is each independently selected from alkyl (C_1 - C_8), and unsubstituted aryl;

with the proviso that X^1 , X^2 , Y^1 and Y^2 are not all simultaneously unsubstituted aryl;

with the proviso that Y^1 and Y^2 are not simultaneously unsubstituted aryl when X^1 and X^2 are both methyl.

With the above subgroup established it is convenient as to the formula I compounds to attach the proviso that when L^1 and L^2 are simultaneously (J1), that R^1 , R^2 , R^3 and R^4 are not all hydrogen simultaneously. Said proviso does not apply as to the three methods disclosed to produce the formula I compounds or the record materials, in that the method and record material aspect of the invention is of broader scope and applicability than just the specific new compounds (Formula I and the above subgroup) recited herein.

According to the first process, the bis-(indolyl)ethylenes, (I) for example, are prepared by condensing the indoles (J1) through (J4) with acid anhydride $[(ZCH_2CO)_2O]$ in the presence of compounds belonging to:

Carboxylic Acids (e.g. Acetic Acid); or
Sulfonic Acids (e.g. p-Toluenesulfonic Acid); or
Acid Chlorides (e.g. Benzoyl Chloride); or
Lewis Acids (e.g. Zinc Chloride, Boron Trifluoride)

in solvents, preferably organic, or more preferably the halogenated organic solvents such as 1,2-dichloroethane and chlorobenzene and the like.

Specifically, the indole (J5) was refluxed with zinc chloride and acetic anhydride in 1,2-dichloroethane. After one hour, the starting material had disappeared and the reaction mixture contained the bis-(indolyl)-ethylene (II) [(I) $L^1 = L^2 = 1$ -ethyl-2-methyl-3-indolyl, $Z = H$] as the major product; and (K5) as the minor product. Further studies on this reaction revealed that the yield of (I1) depended on the relative molar amounts of indole (J5), acetic anhydride and zinc chloride. The results of these studies are summarized in Table 1.

Table 1

Entry	Indole (J1) (Mole)	Acetic Anhydride (Mole)	Zinc Chloride (Mole)	Yield (I1) (%)
1	0.10	0.05	0.10	Incomplete Reaction
2	0.10	0.10	0.10	47.0
3	0.10	0.10	0.15	59.0
4	0.10	0.10	0.05	60.0
Reaction Conditions: Solvent, 1,2-dichloroethane; reflux 2 hours.				

From Table 1, it seems that equimolar amounts of indole (J5) and acetic anhydride are preferred for complete reaction and that half the molar amount of zinc chloride is sufficient to carry out the reaction (of Entry 4). Using these reactions, several bis-(indolyl)ethylenes (I) were prepared and some examples are included in Table 3.

In the second process, bis-(indolyl)ethylenes (I) are prepared by reacting the indoles (J1) through (J4) with acid chloride (ZCH_2COCl) with or without solvent in the temperature range 15-75° C.

This process was studied in detail using the indole (J5) and acetyl chloride (CH_3COCl) by varying the reaction conditions and the results are summarized in Table 2.

Table 2

Entry	Acetylchloride (Mole)	Solvent	Temperature (°C)	Time (Hours)	Yield (I1) (%)
1	0.015	$(\text{CH}_3\text{CO})_2\text{O}$	50-52	14	88.0
2	0.025	$(\text{CH}_3\text{CO})_2\text{O}$	50-52	8	96.0
3	0.05	$(\text{CH}_3\text{CO})_2\text{O}$	15-20*	24	49.0
4	0.05	$(\text{CH}_3\text{CO})_2\text{O}$	50-52	7	95.0
5	0.10	$(\text{CH}_3\text{CO})_2\text{O}$	50-52	3	95.0
6	0.12	$\text{ClCH}_2\text{CH}_2\text{Cl}$	45-50	30	78.0
7	0.06	$\text{ClCH}_2\text{CH}_2\text{Cl}$	65-75	48	41.0
8	0.10	Toluene	15-20*	20	86.0
9	0.12	Toluene	50-55	20	35.0
10	0.10	Diglyme	15-20*	20	65.0
11	0.12	None	15-20*	20	76.0
12	0.20	None	15-20*	20	76.0
Amount of (J5) used, 0.1 mole.					

*Room temperature.

Solvent (15 ml).

For a sample procedure, see Example 3.

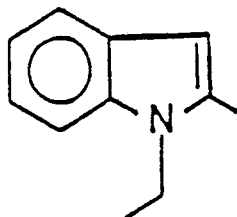
From Table 2, it seems that acetic anhydride is the best solvent for the reaction and that varying amounts of acetyl chloride (0.015-0.1 mole) (entries 2, 4 and 5) can be used with variable reaction times at 50-52°C to get very good yields of (I1). The reaction time is inversely proportional to the acetyl chloride concentration. Several bis-(indolyl)ethylenes (I) were prepared using this process and some examples are included in Table 3.

In the third process for the production of bis-(indolyl)ethylenes, the acylindoles (K1) through (K4) are condensed with indoles (J1) through (J4) using Vilsmeier reagents (such as phosphoryl chloride, phosgene, oxalyl chloride, benzoyl chloride, alkane or arenesulfonylchloride and alkyl or arylchloroformate) with or without solvent. This process is very versatile because symmetrical as well as unsymmetrical indolyl ethylenes can be produced.

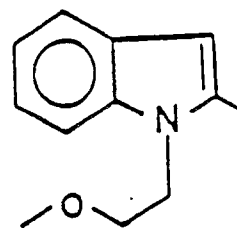
This condensation reaction was studied in detail using the acetylindole (KS) and the indole (J6) using

phosphoryl chloride as a condensing agent in 1,2-dichloroethane as solvent. A solution of acetylindole (K5) in 1,2-dichloroethane was cooled in an ice/salt bath and phosphoryl chloride was added slowly, keeping the temperature of the reaction mixture between 0 and 5°C during the addition. This low temperature was preferred during the initial stages of this reaction to minimize the formation of unwanted byproducts. After 30 minutes stirring while the reaction mixture warmed to room temperature, indole (J6) in 1,2-dichloroethane was added. The reaction mixture was stirred overnight at room temperature and gas chromatographic analysis indicated that the condensation, though not complete, had taken place. The condensation reaction was driven to completion by refluxing the reaction mixture for one hour. The product, unsymmetrical indolyethylene [Table 3, Entry 22], was isolated in good yield (74%, Example 11).

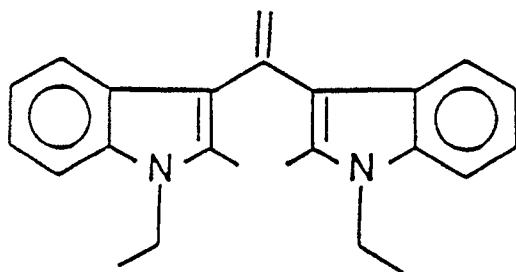
Using a similar procedure discussed above, another unsymmetrical indolyethylene [Table 3, Entry 21] was also prepared in good yield (80%, Example 10).



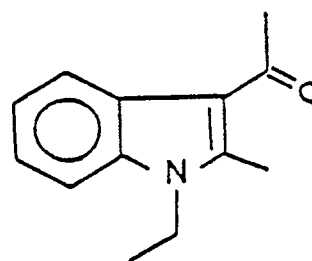
(J5)



(J6)



(I1)



(K5)

Table 3

REFLECTANCE MINIMA AND COLOR OF INDOLYL ETHYLENES ON RESIN-COATED
AND CLAY -COATED PAPERS.

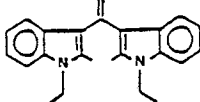
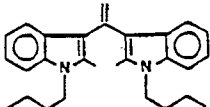
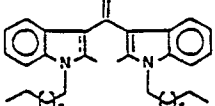
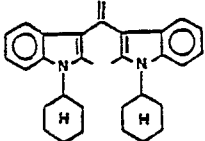
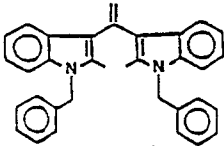
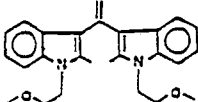
ENTRY	COMPOUND	ENTRY (NO.) M.P. (°C)	REFLECTANCE MINIMA (nm) & COLOR ON RESIN-COATED	REFLECTANCE MINIMA (nm) & COLOR ON CLAY-COATED
1		(1) 179-181 (pale yellow)	517 red	513 red
2		Syrup (pale brown)	520 red	517 red
3		Syrup (pale brown)	522 red	519 red
4		205-207 (Grey)	524 pink	525 purple
5		148-151 (Yellow)	525 pink	526 purple
6		93-95 (Pale Yellow)	517 pink	513 purple

TABLE 3 - CONTINUED

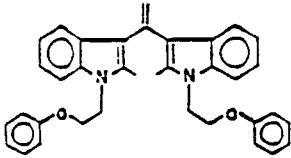
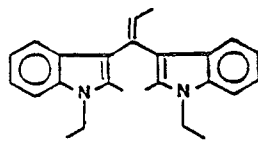
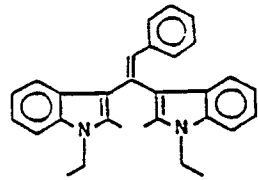
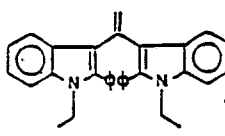
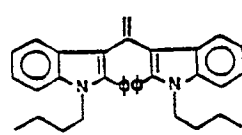
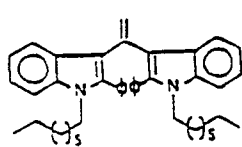
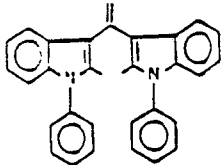
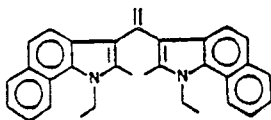
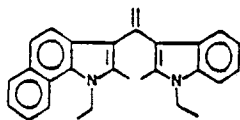
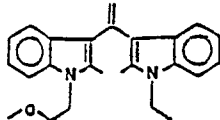
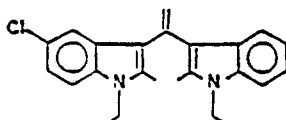
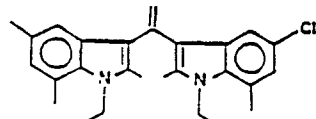
TABLE	COMPOUND	M.P. (°C)	REFLECTANCE MINIMA (nm) & COLOR ON	
			RESIN-COATED	CLAY-COATED
7		128-129 (Yellow)	520 red	514 red
8		109-110 (Beige)	521 light red	534 brownish red
9		157-159 (Pale Yellow)	--- light red	536 purple
10		171-173 (Pale Brown)	535 pink	591 blue
11		95-98 (Pale Brown)	540 light pink	563 purple
12		Syrup (Pale Brown)	535 light pink	561 purple

TABLE 3- CONTINUED

ENTRY	COMPOUND	M.P. (°C)	REFLECTANCE MINIMA (nm) & COLOR ON RESIN-COATED CLAY-COATED	
13		125-127 (Grey)	521 red	515 purple
14		138-140 (White)	512 light red	512 red
15		100-101 (Pale Orange)	520 red	517 red
16		156-158 (White)	522 red	518 red
17		160-161 (Grey)	534 purple	535 violet
18		156-157 (White)	533 light pink	533 violet

TABLE 3 - CONTINUED

ENTRY	COMPOUND	M.P. (°C)	REFLECTANCE MINIMA (nm) & COLOR ON RESIN-COATED	CLAY - COATED
19		150-154 (Yellow)	526 light pink	527 pink
20		182-184 (Pale Brown)	526 light violet	520 violet
21		138-140 (Yellow)	516 red	511 red
22		123-125 (Pale Yellow)	519 red	513 purple
23		143-145	516 red	510 red
24		141-143	529 pink	532 purple

In the above table:-

- i) the symbol $\emptyset$ is for phenyl
- ii) the colour shown with the melting point is that of the compound as prepared
- iii) the third and fourth columns give the print colour it develops. In these columns:-
 - a) "resin" is zincated phenol-formaldehyde resin colour developer
 - b) "clay" is acid washed montmorillonite clay colour developer

All of these processes discussed so far for the production of bis-(indolyl)ethylenes (I) are very conducive to scale-up.

In forming pressure sensitive or heat sensitive mark forming record systems with the bis-(indolyl)-ethylenes, the eligible acidic, or electron acceptor materials include, but are not limited to, acid clay

substances such as attapulgite, bentonite and montmorillonite and treated clays such as siltan clay as disclosed in U.S. Patent Nos. 3,622,364 and 3,753,761, phenols and diphenols as disclosed in U.S. Patent No. 3,539,375, aromatic carboxylic acids such as salicylic acid, metal salts of aromatic carboxylic acids as disclosed in U.S. Patent No. 4,022,936 and acidic polymeric material such as phenol-formaldehyde polymers as disclosed in U.S. Patent No. 3,672,935 and oil-soluble metal salts of phenol-formaldehyde polymers as disclosed in U.S. Patent No. 3,732,120. The compounds of this invention are useful as color formers in recording materials such as, for example, pressure-sensitive copying paper, thermally-responsive record material, electro heat-sensitive recording paper and thermal ink.

Pressure-sensitive copying paper systems provide a marking system and can be assembled by disposing on and/or within sheet support material unreacted mark-forming components and a liquid solvent in which one or both of the mark-forming components is soluble, said liquid solvent being present in so much form that it is maintained isolated by a pressure-rupturable barrier from at least one of the mark-forming components until application of pressure causes a breach of the barrier in the area delineated by the pressure pattern. The mark-forming components are thereby brought into reactive contact, producing a distinctive mark.

The pressure-rupturable barrier, which maintains the mark-forming components in isolation, preferably comprises microcapsules containing liquid solvent solution. The microencapsulation process utilized can be chosen from the many known in the art. Well known methods are disclosed in U.S. Patent Nos. 2,800,457; 3,041,289; 3,533,958; 3,755,190; 4,001,140 and 4,100,103. Any of these and other methods are suitable for encapsulating the liquid solvent containing the chromogenic compounds of this invention.

The chromogenic compounds are particularly useful in pressure-sensitive copying paper systems which incorporate a marking liquid comprising a vehicle in which is dissolved a complement of several colorless chromogenic compounds each exhibiting its own distinctive color on reaction with an eligible acidic record material sensitizing substance. Such marking liquids are disclosed in U.S. Patent No. 3,525,630.

Thermally-responsive record material systems provide a marking system of color-forming components which relies upon melting or subliming one or more of the components to achieve reactive, color-producing contact. The record material includes a substrate or support material which is generally in sheet form. The components of the color-forming system are in a substantially contiguous relationship, substantially homogeneously distributed throughout a coated layer material deposited on the substrate. In manufacturing the record material, a coating composition is prepared which includes a fine dispersion of the components of the color-forming system, polymeric binder material, surface active agents and other additives in an aqueous coating medium.

The chromogenic compounds are useful in thermally-responsive record material systems either as single chromogenic compounds or in mixtures with other chromogenic compounds. Examples of such systems are given in U.S. Patent Nos. 3,539,375 and 4,181,771.

Thermally-responsive record material systems are well known in the art and are described in many patents, for example U.S. Patent Nos. 3,539,375; 3,674,535; 3,746,675; 4,151,748; 4,181,771; and 4,246,318 which are hereby incorporated by reference. In these systems, basic chromogenic material and acidic color developer material are contained in a coating on a substrate which, when heated to a suitable temperature, melts or softens to permit said materials to react, thereby producing a colored mark.

In the field of thermally-responsive record material, thermal sensitivity (response) is defined as the temperature at which a thermally-responsive record material produces a colored image of satisfactory intensity (density). Background is defined as the amount of coloration of a thermally-responsive record material before imaging and/or in the unimaged areas of an imaged material. The ability to maintain the thermal sensitivity of a thermally-responsive record material while reducing the background coloration is a much sought after and very valuable feature.

One of the uses for thermally-responsive record material which is enjoying increasing importance is facsimile reproduction. Alternative terms for facsimile are telecopying and remote copying. In the facsimile system, images transmitted electronically are reproduced as hard copy. One of the important requirements for thermally-responsive record material to be used in facsimile equipment is that it have good (low coloration) background properties.

Increases in the sensitivity of thermally-responsive record material have been achieved through the incorporation of a phenylhydroxynaphthoate compound or a hydroxylanilide compound in the color-forming composition along with the chromogenic material and developer material as disclosed in U.S. Patent No. 4,470,057 or U.S. Patent No. 4,535,347, respectively, by Kenneth D. Glanz. Such sensitizer materials can be advantageously used in combination with the present invention.

The record material includes a substrate or support material which is generally in sheet form. For purposes of this invention, sheets also mean webs, ribbons, tapes, belts, films, cards and the like. Sheets

denote articles having two large surface dimensions and a comparatively small thickness dimension. The substrate or support material can be opaque, transparent or translucent and could, itself, be colored or not. The material can be fibrous including, for example, paper and filamentous synthetic materials. It can be a film including, for example, cellophane and synthetic polymeric sheets cast, extruded, or otherwise formed.

5 The gist of this invention resides in the color-forming composition coated on the substrate. The kind or type of substrate material is not critical.

Although not required to practice and demonstrate the beneficial properties, the inclusion of certain sensitizing materials in the color-forming system provides a further improvement in properties, especially increases in sensitivity. Materials such as phenyl-1-hydroxy-2-naphthoate, stearamide, 1,2-diphenoxyethane
10 and p-hydroxyoctadecanilide are useful as such sensitizing materials.

The components of the color-forming system are in a contiguous relationship, substantially homogeneously distributed throughout the color-forming system, preferably in the form of a coated layer deposited on the substrate. In manufacturing the record material, a coating composition is prepared which includes a fine dispersion of the components of the color-forming system, polymeric binder material, surface active
15 agents and other additives in an aqueous coating medium. The composition can additionally contain inert pigments, such as clay, talc, aluminum hydroxide, calcined kaolin clay and calcium carbonate; synthetic pigments, such as urea-formaldehyde resin pigments; natural waxes such as carnauba wax; synthetic waxes; lubricants such as zinc stearate; wetting agents and defoamers.

The color-forming system components are substantially insoluble in the dispersion vehicle (preferably
20 water) and are ground to an individual average particle size of between about 1 micron to 10 microns, preferably about 1 to 3 microns. The polymeric binder material is substantially vehicle soluble, although latexes are also eligible in some instances. Preferred water-soluble binders include polyvinyl alcohol, hydroxy ethylcellulose, methylcellulose, hydroxypropylmethylcellulose, starch, modified starches, gelatin and the like. Eligible latex materials include polyacrylates, polyvinylacetates, polystyrene, and the like. The
25 polymeric binder is used to protect the coated materials from brushing and handling forces occasioned by storage and use of the thermal sheets. Binder should be present in an amount to afford such protection and in an amount less than will interfere with achieving reactive contact between color-forming reactive materials.

Coating weights can effectively be about 3 to about 9 grams per square meter (gsm) and preferably
30 about 5 to about 6 gsm. The practical amount of color-forming materials is controlled by economic considerations, functional parameters and desired handling characteristics of the coated sheets.

BRIEF DESCRIPTION OF THE DRAWINGS, PRESENT ASPECT

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In the drawings Figs. 1 and 2 are the reflectance spectra of respectively 1,1-bis(1-ethyl-2-methylindole-3-yl)ethylene on resin-coated and "Silton" (Trade Mark) - coated paper, and Figs. 3 and 4 correspondingly the spectra of 1-(1- β -methoxyethyl-2-methyl-indole-3-yl)-1-(1-ethyl-2-methylindole-3-yl) ethylene. The resin is a zincated phenol-formaldehyde resin colour developer and the "Silton" an acid washed montmorillonite
40 clay colour developer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE PRESENT ASPECT

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In the following examples, general procedures for preparing certain bis(indolyl)ethylenes of formula (I) are described; the examples are not intended to be exhaustive and the moieties, as previously defined, are all eligible for use in any combination in preparing the compounds. Unless otherwise noted, all measurements, percentages and parts are by weight.

Satisfactory spectroscopic data were obtained for the new compounds synthesized.

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Example 1

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Preparation of 1,1-bis(1-ethyl-2-methylindole-3-yl) ethylene

[Table 3, Entry 1]

1-ethyl-2-methylindole (16.0 g, 0.1 mole) and finely powdered zinc chloride (7.0 g, 0.05 mole) were placed in a 250 ml round bottom flask equipped with a dropping funnel, magnetic stirrer and a reflux condenser carrying a drying tube. 1,2-dichloroethane (50 ml) was added, followed by acetic anhydride (10.2 g, 0.1 mole) in 1,2-dichloroethane (30 ml). Then, the reaction mixture was refluxed with stirring. After one hour, GC analysis of the reaction mixture indicated that almost all the starting indole had been used up. The reaction mixture was cooled to room temperature; treated with water (150 ml) to remove most of the zinc salts; the organic layer separated, washed with 10% aqueous sodium hydroxide and brine; dried over anhydrous magnesium sulfate; filtered and the filtrate concentrated under reduced pressure. The residue was dissolved in methanol and cooled in an ice bath. The precipitated solid was isolated and recrystallized from toluene/methanol. Yield (1st crop): 10.3 g (60%), M.P.: 179-181°C.

The calculated analysis for $C_{24}H_{26}N_2$, the title compound, is C, 84.17%; H, 7.65%; and N, 8.18%. Found on analysis: C, 83.08%; H, 7.68%; and N, 7.88%.

Example 2

Preparation of 1,1-bis(1-ethyl-2-methylindole-3-yl)ethylene

[Table 3, Entry 1]

A mixture of 1-ethyl-2-methylindole (15.9 g, 0.1 mole) and acetyl chloride (9.4 g, 0.12 mole) was stirred at room temperature for 20 hours. Then, water (100 ml) was added to the reaction mixture and the resulting grains were filtered and dried. The dried product was recrystallized from toluene/methanol. Yield: 13.0 g (77.0%). M.P.: 183-185°C. IR (KBr) spectrum was identical to that of the product in Example 1.

Example 3

Preparation of 1,1-bis(1-ethyl-2-methylindole-3-yl)ethylene

[Table 3, Entry 2]

A mixture of 1-ethyl-2-methylindole (15.9 g, 0.1 mole), acetyl chloride (2.0 g, 0.025 mole) and acetic anhydride (15 ml) was stirred at 50-52°C for 8 hours. Then, the reaction mixture was cooled to room temperature and poured into ice, water and sodium hydroxide (10%, 50 ml). After stirring for 20 minutes, the precipitated solid was filtered off, washed with water, refluxed with methanol for 1 hour and cooled. The solid was filtered, washed with methanol and dried. Yield of the product: 16.5g (96%), pale yellow powder, m.p.: 179-182°C. IR(KBr) spectrum was identical to that of the product in Example 1.

Example 4

Preparation of 1,1-bis(1-ethyl-2-methylindole-3-yl)-2-phenylethylene

[Table 3, Entry 9]

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A mixture of 1-ethyl-2-methylindole (159.0 g, 1 mole), phenacetyl chloride (185.4 g, 1.2 moles) and 1,2-dichloroethane (500 ml) was stirred at 45-50°C for 20 hours. Then, the reaction mixture was cooled to room temperature and stirred with ice, water and sodium hydroxide (10%, 600 ml) for 20 minutes. The organic layer was separated, washed with water, dried and concentrated. The residue was refluxed with methanol (1 liter) for 1 hour and cooled. The solid precipitated, was filtered off, washed twice with methanol and dried. Yield of the product: 157 g (75%), white powder, m.p.: 157-159°C.

The calculated analysis for $C_{30}H_{30}N_2$, the title compound, is C, 86.07%; H, 7.24%; and N, 6.69%. Found on analysis: C, 86.31%; H, 7.08; and N, 6.65%.

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Example 5

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Preparation of 1,1-bis(1-ethyl-2-phenylindole-3-yl)-ethylene

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[Table 3, Entry 10]

A mixture of 1-ethyl-2-phenylindole (110.5 g, 0.5 mole) acetyl chloride (78.5 g, 1 mole) and 1,2-dichloroethane (200 ml) was stirred at 50-55°C for 20 hours. After cooling to room temperature, the reaction mixture was stirred vigorously with ice, water and sodium hydroxide (10%, 500 ml) for 20 minutes. The organic layer was separated, washed with water, dried and concentrated. The residue was refluxed with methanol (300 ml) and cooled. The resulting solid mass was filtered off, dried and pulverized. The pulverized product was refluxed with isopropanol (30 ml) for 1 hour, cooled, filtered and the residue washed with methanol (200 ml) and dried. Yield of the product: 104 g (89%), pale brown powder, m.p.: 165-167°C.

The calculated analysis for $C_{34}H_{30}N_2$, the title compound, is C, 87.50%; H, 6.49; and N, 6.00%. Found on analysis: C, 87.72%; H, 6.55%; and N, 6.00%.

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Example 6Preparation of 1,1-bis(1-n-octyl-2-phenylindole-3-yl)ethylene

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[Table 3, Entry 12]

A mixture of 1-n-octyl-2-phenylindole (122.0 g, 0.4 mole) and acetyl chloride (37.7 g, 0.48 mole) was stirred at 50-55°C for 18 hours. TLC analysis of the reaction mixture showed the presence of starting indole. The reaction mixture was stirred with more acetyl chloride (15.7 g, 0.2 mole) for 24 hours. Then, water (3 liters) was added to the reaction mixture, followed by extraction with toluene (300 ml). The toluene extract was washed twice with hot water, dried over anhydrous sodium sulfate, filtered and the filtrate concentrated. The residue was chromatographed on alumina with toluene as eluent. The desired fractions were collected, combined and concentrated under reduced pressure. Yield: 115 g (45%) Pale Brown Oil.

The calculated analysis for $C_{46}H_{54}N_2$, the title compound, is C, 87.00%; H, 8.59%; and N, 4.41%. Found on analysis: C, 87.10%; H, 8.58%; and N, 4.18%.

Example 75 Preparation of 1,1-bis(2,5-dimethyl-1-ethylindole-3-yl)ethylene

[Table 3, Entry 13]

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A mixture of 2,5-dimethyl-1-ethylindole (95.2 g, 0.55 mole) and acetyl chloride (86.4 g, 1.1 moles) was stirred at room temperature for 20 hours. Then, the reaction mixture was poured into ice, water and sodium hydroxide (10%, 300 ml) and stirred vigorously for 20 minutes. The precipitated solid was filtered off, washed with water, refluxed with methanol (500 ml) for 1 hour and cooled. The solid was filtered, washed with methanol and dried. Yield of the product: 94.0 g (92%), pale grey powder, m.p.: 125-127°C.

The calculated analysis for $C_{26}H_{30}N_2$ the title compound, is C, 84.26%; H, 8.18%; and N, 7.56%. Found on analysis: C, 84.11%; H, 8.36%; and N, 7.53%.

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Example 825 Preparation of 1,1-bis(2,7-dimethyl-1-ethylindole-3-yl)ethylene

[Table 3, Entry 17]

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A mixture of 2,7-dimethyl-1-ethylindole (65.7 g, 0.38 mole) and acetyl chloride (59.7 g, 0.76 mole) was stirred at room temperature for 20 hours. Then, the reaction mixture was added to ice, water and sodium hydroxide (10%, 300 ml) and stirred for 20 minutes. The solid precipitated was worked-up as in Example 6. Yield of the product: 63.0 g (90%), grey powder, m.p.: 160-161°C.

The calculated analysis for $C_{26}H_{30}N_2$ the title compound, is C, 84.26%; H, 8.18%; and N, 7.56%. Found on analysis: C, 84.50%; H, 8.02%; and N, 7.58%.

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Example 9

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Preparation of 3-acetyl-1-ethyl- 2-methylindole

(K5)

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Phosphoryl chloride (33.7 g, 21.0 ml, 0.22 mole) was added dropwise to vigorously stirred N,N-dimethylacetamide (19.2 g, 20.5 ml, 0.22 mole) cooled in an ice/salt bath, keeping the temperature of the reaction mixture between 10 and 20°C during the addition. Then, the reaction mixture was stirred for 30 minutes as it warmed to room temperature. 1,2-dichloroethane (50 ml) was added to the reaction mixture, cooled in an ice/salt bath and followed by the addition of 1-ethyl-2-methylindole (32.0g, 0.20 mole) in 1,2-dichloroethane (30 ml.) while the reaction mixture was kept at 5°C. The reaction mixture was then refluxed for one hour, cooled to room temperature, stirred with aqueous sodium hydroxide (10%) and the organic layer was separated. The organic layer was washed with aqueous sodium hydroxide (10%) and then with

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brine (2x), dried and filtered, and the filtrate concentrated. The residue was chromatographed on silica gel using toluene:acetone::4:1 as eluent. The fractions containing the product were collected, combined and concentrated. The residue was recrystallized from toluene/petroleum ether. Yield: - 33.5 g (83%), pale yellow solid, m.p.: -90-92 °C.

5 The calculated analysis for $C_{13}H_{15}NO$, the title compound, is C, 77.58%; H, 7.51%; N, 6.96%; and O, 7.95%. Found on analysis: C, 77.71%; H, 7.45%; and N, 6.94%.

Example 10

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Preparation of 1-(1-ethyl-2-methylindole-3-yl)-1-(1-ethyl-2-methyl-6,7-benzoinidole-3-yl)-ethylene. (Table 3, Entry 21].

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Phosphoryl chloride (1.6 g, 0.01 mole) was added slowly to a well-stirred solution of 3-acetyl-1-ethyl-2-methylindole (2.2g, 0.011 mole) in 1,2-dichloroethane (10 ml) cooled in an ice/salt bath. Stirring was continued for one hour as the reaction mixture warmed to room temperature. Then, 1-ethyl-2-methyl-6,7-benzoinidole (2.1 g, 0.01 mole) was added and the reaction mixture was refluxed for one hour, cooled to room temperature, treated with aqueous sodium hydroxide (10%, 30 ml); the organic layer was separated, washed with water, dried and concentrated. The residue was chromatographed on silica gel using toluene as eluent. Fractions containing the product were collected, combined and concentrated. The residue was recrystallized from isopropanol. Yield: 3.1 g (80%), yellow solid, m.p.: -138-140°C.

25 The calculated analysis for $C_{28}H_{28}N_2$, the title compound, is C, 85.67%; H, 7.19%; and N, 7.14%. Found on analysis: C, 85.81%; H, 7.26%; and N, 7.19%.

Example 11

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Preparation of 1-(1-ethyl-2-methylindole-3-yl)-1-(1-β-methoxyethyl-2-methylindole-3-yl)-ethylene. [Table 3, Entry 22]

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3-acetyl-1-ethyl-2-methylindole (4.4 g, 0.022 mole) was dissolved in 1,2-dichloroethane (30 ml) and the solution was cooled in an ice/salt bath. Phosphoryl chloride (3.1 g, 0.02 mole) was added and the reaction mixture was stirred for 30 minutes as it warmed to room temperature. Then, 1-(β-methoxyethyl)-2-methylindole (3.8 g, 0.02 mole) in 1,2-dichloroethane (10 ml) was added and the reaction mixture was stirred overnight at room temperature. After refluxing for one hour, the reaction mixture was cooled; poured into ice, water and sodium hydroxide (10%, 100 ml); stirred for 20 minutes and the organic layer separated. The organic layer was washed with water, dried and concentrated under reduced pressure. The residue was chromatographed on silica gel using toluene as eluent. The fractions containing the product were collected, combined and concentrated. The residue was recrystallized from toluene/methanol. Yield: 5.5g (74%), pale yellow solid, m.p.: -123-125°C.

45 The calculated analysis for $C_{25}H_{28}N_2O$, the title compound, is C, 80.61%; H, 7.58%; N, 7.52%; and O, 4.29%. Found on analysis: C, 80.82%; H, 7.65%; and N, 7.50%.

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Example 12

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Example of Pressure-Sensitive Record Material

Formulations and techniques for the preparation of carbonless copy paper are well known in the art, for

example, as disclosed in U.S. Patent Nos. 3,627,581; 3,775,424; and 3,853,869 incorporated herein by reference. CF sheets used with the CB sheets to form a manifold assembly are well known in the art. Substrate sheets containing oil-soluble metal salts of phenol-formaldehyde novolak resins of the type disclosed in U.S. Patent Nos. 3,675,935; 3,732,120; and 3,737,410 are exemplary thereof. A typical example
 5 of a suitable acidic resin is a zinc modified, oil-soluble phenol-formaldehyde resin such as the zinc salt of a para-octylphenol-formaldehyde resin or the zinc salt of a para-phenylphenol-formaldehyde resin.

Color former solution:	
	Parts
bis indolyethylene ex. (1,1-bis(1-ethyl-2-methyl-3-indolyl)ethylene	5.6
C ₁₀ -C ₁₅ alkylbenzene ex. Alkylate 215	130.0
(ethylphenyl)phenylmethane	70.0

The color former solution is emulsified into a mixture of 35 parts of 10% EMA 31 [ethylene-maleic anhydride copolymer with a molecular weight range of 75,000 to 90,000 (Monsanto)] in water, 32 parts of 20% EMA 1103 [ethylene maleic anhydride copolymer with a molecular weight range of 5,000 to 7,000 (Monsanto)] in water, 133 parts water, 10 parts urea, and 1 part resorcinol, adjusted to pH 3.5. Following
 20 emulsification 29 parts 37% formaldehyde is added and the mixture placed in a 55°C water bath with stirring. After two hours, with stirring maintained, the temperature of the water bath is allowed to equilibrate with ambient temperature. The capsules are used to prepare a paper coating slurry.

	Parts Wet	Parts Dry
capsule slurry	80	40
wheat starch granules	10	10
etherified corn starch binder ex. Penford 230, 10% (Penwick and Ford Ltd.)	40	4
water	100	--

The slurries are applied to a paper base and drawn down with a No. 12 wire wound coating rod and the coatings dried. The resulting CB coatings are coupled with a sheet comprising a zinc-modified phenolic resin as disclosed in U.S. Patent Nos. 3,732,120 and 3,737,410. Upon pressure contact, a visible image forms corresponding to the localized contact. Dyes can be versatily mixed for color customization.

Example 13

Example of Heat-Sensitive Record Material

The coating is prepared by milling the components in an aqueous solution of the binder until a particle size of between 1 and 10 microns is achieved. The milling is accomplished in an attritor, small media mill, or other suitable dispensing vehicle. The desired average particle size is 1 to 3 microns.

Separate dispersions of chromogenic compound, acidic developer material, and sensitizer are prepared.

Chromogenic Dispersion A		Parts
bis-indolyethylene ex. 1,1-bis(2,5-dimethyl-1-ethyl-3-indolyl)ethylene of Example 7		39.10
binder, 20% polyvinylalcohol in water		28.12
water		45.00
defoamer and dispersing agent ex Nopko NDW (sulfonated castor oil of Nopko Chemical Co.)		00.28
Surfynol 104 (a ditertiary acetylene glycol surface active agent)		10.60

Acidic Developer Material Dispersion B	
acidic developer material ex. 4,4'-isopropylidenediphenol	13.60
binder, 10% polyvinylalcohol in water	24.00
water	42.35
defoamer, Nopko NDW	00.05
Surfynol	00.60

Sensitizer Dispersion C (optional)	
sensitizer ex. phenyl-1-hydroxy-2-naphthoate or 1,2-diphenoxyethane U.S. 4,531,140	13.60
binder, 10% polyvinylalcohol in water	24.00
water	42.35
defoamer, Nopko NDW	00.05
Surfynol	00.60

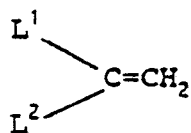
The above separate dispersions, A, B, and C, can be combined as follows, and optionally include zinc stearate, 21% dispersion, urea formaldehyde resin, and micronized silica.

The above dispersions are combined 0.6 parts A, 4.9 parts B, 3.3 parts C, along with 1.4 parts zinc stearate dispersion, 4.3 parts water, 1.9 parts polyvinylalcohol and 0.6 parts urea formaldehyde resin. This mix is applied to paper and dried yielding a dry coat weight of 5.2 to 5.9 gsm. The resultant paper is sensitive to applied heat such as via a thermal print head.

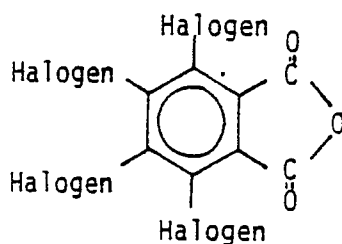
SECOND ASPECT OF INVENTION

In this aspect the invention provides chromogenic di-[bis-(indolyl)ethylenyl]tetrahalophthalides methods for their production, and use to give intense colors when reacted with an electron accepting coreactant material. More specifically, this aspect relates to methods for the production of such chromogenic compounds for use in novel pressure-sensitive or heat-sensitive mark-forming record systems. As used in mark-forming systems, marking in desired areas on support webs or sheets may be accomplished by effecting localized reactive contact between the chromogenic material and the electron-accepting material on or in such web or sheet, such material being brought thereto by transfer or originally there in situ, the desired reactive contact forming colored images in the intended image marking areas.

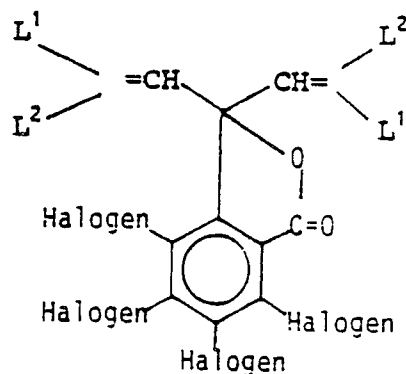
In related art, Sheldon Farber, U.S. Patent No. 4,119,776 issued October 10, 1978, described vinyl phthalide color formers. Several divinyl phthalide chromogenic compounds (C1) [(C) L¹, L²=substituted phenyl] (read as Compound C1 arrived at by referring to formula C wherein L¹ and L² are as stated) have been prepared by the condensation of ethylenes (A1) [(A) L¹, L²=substituted phenyl] with phthalic anhydrides (B) [(B) Each Halogen is independently Cl or Br] in acetic anhydride.



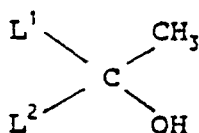
(A)



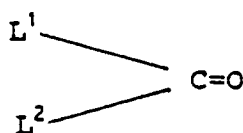
(B)



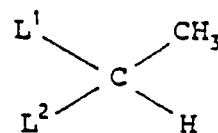
(C)



(D)



(E)



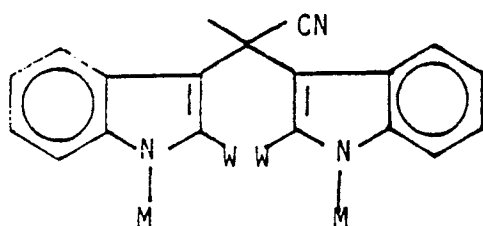
(F)

Substituted ethylenes (A1) or their precursors (D1) [(D) L^1, L^2 = substituted phenyl] were prepared by the reaction of methylmagnesium bromide (also known as methyl Grignard reagent) with ketones (E1) [(E) L^1, L^2 = substituted phenyl]. The use of Grignard reaction to prepare (A1) imposes severe restrictions on the scale up synthesis of (A1) and consequently on the manufacture of divinyl phthalides (C1).

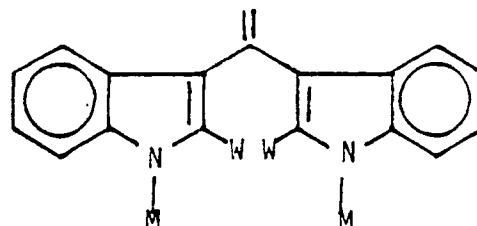
In another synthetic approach, the alcohol (D1) was obtained by reacting the ethane (F1) [(F) L^1, L^2 = substituted phenyl] with lead peroxide in either nitric acid or formic acid; and the substituted ethylene (A1) was obtained from (D1) by dehydration [Yamada Kagaku, Japan Kokai 1988-8360, filed June 30, 1986].

When indole was heated with acetic anhydride containing 10% acetic acid a bis(indolyl)ethylene (A2) [(A) L^1, L^2 = 1-acetylindole-3-yl] was obtained as a by-product in 5-10% yield (J. E. Saxton, J. Chem. Soc., 3592 (1952)).

Substituted (2- and 1,2-) indoles when reacted with acetyl cyanide in the presence of hydrogen chloride yielded 1-cyano-1,1-di(3-indolyl)ethanes (G) and these products can be converted to bis(indolyl)ethylenes (H) by heating them under vacuum either alone or with soda lime. In some cases, depending on the substituents M and W, (G) yields (H) on refluxing with aqueous-ethanolic 10% potassium hydroxide [A. K. Kiang and F. G. Mann, J. Chem., Soc., 594 (1953)].



(G)



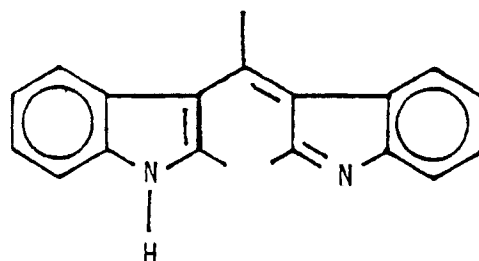
(H)

M=H, Ph

W=Me, Ph

Bis(indolyl)ethylene (H1) [(H) M=H and W=Me] was speculated to be a product, (m.p. 203 °C) from the reaction of 2-methylindole with ethyl acetate and sodium ethoxide. No other data were given to substantiate the structure [A. Angeli and G. Marchetti, Atti. Accad. Lincei, 16 (II), 179 (1907)].

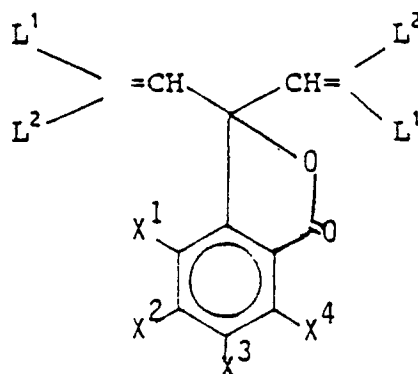
In another report (W. Borsche and H. Groth, Annalen, 549, 238 (1941)), 2-methylindole when boiled with acetyl chloride formed a product that on treatment with alkali gave a pseudobase, (C₂₀H₁₈N₂, pale rose, m.p. 208 °C). The pseudobase was suggested to be 1-(2-methylindole-3-yl)-1-(2-methyl-3-indolidene)ethane (H2). Again, insufficient data precludes the substantiation of this structure. Furthermore, similar structure was proposed for the pseudobase obtained by substituting 2-phenylindole for 2-methylindole.



(H2)

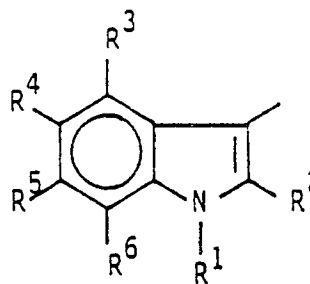
SUMMARY OF PRESENT ASPECT

A. Novel symmetrical and unsymmetrical chromogenic di-[bis-(indolyl)ethylenyl]tetrahalophthalides. Specifically these compounds are chromogenic di-[bis-(indolyl)ethylenyl]tetrahalophthalides of the formula



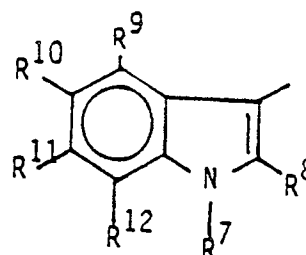
wherein

$L^1 =$

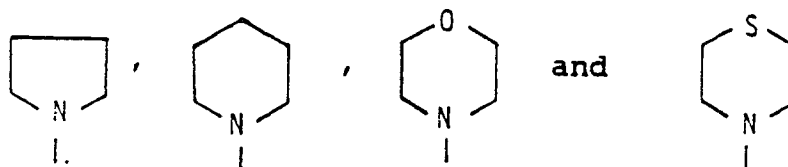


and

$L^2 =$

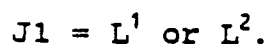
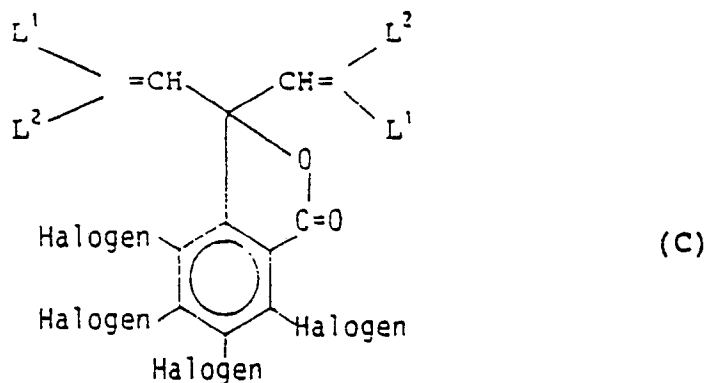


wherein each X^1 , X^2 , X^3 , and X^4 is independently selected from chlorine or bromine;
 wherein each of R^1 and R^7 is independently selected from cycloalkyl (e.g. cyclohexyl, cyclopentyl, cyclobutyl and cyclopropyl), aralkyl, alkoxyalkyl (e.g. β -methoxyethyl), aroxyalkyl (e.g. β -phenoxyethyl);
 wherein each of R^2 and R^8 is independently selected from alkyl ($C_1 - C_8$) and aryl (substituted or unsubstituted);
 wherein each of R^3 , R^4 , R^5 , R^6 , R^9 , R^{10} , R^{11} , and R^{12} is independently selected from hydrogen, halogen, alkyl ($C_1 - C_8$), cycloalkyl, aryl (substituted or unsubstituted), halogen, alkoxy ($C_1 - C_8$), aroxy, cycloalkoxy, dialkylamino including symmetrical and unsymmetrical alkyl ($C_1 - C_8$), alkylcycloalkylamino, dicycloalkylamino, alkylarylamino,



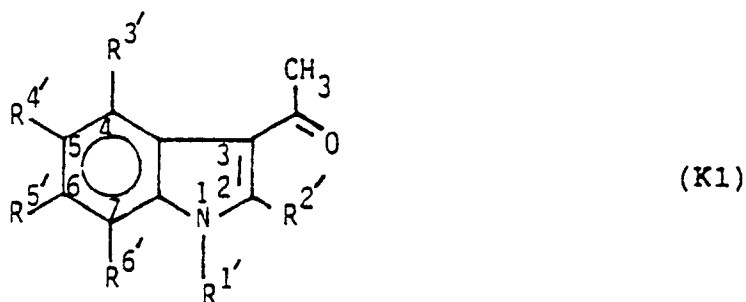
$J1 = L^1 \text{ or } L^2.$

B. Novel methods for producing these di-[bis(indolyl)ethylenyl]tetrahalophthalides. The above formula, for ease of reference, can also be expressed as (C2) [(C) wherein each Halogen is independently selected from chlorine or bromine; wherein each L namely, L^1 and L^2 is the same or different and is each independently selected from indole moieties (J1). This is read as new compound C2 arrived at by reference to formula C wherein L^1 and L^2 are as stated.



Preparation of di-[bis-(indolyl)ethylenyl]tetrahalophthalides (C2) comprises condensation of bis(indolyl)-ethylenes (A3) [(A) wherein each L^1 and L^2 is the same or different and is each independently selected from indole moieties (J1), with tetrahalophthalic anhydrides (B) in acetic anhydride with or without acetate of Group I or Group II elements of the periodic table

The first route uses the corresponding indoles, acetic anhydride and Lewis acid such as zinc chloride or other electron acceptor preferably in approximately 1:1:0.5 molar ratios respectively in a suitable solvent. The second route uses the corresponding indoles with acetyl chloride preferably in approximately 1:(0.5-2.0) molar amounts at temperatures (15-75°C) with or without solvent. The third route involves a condensation of component (K1) with indole (J1) in the presence of a Vilsmeier reagent (such as phosphoryl chloride, phosgene, oxalyl chloride, benzoyl chloride, alkanesulfonyl chloride, arenesulfonyl chloride, alkyl chloroformate and aryl chloroformate) with or without solvent. This third route can be used to conveniently prepare unsymmetrical indolyl ethylenes (i.e. (A3) with different L^1 and L^2).



wherein $R^1, R^2, R^3, R^4, R^5, R^6$ of K1 are defined identically as R^1, R^2, R^3, R^4, R^5 and R^6 respectively in formula L¹, i.e. R^1 is defined the same as R^1 , R^2 is defined as R^2 , $R^3 = R^3$, $R^4 = R^4$, $R^5 = R^5$ and $R^6 = R^6$.

The processes disclosed herein are versatile and can be used to prepared di[bis-(indolyl)ethylenyl]-tetrahalophthalides using indoles with broader substitution patterns than simply J1, i.e., can be used to make compounds broader in scope than (C). In other words, if desired, in the disclosed processes, K1's substituents R^1 and R^2 can be broader than R^1 and/or R^2 of J1. Thus, R^1 can additionally, in the disclosed processes, include hydrogen, alkyl ($C_1 - C_8$), substituted or unsubstituted aryl, and alkoxy. R^2 can additionally in the processes include hydrogen.

Solvents as referred to herein are preferably organic and more preferably the halogenated organic solvents such as 1,2-dichloroethane and chlorobenzene and the like.

Di-[bis(indolyl)ethylenyl]tetrahalophthalides (C2) are prepared via two major routes from bis(indolyl)-

ethylenes (A3) and tetrahalophthalic anhydrides (B). In the first route bis(indolyl)ethylene (A3) and tetrahalophthalic anhydride (B) in 2:1 molar ratio respectively were heated at 100-110 °C in acetic anhydride for 2-3 hours. In the case of acid sensitive bis(indolyl)ethylene, acetate of Group I or Group II elements was added to the above reaction mixture to improve the yield of (C2). In the second route, the bis(indolyl)-ethylene (A3) is generated in situ from the indole (J1) and acetyl chloride with or without solvent and then condensed with tetrahalophthalic anhydride (B) in the presence of acetate of Group I or Group II elements and acetic anhydride at 100-110 °C for 2-3 hours. This procedure, referred to as one-pot two-step synthesis, has several advantages over the first route; for example, (a) it simplifies the process for the manufacture of di-[bis-(indolyl)ethylenyl]tetrahalophthalides (C2) by eliminating the isolation and purification of intermediate bis(indolyl)ethylenes; and (b) unstable or difficult to isolate bis(indolyl)ethylenes (A3) are condensed in situ with tetrahalophthalic anhydrides (B) to give (C2) that are difficult to prepare otherwise.

All the above-mentioned methods are conducive to scale-up and are used to prepare a variety of di-[bis-(indolyl)ethylenyl]tetrahalophthalides (C2). Some examples are illustrated in Table 1'.

Table 1'

Entry	Compound	M.P. (°C)	Color
1.		238-240	Grey
2.		252-253	Pale Yellow
3.		140-142	Pale Yellow
4.		137-140	Pale Yellow

Table 1 (Continued)

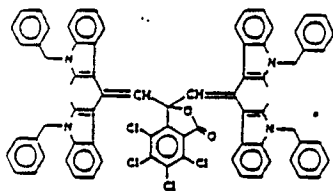
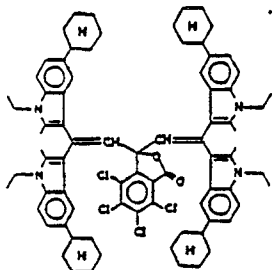
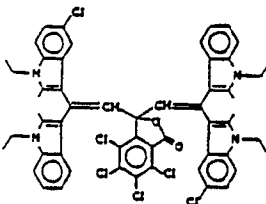
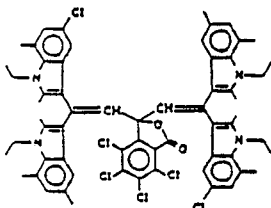
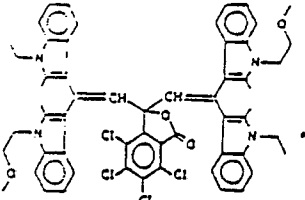
Entry	Compound	M.P. (°C)	Color
5.		255-260	Grey
6.		225-228	Pale Yellow
7.		172-175	White
9.		269-271	White

Table 1 (Continued)

Entry	Compound	M.P. (°C)	Color
5			
10		213-217	Brown
15			

BRIEF DESCRIPTION OF THE DRAWINGS, PRESENT ASPECT

Figure 5 is a graph of reflectance (%) from 400 to 1200 nm for the compound shown in the graph 1 when coated on resin-coated paper:

3,3-bis[1-(1-ethyl-2-methylindole-3-yl)-1-(1-β-methoxyethyl-2-methylindole-3-yl)ethylene-2-yl]-4,5,6,7-tetrachlorophthalide.

Figure 6 is a graph of reflectance of the above compound when coated on silton-coated paper. Example 2 details the synthesis of this specific compound.

Figure 7 is a graph of reflectance (%) from 400 to 1200 nm for the compound shown on the graph when coated on resin-coated paper:

3,3-bis[1,1-bis(1-cyclohexyl-2-methylindole-3-yl)ethylene-2-yl]-4,5,6,7-tetrabromophthalide.

Figure 8 is a graph of reflectance of the above compound when coated on silton-coated paper.

The resin is a zincated phenol-formaldehyde resin colour developer. The "Silton" (trade mark) is an acid washed montmorillonite clay colour developer

DETAILED DESCRIPTION OF PRESENT ASPECT

Teaches a process for the preparation of chromogenic compounds which in color form have absorbance in the infrared region of the spectrum at approximately 700-1200 nm and thus are eligible for use in pressure-sensitive and thermal recording systems. Compounds which are chromogenic and absorptive in the near infrared region of the spectrum have commercial utility by being capable, when imaged, of being detected by optical reading machines.

More particularly, describes novel methods for the preparation of substantially colorless but colorable chromogenic compounds eligible for use in pressure-sensitive recording and thermal recording systems. Advantageously recording systems utilizing these compounds can be read by optical reading machines, particularly those capable of reading for the infrared wavelength range of 700-1200 nm.

The colorable chromogenic compounds can be combined with other chromogenic materials covering other or wider spectral ranges and can be used in pressure-sensitive and thermal recording systems to provide images which absorb over wider ranges of the electromagnetic spectrum. The commercial significance is that a larger assortment of available optical readers can thus be effectively useful with such imaged record systems.

The chromogenic compounds also find use in photosensitive printing material, typewriter ribbons, inks and the like.

More specifically the process relates to the preparation of chromogenic compounds having two vinyl linkages. These compounds are substantially colorless or slightly colored solids but can be converted to colored forms upon reactive contact with an electron accepting material. The compounds in imaged or colored form are typically dark colored and are remarkably absorptive of near infrared light such that images formed of these compounds can be detected by conventional optical readers capable of detecting in the infrared wavelength range of 700-1200 nm.

In the above, di-[bis-(indolyl)ethylenyl]tetrahalophthalides (C₂) [(C) wherein each halogen is indepen-

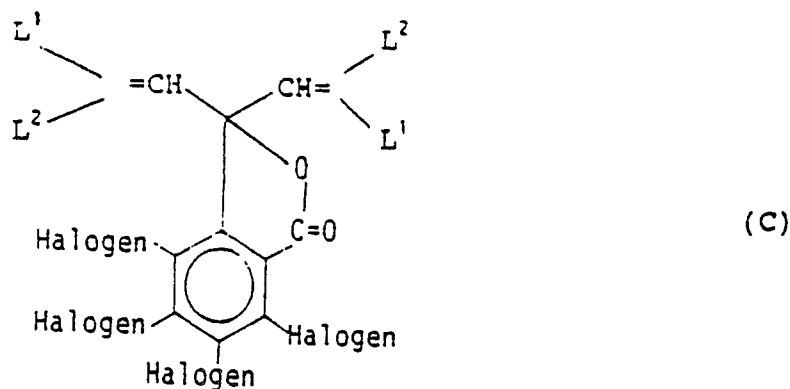
dently selected from chlorine or bromine; wherein each L namely, L¹ and L² is the same or different and is each independently selected from indole moieties of the formulae (J1)] are prepared. (C2) is understood or read to be compound (C) as described in the brackets and with reference to the formula set forth below.

The processes described for the preparation of (C2) are very conducive to scale up.

5

10

15



20

J1 = L¹ or L² are as earlier defined herein. The halogen is each independently chlorine or bromine.

25

30

In forming pressure-sensitive or heat-sensitive mark-forming record systems with di-[bis-(indolyl)-ethylenyl]tetrahalophthalides of the invention, the eligible acidic, or electron acceptor materials include, but are not limited to, acid clay, substances such as attapulgite, bentonite and montmorillonite and treated clays such as siltan clay as disclosed in U.S. Patent Nos. 3,622,364 and 3,753,761, phenols and diphenols as disclosed in U.S. Patent No. 3,539,375, aromatic carboxylic acids such as salicylic acid, metal salts of aromatic carboxylic acids as disclosed in U.S. Patent No. 4,022,936 and acidic polymeric material such as phenol-formaldehyde polymers as disclosed in U.S. Patent No. 3,672,935 and oil-soluble metal salts of phenol-formaldehyde polymers as disclosed in U.S. Patent No. 3,732,120. The compounds of this invention are useful as color formers in recording materials such as, for example, pressure-sensitive copying paper, thermally-responsive record material, electro heat-sensitive recording paper and thermal ink.

35

Pressure-sensitive copying paper systems provide a marking system and can be assembled by disposing on and/or within sheet support material unreacted mark-forming components and a liquid solvent in which one or both of the mark-forming components is soluble, said liquid solvent being present in such form that it is maintained isolated by a pressure-rupturable barrier from at least one of the mark-forming components until application of pressure causes a breach of the barrier in the area delineated by the pressure pattern. The mark-forming components are thereby brought into reactive contact, producing a distinctive mark.

40

The pressure-rupturable barrier, which maintains the mark-forming components in isolation, preferably comprises microcapsules containing liquid solvent solution. The microencapsulation process utilized can be chosen from the many known in the art. Well known methods are disclosed in U.S. Patent Nos. 2,800,457; 3,041,289; 3,533,958; 3,755,190; 4,001,140 and 4,100,103. Any of these and other methods are suitable for encapsulating the liquid solvent containing the chromogenic compounds of this invention.

45

The chromogenic compounds are particularly useful in pressure-sensitive copying paper systems which incorporate a marking liquid comprising a vehicle in which is dissolved a complement of several colorless chromogenic compounds each exhibiting its own distinctive color on reaction with an eligible acidic record material sensitizing substance. Such marking liquids are disclosed in U.S. Patent No. 3,525,630.

50

Thermally-responsive record material systems provide a marking system of color forming components which relies upon melting or subliming one or more of the components to achieve reactive, color-producing contact. The record material includes a substrate or support material which is generally in sheet form. Components of the color-forming system are in a substantially contiguous relationship, preferably substantially homogeneously distributed throughout a coated layer or layers of material deposited on the substrate. In manufacturing the record material, a coating composition is preferred which includes a fine dispersion of the components of the color-forming system, polymeric binder material, surface active agents and other additives in an aqueous coating medium.

55

The chromogenic compounds are useful in thermally-responsive record material systems either as single chromogenic compounds or in mixtures with other chromogenic compounds. Examples of such systems are given in U.S. Patent Nos. 3,539,375 and 4,181,771.

Thermally-responsive record material systems are well known in the art and are described in many

patents, for example U.S. Patent Nos. 3,539,375; 3,674,535; 3,746,675; 4,151,748; 4,181,771; and 4,246,318 which are hereby incorporated by reference. In these systems, basic chromogenic material and acidic color developer material are contained in a coating on a substrate which, when heated to a suitable temperature, melts or softens to permit said materials to react, thereby producing a colored mark.

5 In the field of thermally-responsive record material, thermal sensitivity (response) is defined as the temperature at which a thermally responsive record material produces a colored image of satisfactory intensity (density). Background is defined as the amount of coloration of a thermally-responsive record material before imaging and/or in the unimaged areas of an imaged material. The ability to maintain the thermal sensitivity of a thermally-responsive record material while reducing the background coloration is a
10 much sought after and very valuable feature.

One of the uses for thermally responsive record material which is enjoying increasing importance is facsimile reproduction. Alternative terms for facsimile are telecopying and remote copying. In the facsimile system, images transmitted electronically are reproduced as hard copy. One of the important requirements for thermally-responsive record material to be used in facsimile equipment is that it have good (low
15 coloration) background properties.

Increases in the sensitivity of thermally-responsive record material have been achieved through the incorporation of a phenylhydroxynaphthoate compound or a hydroxylanilide compound in the color-forming composition along with the chromogenic material and developer material as disclosed in U.S. Patent No. 4,470,057 or U.S. Patent No. 4,535,347, respectively, by Kenneth D. Glanz. Such sensitizer materials can be
20 advantageously used in combination with the present invention.

The record material includes a substrate or support material which is generally in sheet form. For purposes of this invention, sheets also mean webs, ribbons, tapes, belts, films, cards and the like. Sheets denote articles having two large surface dimensions and a comparatively small thickness dimension. The substrate or support material can be opaque, transparent or translucent and could, itself, be colored or not.
25 The material can be fibrous including, for example, paper and filamentous synthetic materials. It can be a film including, for example, cellophane and synthetic polymeric sheets cast, extruded, or otherwise formed. The gist of this invention resides in the color-forming composition coated on the substrate. The kind or type of substrate material is not critical.

Although not required to practice and demonstrate the beneficial properties of the claimed invention, the
30 inclusion of certain sensitizing materials in the color-forming system provides a further improvement in properties, especially increases in sensitivity. Materials such as 1,2-diphenoxyethane, N-acetoacetyl-o-toluidine, para- benzylbiphenyl; phenyl-1-hydroxy-2-naphthoate, stearamide and p-hydroxyoctadecanilide are useful as such sensitizing materials. A listing of additional sensitizers can be found in U.S. Patent No. 4,531,140.

The components of the color-forming system are in a contiguous relationship, substantially homogeneously distributed throughout the color-forming system, preferably in the form of a coated layer deposited on the substrate. In manufacturing the record material, a coating composition is preferred which includes a fine dispersion of the components of the color-forming system, polymeric binder material, surface active agents and other additives in an aqueous coating medium. The composition can additionally contain inert
40 pigments, such as clay, talc, aluminum hydroxide, calcined kaolin clay and calcium carbonate; synthetic pigments, such as urea-formaldehyde resin pigments; natural waxes such as carnauba wax; synthetic waxes; lubricants such as zinc stearate; wetting agents and defoamers.

The color-forming system components are substantially insoluble in the dispersion vehicle (preferably water) and are ground to an individual average particle size of between about 1 micron to about 10 microns,
45 preferably about 1 to about 3 microns. The polymeric binder material is substantially vehicle soluble, although latexes are also eligible in some instances. Preferred water-soluble binders include polyvinyl alcohol, hydroxyethylcellulose, methylcellulose, hydroxypropylmethylcellulose, starch, modified starches, gelatin and the like. Eligible latex materials include polyacrylates, polyvinylacetates, polystyrene, and the like. The polymeric binder is used to protect the coated materials from brushing and handling forces
50 occasioned by storage and use of the thermal sheets. Binder should be present in an amount to afford such protection and in an amount less than will interfere with achieving reactive contact between color-forming reactive materials.

Coating weights can effectively be about 3 to about 9 grams per square meter (gsm) and preferably about 5 to about 6 gsm. The practical amount of color-forming materials is controlled by economic
55 considerations, functional parameters and desired handling characteristics of the coated sheets.

DESCRIPTION OF THE PREFERRED EMBODIMENTS, PRESENT ASPECT

In the following examples, general procedures for preparing certain di-[bis-(indolyl)ethylenyl]-tetrachlorophthalides of formula (C2) are described; and the examples are not intended to be exhaustive and the moieties, as previously defined, are all eligible for use in any combination in preparing the compounds. Unless otherwise noted, all measurements, percentages and parts are by weight and in the metric system.

5 Satisfactory spectroscopic data were obtained for new compounds synthesized.

Example 1'

10

One-pot two-step preparation of 3,3-bis[1,1-bis(1-β-methoxyethyl-2-methylindole-3-yl)ethylene-2-yl]-4,5,6,7-tetrachlorophthalide

15

[Table 1', Entry 3]

1-β-methoxyethyl-2-methylindole (19.0g,0.1 mole) was stirred with acetyl chloride (16.0g,0.2 mole) at
20 room temperature for 5 hours. Sodium acetate (16.4g,0.2 mole), acetic anhydride (30 ml) and tetrachlorophthalic anhydride (7.2g,0.025 mole) were added to the reaction mixture and the reaction mixture was heated at 100 °C for two hours, cooled to room temperature, stirred with excess aqueous sodium hydroxide (10%) and toluene. After stirring for 30 minutes at 60 °C, toluene layer was separated, washed twice with hot water, dried and concentrated. The residue was warmed with isopropanol and filtered. The product was
25 purified by column chromatography on silica gel, followed by recrystallization from chloroform/isopropanol. Yield:- 11.3g(43%), pale yellow solid, m.p.:- 140-142 °C.

A solution of the product gives a greenish blue color to paper coated with a phenolic resin, with reflectance minima at 607 and 815 nm; and a blue color to paper coated with siltan clay, with reflectance minima at 610 and 808 nm.

30 The calculated analysis for C₆₀H₅₈N₄O₆Cl₄, the title compound, is C,67.16%; H,5.45%; N,5.22%; and Cl,13.22%. Found on analysis: C,67.17%; H,5.44%; N,5.10%; and Cl,13.19%.

Example 2'

35

Preparation of 3,3-bis[1-(1-ethyl-2-methylindole-3-yl)-1-(1-β-methoxyethyl-2-methylindole-3-yl)ethylene-2-yl]-4,5,6,7-tetrachlorophthalide

40

[Table 1', Entry 9]

45 1-(1-ethyl-2-methylindole-3-yl)-1-(1-β-methoxyethyl-2-methylindole-3-yl)ethylene (3.7g,0.01 mole) and tetrachlorophthalic anhydride(1.5g,0.005 mole) in acetic anhydride (15 ml) were heated at 120 °C for two hours, cooled down to room temperature and treated with aqueous sodium hydroxide (100 ml,10%) and toluene (100 ml). After vigorous stirring for 30 minutes. The toluene layer was separated, washed with hot water, dried and concentrated under reduced pressure. The residue was purified by chromatography on
50 silica gel. The product obtained was heated with methanol, allowed to cool to room temperature and filtered; and, this process was repeated twice. Yield:-2.6g(51%), brown powder, m.p.:- 213-217 °C.

A solution of the product gives a green color to paper coated with a phenolic resin, with reflectance minima at 612 and 808 nm; and bluish green color to paper coated with siltan clay, with reflectance minima at 609 and 809 nm.

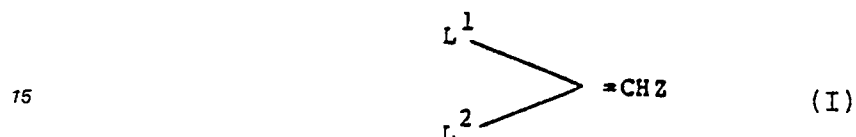
55 The calculated analysis for C₅₈H₅₄N₄O₄Cl₄, the title compound, is C,68.77%; H,5.37%; N,5.53%; and Cl,14.00%. Found on analysis:-C,68.44%; H,5.15%; N,5.30%; and Cl,14.61%.

The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is

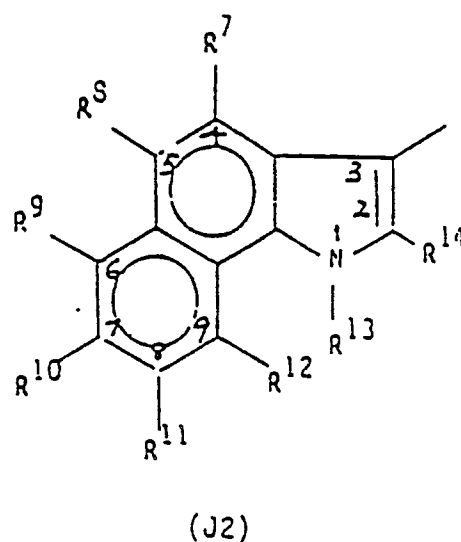
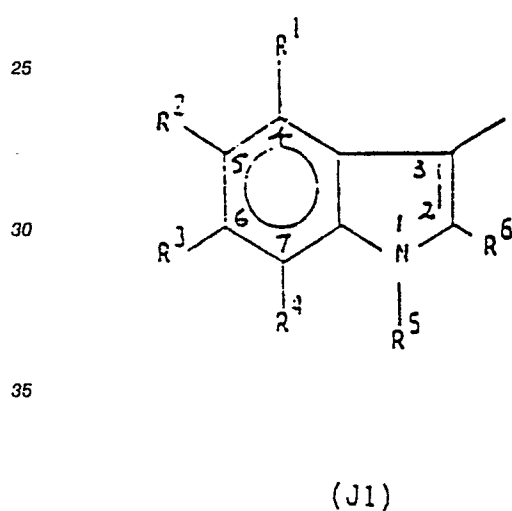
not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes can be made by those skilled in the art without departing from the spirit and scope of the invention as claimed. Further it is to be noted that substituents are as defined within a given claim; for example the substituents R¹ to R⁶ for formula J1 in claim 1 and for
 5 substituent L¹ in claim 13 are independently defined.

Claims

10 1. Chromogenic compounds of the formula



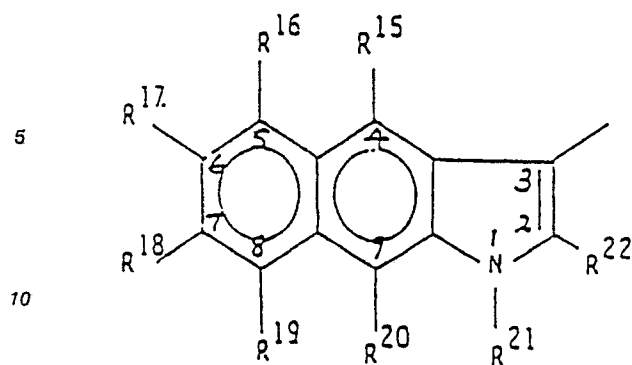
wherein either L¹ L² and Z are as set out in claim 13, 15 or 17 or each L¹ and L² is the same or different
 20 and is each independently selected from indole moieties (J1) through (J4), with the proviso that when L¹ and L² are simultaneously (J1), that R¹, R², R³ and R⁴ are not all hydrogen simultaneously,



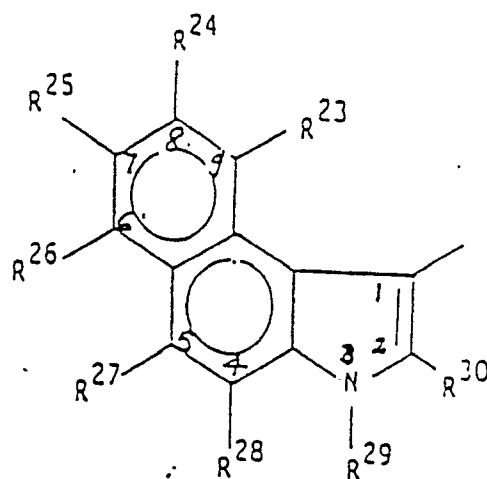
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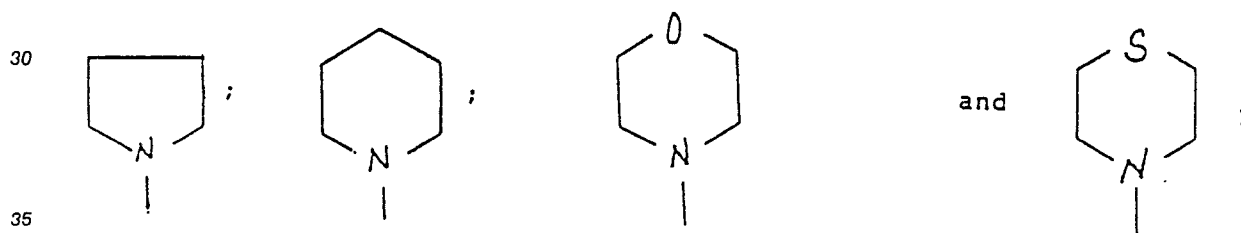


(J3)



(J4)

and wherein in each of formulae (J1) through (J4) each of R⁵, R⁶, R¹³, R¹⁴, R²¹, R²², R²⁹, and R³⁰ need not be the same and is each independently selected from hydrogen, alkyl (C₁-C₈), cycloalkyl, aroxyalkyl, alkoxyalkyl, substituted aryl, and unsubstituted aryl, wherein each of R¹, R², R³, R⁴, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²³, R²⁴, R²⁵, R²⁶, R²⁷ and R²⁸ need not be the same and is independently selected from hydrogen, alkyl (C₁-C₈), cycloalkyl, substituted or unsubstituted aryl, halogen, alkoxy (C₁-C₈), aroxy, cycloalkoxy, dialkylamino including symmetrical and unsymmetrical alkyl groups with one to eight carbons, alkylcycloalkylamino, dicycloalkylamino, and the following



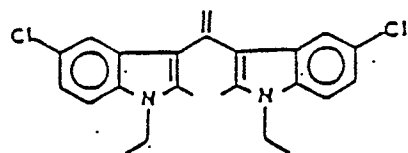
and wherein Z is selected from the group consisting of hydrogen, alkyl (C₁-C₈), substituted or unsubstituted aryl, aralkyl, aroxyalkyl, alkoxyalkyl and halogen.

2. Chromogenic bis-(indolyl)ethylene according to Claim 1 comprising 1,1-bis(2,5-dimethyl-1-ethylindole-3-yl)ethylene

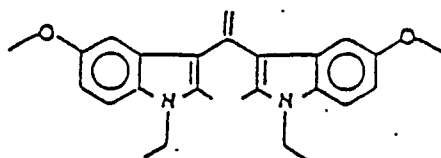
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1,1-bis(2,7-dimethyl-1-ethylindole-3-yl)ethylene

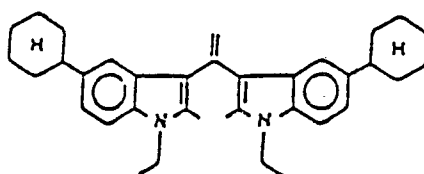
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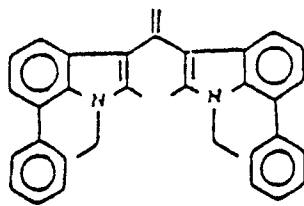


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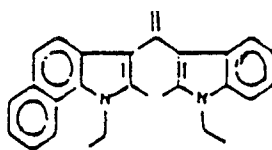


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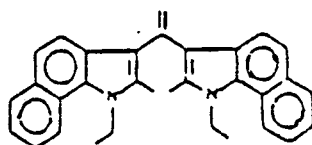




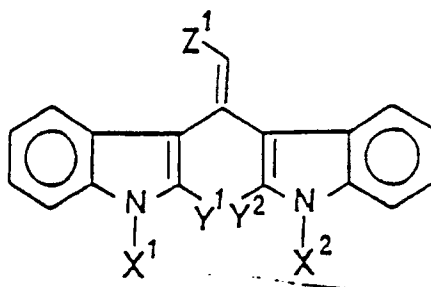
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3. Chromogenic bis(indolyl)ethylene of the formula



wherein Z^1 is hydrogen, alkyl (C_1-C_8), substituted or unsubstituted aryl, aralkyl, aroxyalkyl, alkoxyalkyl and halogen,

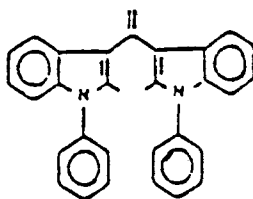
wherein X^1 and X^2 need not be the same and is each independently selected from alkyl (C_1-C_8), cycloalkyl, aroxyalkyl, alkoxyalkyl, substituted aryl and unsubstituted aryl,

wherein Y^1 and Y^2 need not be the same and is each independently selected from alkyl (C_1-C_8), and unsubstituted aryl,

with the proviso that X¹, X², Y¹ and Y² are not all simultaneously unsubstituted aryl,
with the proviso that Y¹ and Y² are not simultaneously unsubstituted aryl when X¹ and X² are both methyl.

4. Chromogenic bis-(indolyl)ethylene according to Claim 3 comprising

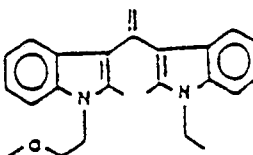
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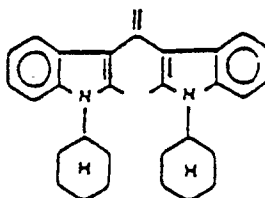


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- or -

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- or -

1,1-bis(1-ethyl-2-methylindole-3-yl)ethylene.

- or -

1,1-bis(1-n-butyl-2-methylindole-3-yl)ethylene.

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- or -

1,1-bis(1-n-octyl-2-methylindole-3-yl)ethylene.

- or -

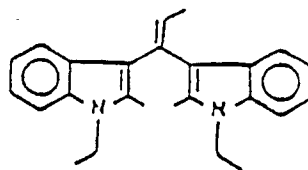
1,1-bis(1-ethyl-2-methylindole-3-yl)-2-phenylethylene.

- or -

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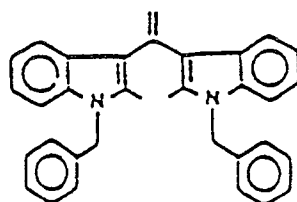
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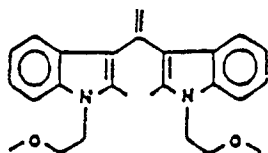
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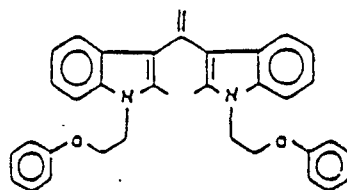


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5. A process for the manufacture of bis-(indolyl)ethylenes comprising condensing corresponding indoles with acetic anhydride in the presence of carboxylic acids, sulfonic acids, acid chlorides, and Lewis acids, in

halogenated or other organic solvent.

6, A process for the manufacture of bis-(indolyl)ethylenes comprising reacting corresponding indoles with acetyl chloride, reaction being carried out at a temperature of from 15-75°C, optionally in the presence of acetic anhydride or other solvent.

5 7. A method for the manufacture of bis-(indolyl)ethylenes of the formula



wherein each L¹ and L² is the same or different and is each independently selected from indole moieties (J1) through (J4) as set out in claim 1 (but without the proviso), said method comprising:

15 a) reacting indoles corresponding to each respective L¹ and L² with acetic anhydride in the presence of an acid, selected from carboxylic acid, sulfonic acid, acid chloride, and Lewis acid, in a halogenated organic or other solvent

- or -

20 b) reacting indoles corresponding to each respective L¹ and L² with an acid chloride, optionally in the presence of acetic anhydride or other solvent

- or -

c) condensing acylindoles (K1) through (K4) below with indoles (J1) through (J4) using Vilsmeier reagents with or without solvent,

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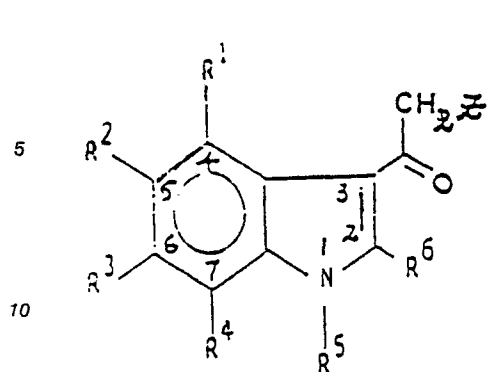
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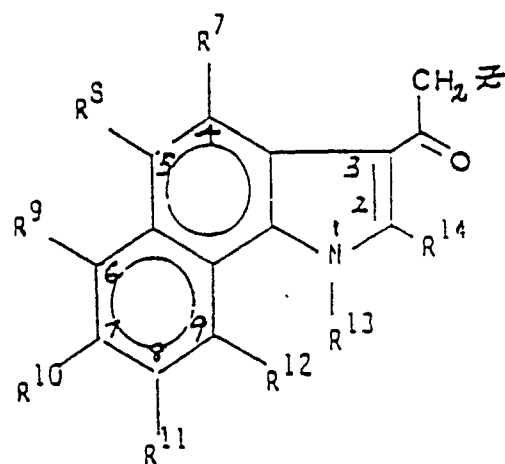
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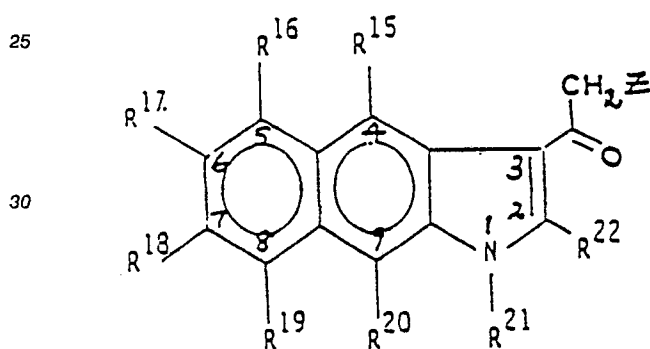
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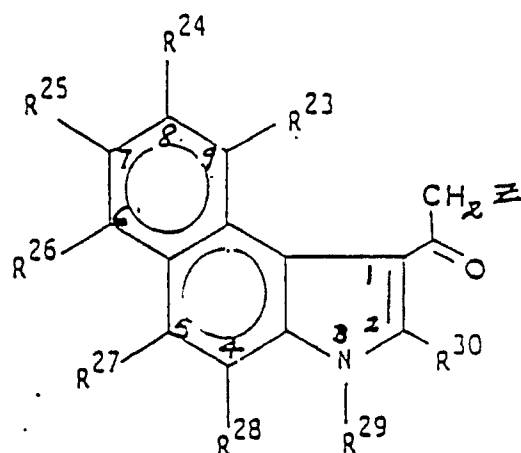
(K1)



(K2)



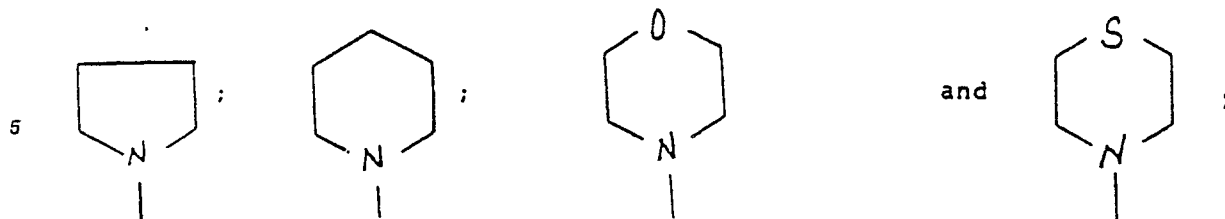
(K3)



(K4)

wherein in (K1) through (K4) each of R⁵, R⁶, R¹³, R¹⁴, R²¹, R²², R²⁹ and R³⁰ need not be the same and is each independently selected from hydrogen, alkyl (C₁-C₈), cycloalkyl, aroxyalkyl, alkoxyalkyl, substituted aryl, and unsubstituted aryl, such as phenyl, naphthyl, or heterocyclyl,

each R¹, R², R³, R⁴, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²³, R²⁴, R²⁵, R²⁶, R²⁷ and R²⁸ need not be the same and is independently selected from hydrogen, alkyl (C₁-C₈), cycloalkyl, substituted or unsubstituted aryl, halogen, alkoxy (C₁-C₈), aroxy, cycloalkoxy, dialkylamino including symmetrical and unsymmetrical alkyl groups with one to eight carbons, alkylcycloalkylamino, dicycloalkylamino, and the following



10 and wherein Z is hydrogen, alkyl (C₁-C₈), substituted or unsubstituted aryl, aralkyl, aroxyalkyl, alkoxyalkyl and halogen.

8. The method according to Claim 7 wherein the Vilsmeier reagents are selected from the group consisting of phosphoryl chloride, phosgene, oxalyl chloride, benzoyl chloride, alkane sulfonyl chloride, arene sulfonyl chloride, alkylchloroformate, and arylchloroformate.

15 9. A record material comprising a substrate having coated thereon an electron accepting developer material and a chromogenic mark forming bis-(indolyl)ethylene of the formula,



wherein each L¹ and L² is the same or different and is each independently selected from indole moieties of the formulae J1 through J4 as set out in claim 1 (but without the proviso) and wherein Z is as set out in claim 1.

10. The record material according to Claim 9 wherein the chromogenic bis-(indolyl)ethylene comprises 1,1-bis(1-ethyl-2-methylindole-3-yl)ethylene.

- or -

30 1,1-bis(1-n-butyl-2-methylindole-3-yl)ethylene.

- or -

1,1-bis(1-n-octyl-2-methylindole-3-yl)ethylene.

- or -

1,1-bis(1-ethyl-2-methylindole-3-yl)-2-phenylethylene.

35 - or -

1-(1-ethyl-2-methylindole-3-yl)-1-(1-ethyl-2-methyl-6,7-benzoindole-3-yl)ethylene.

- or -

1-(1-ethyl-2-methylindole-3-yl)-1-(1-β-methoxyethyl-2-methylindole-3-yl)ethylene.

- or -

40 1,1-bis(2,5-dimethyl-1-ethylindole-3-yl)ethylene.

- or -

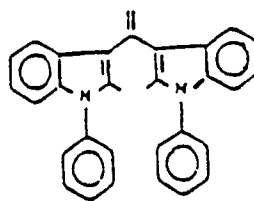
1,1-bis(2,7-dimethyl-1-ethylindole-3-yl)ethylene.

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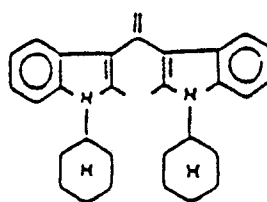
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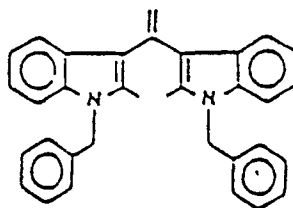


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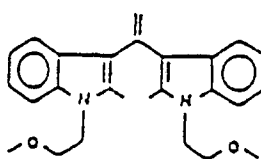


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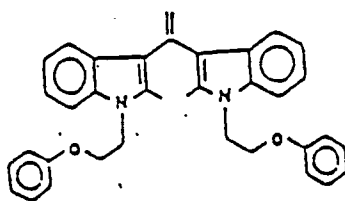
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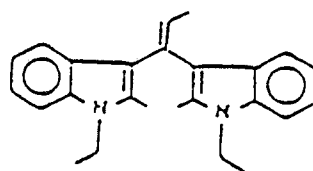
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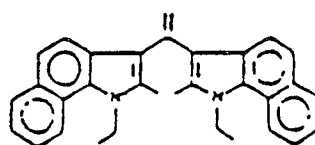
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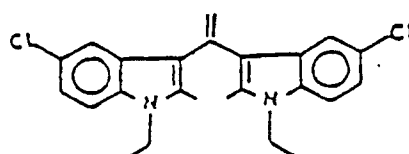
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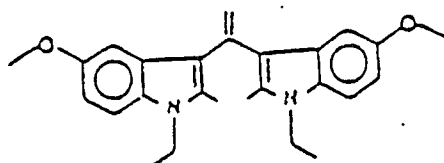
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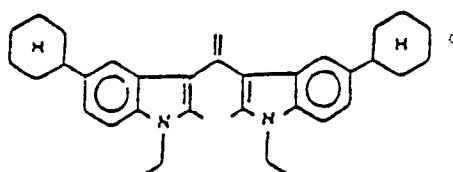
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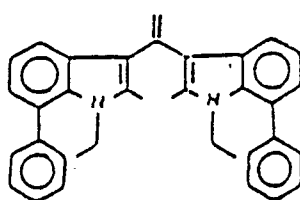
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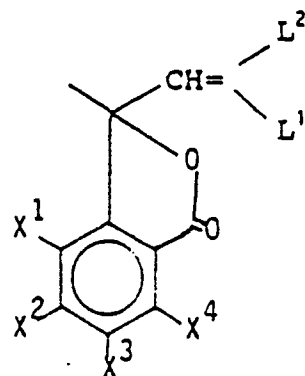
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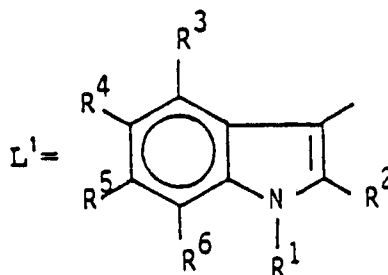
11. The record material according to Claim 9 wherein the record material is, specifically, pressure sensitive or heat sensitive.

12. A record material comprising, for reaction with a colour developer, a chromogenic compound as claimed in any of claims 1 to 4 or as prepared according to the process of claim 5 or 6 or the method of claim 7 or 8.

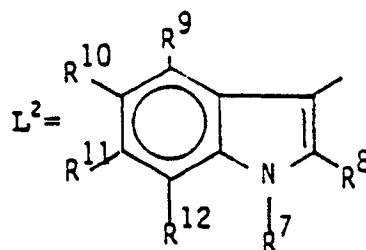
13. A chromogenic compound of the formula (I) set out in claim 1 wherein Z is



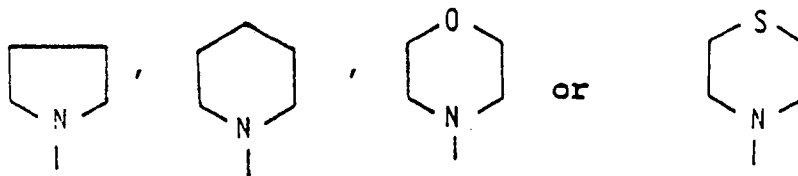
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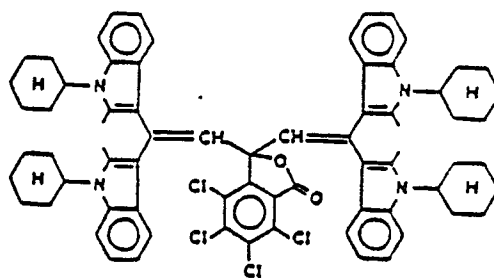
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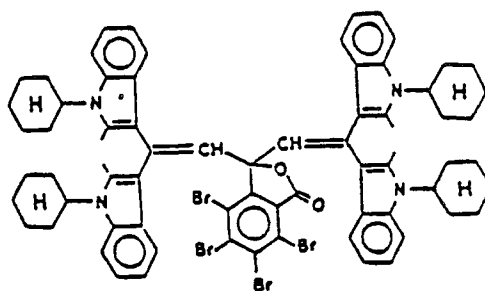
- 35 wherein each X^1 , X^2 , X^3 and X^4 is independently selected from chlorine or bromine;
 wherein each of R^1 and R^7 is independently selected from cycloalkyl, aralkyl, alkoxyalkyl, or aroxyalkyl;
 wherein each of R^2 and R^8 is independently selected from alkyl (C_1 - C_8) or, substituted or unsubstituted
 aryl;
 wherein each of R^3 , R^4 , R^5 , R^6 , R^9 , R^{10} , R^{11} , and R^{12} is independently selected from hydrogen, alkyl (C_1 -
 40 C_8), cycloalkyl, substituted or unsubstituted aryl, halogen, alkoxy (C_1 - C_8), aroxy, cycloalkoxy, dialkylamino
 including symmetrical and unsymmetrical alkyl (C_1 - C_8), alkylcycloalkylamino, dicycloalkylamino, al-
 kylarylamino, and the following



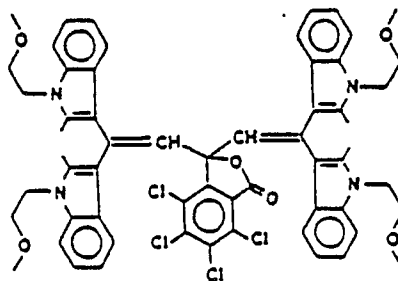
14. A compound according to Claim 13, being the di-[bis-(indolyl)ethylenyl]tetrahalophthalide



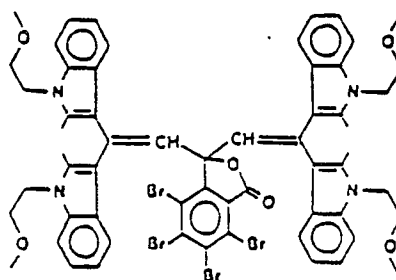
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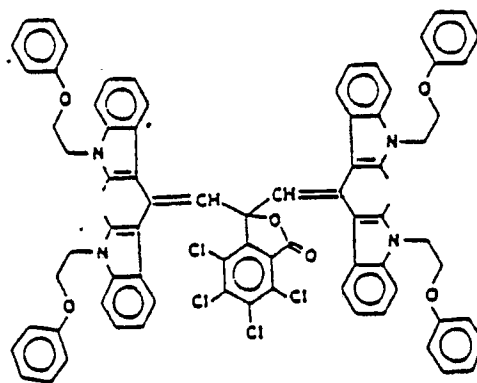
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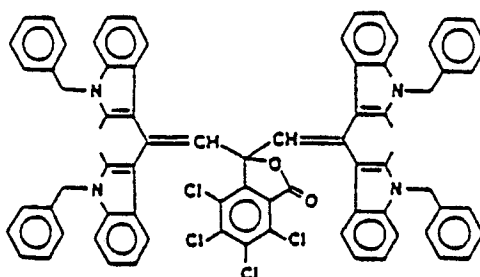


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the chromogenic di-[bis-(indolyl)ethylenyl]tetrahalophthalide according to Claim 1 wherein each of R², and R⁸ is alkyl and wherein each of R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹, and R¹² is hydrogen.

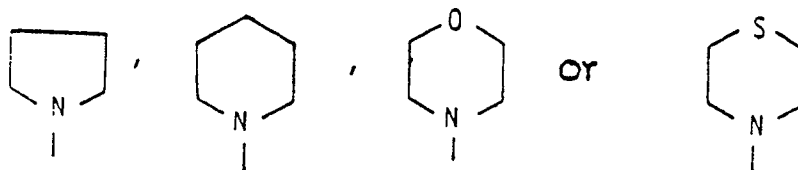
15. A chromogenic compound of the formula (I) set out in claim 1 wherein Z, L¹ and L² are as set out in claim 13 except that

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each X¹, X², X³ and X⁴ is independently selected from chlorine or bromine;

when at least one of R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹, and R¹² is cycloalkyl, alkylarylamino,

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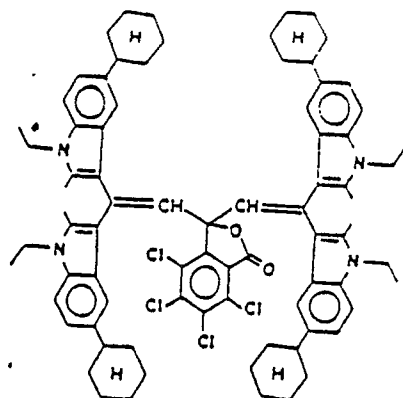
the balance of R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹, and R¹² is independently selected from hydrogen, alkyl (C₁ - C₈), cycloalkyl, substituted or unsubstituted aryl, halogen, alkoxy (C₁ - C₈), aroxy, cycloalkoxy, dialkylamino having symmetrical and unsymmetrical alkyl (C₁ - C₈), alkylcycloalkylamino, dicycloalkylamino, or alkylarylamino,

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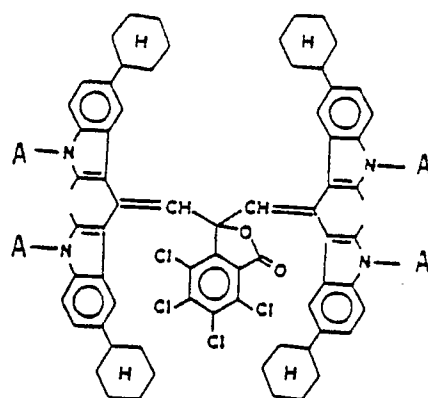
each of R¹, R², R⁷ and R⁸ is independently selected from alkyl (C₁ - C₈) or, substituted or unsubstituted aryl.

16. A compound according to Claim 15, being the di-[bis-(indolyl)ethylenyl]tetrahalophthalide

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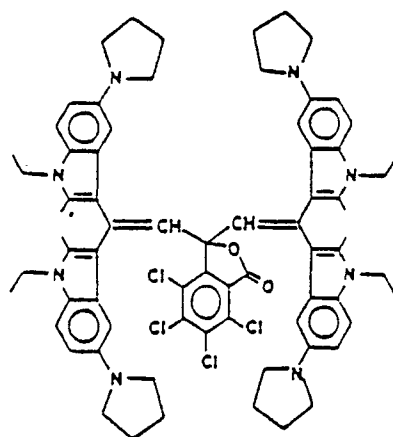
wherein A is C₁ - C₈ alkyl.
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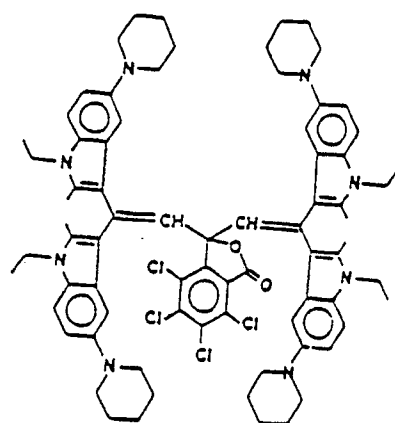
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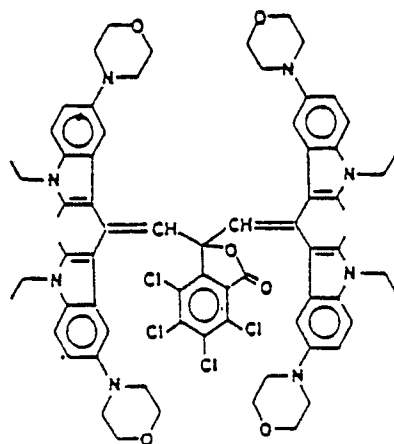


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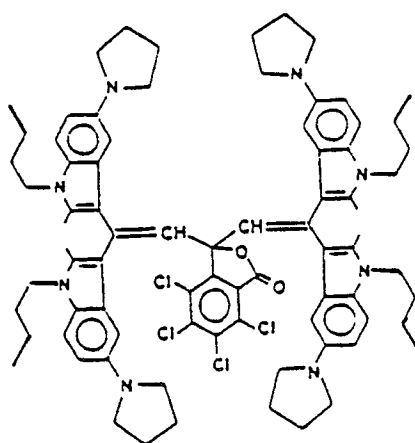
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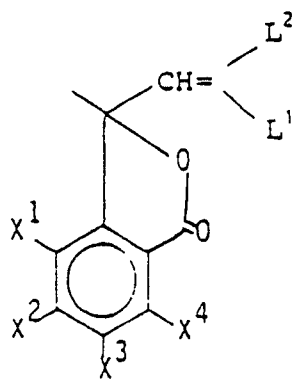
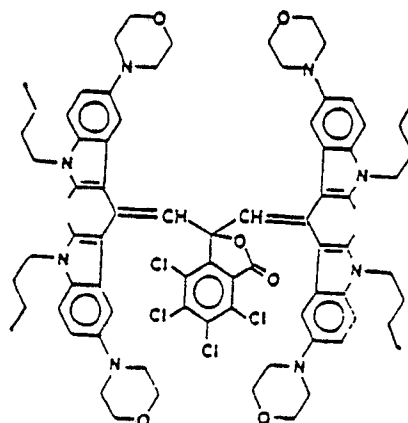
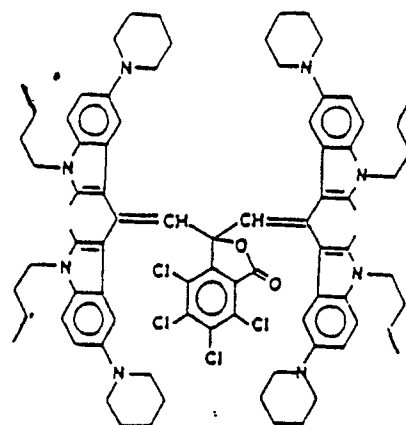
17. A chromogenic compound of the formula I set out in claim 1 wherein Z is

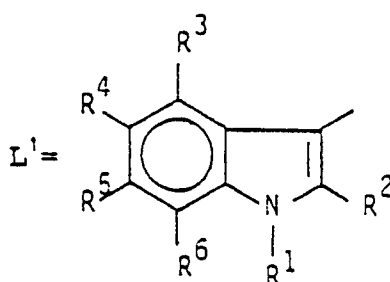
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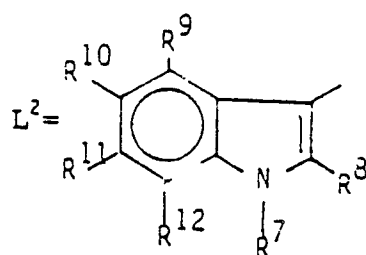
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and indole moieties L^1 and L^2 are





and

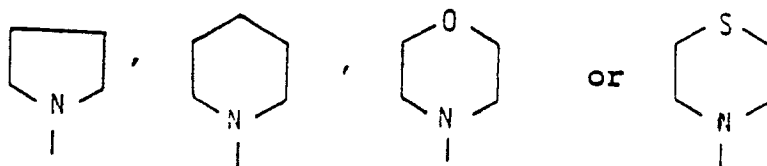


wherein each X^1 , X^2 , X^3 , and X^4 is independently selected from chlorine or bromine;

wherein each of R^1 and R^7 is independently selected from alkyl ($C_1 - C_8$), substituted or unsubstituted aryl, cycloalkyl, alkoxyalkyl or aroxyalkyl;

wherein each of R^2 and R^8 is independently selected from alkyl ($C_1 - C_8$) or, substituted or unsubstituted aryl,

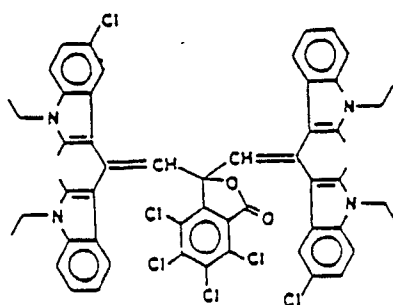
wherein each of R^3 , R^4 , R^5 , R^6 , R^9 , R^{10} , R^{11} , and R^{12} is independently selected from hydrogen, halogen, alkyl ($C_1 - C_8$), cycloalkyl, substituted or unsubstituted aryl, halogen, alkoxy ($C_1 - C_8$), aroxy, cycloalkoxy, dialkylamino including symmetrical and unsymmetrical alkyl ($C_1 - C_8$), alkylcycloalkylamino, dicycloalkylamino, alkylaryl amino, and the following



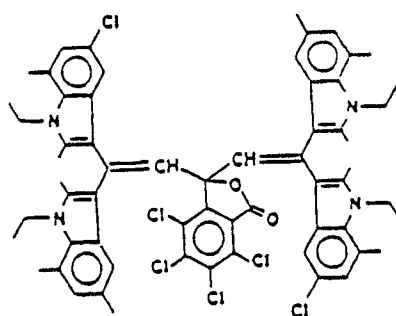
wherein each L^1 is the same or different;

wherein each L^2 is the same or different with the proviso however that at least one L^1 is not identical to at least one L^2 .

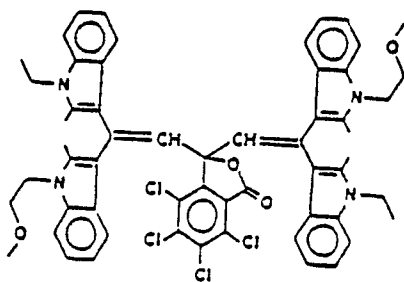
18. The compound according to Claim 17, being the unsymmetrical chromogenic di-[bis-(indolyl)-ethylenyl]tetrahalophthalide



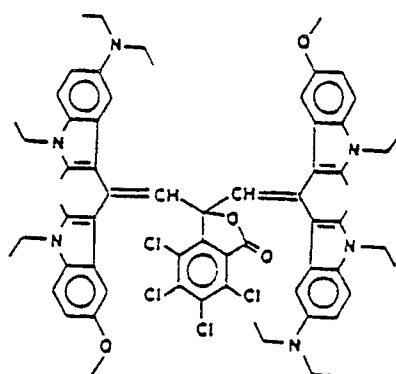
- or -



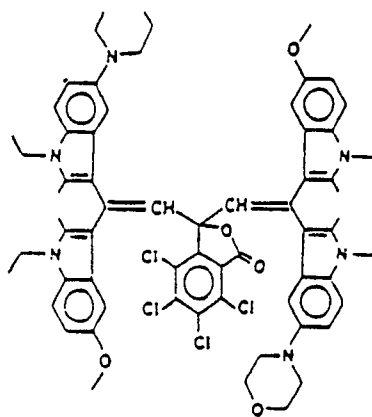
- or -



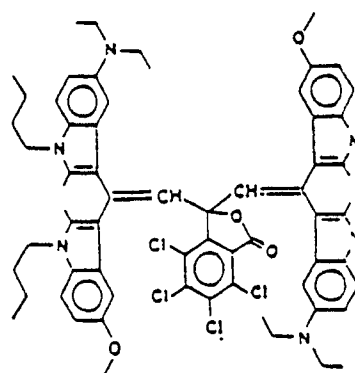
- or -



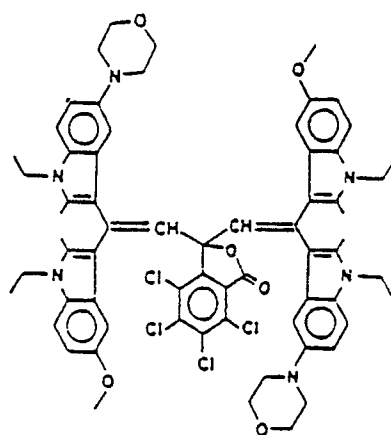
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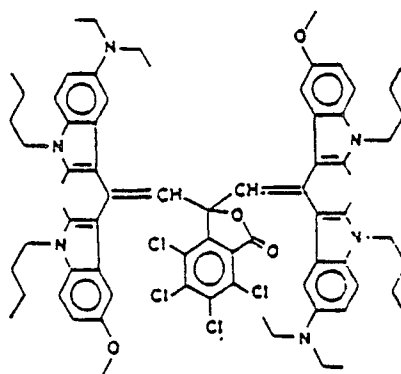
- or -



- or -



- or -

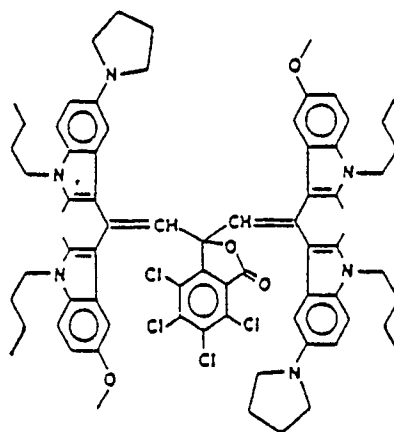


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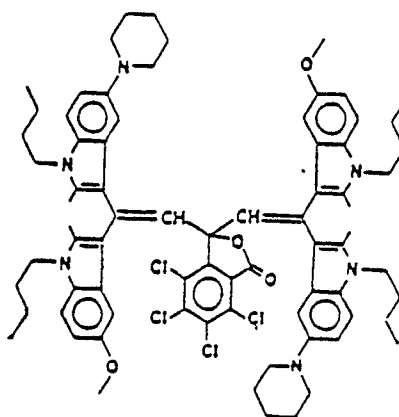
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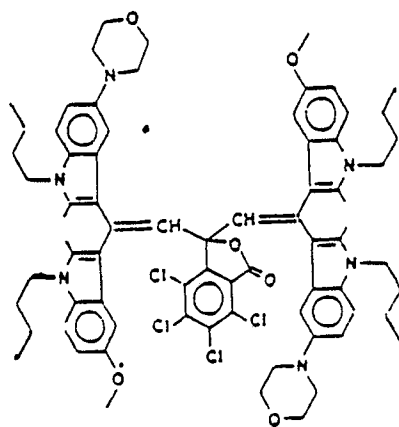
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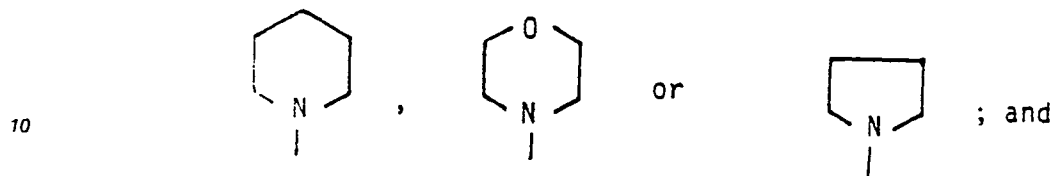
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- or -

- or -

the chromogenic di-[bis-(indolyl)ethylenyl]tetrahalophthalide
 wherein each R¹ and R⁷ independently is alkyl or alkoxyalkyl;
 wherein each R² and R⁸ independently is alkyl;
 wherein each of R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹, and R¹² is independently selected from hydrogen, alkoxy,
 5 dialkylamino, and the following



wherein at least one L¹ is not identical to at least one L².

15 - or -

the chromogenic di-[bis-(indolyl)ethylenyl]tetrahalophthalide
 wherein each R¹ and R⁷ independently is alkyl or alkoxyalkyl;
 wherein each R² and R⁸ independently is alkyl;
 wherein each of R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹, and R¹² is independently selected from hydrogen, alkyl, or
 20 halogen;
 wherein at least one L¹ is not identical to at least one L².

19. A record material comprising, for reaction with a colour developer, a chromogenic compound
 according to any of claims 13 to 18.

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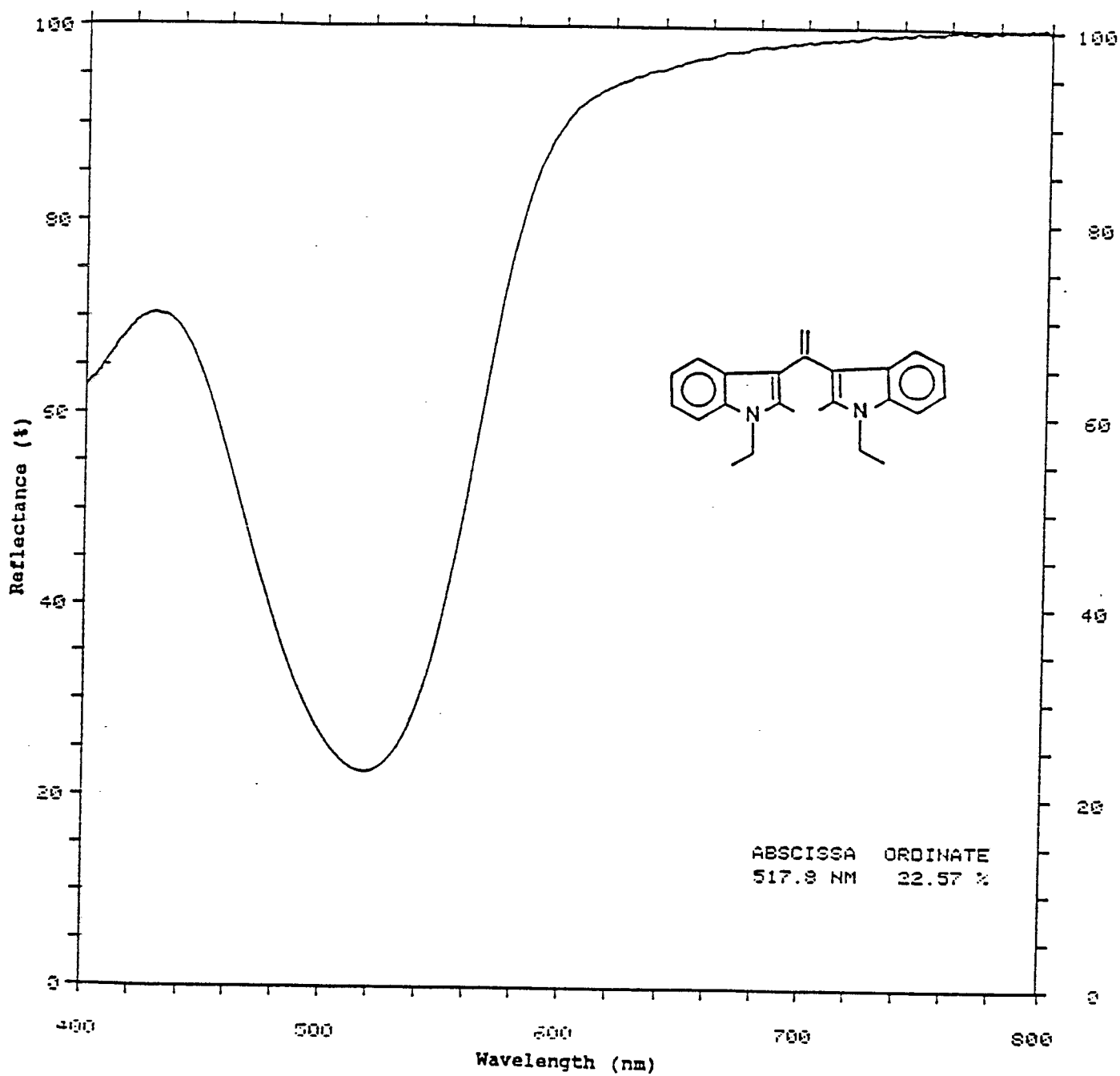


Figure 1. Reflectance spectrum of 1,1-bis(1-ethyl-2-methylindole-3-yl)ethylene on resin-coated paper.

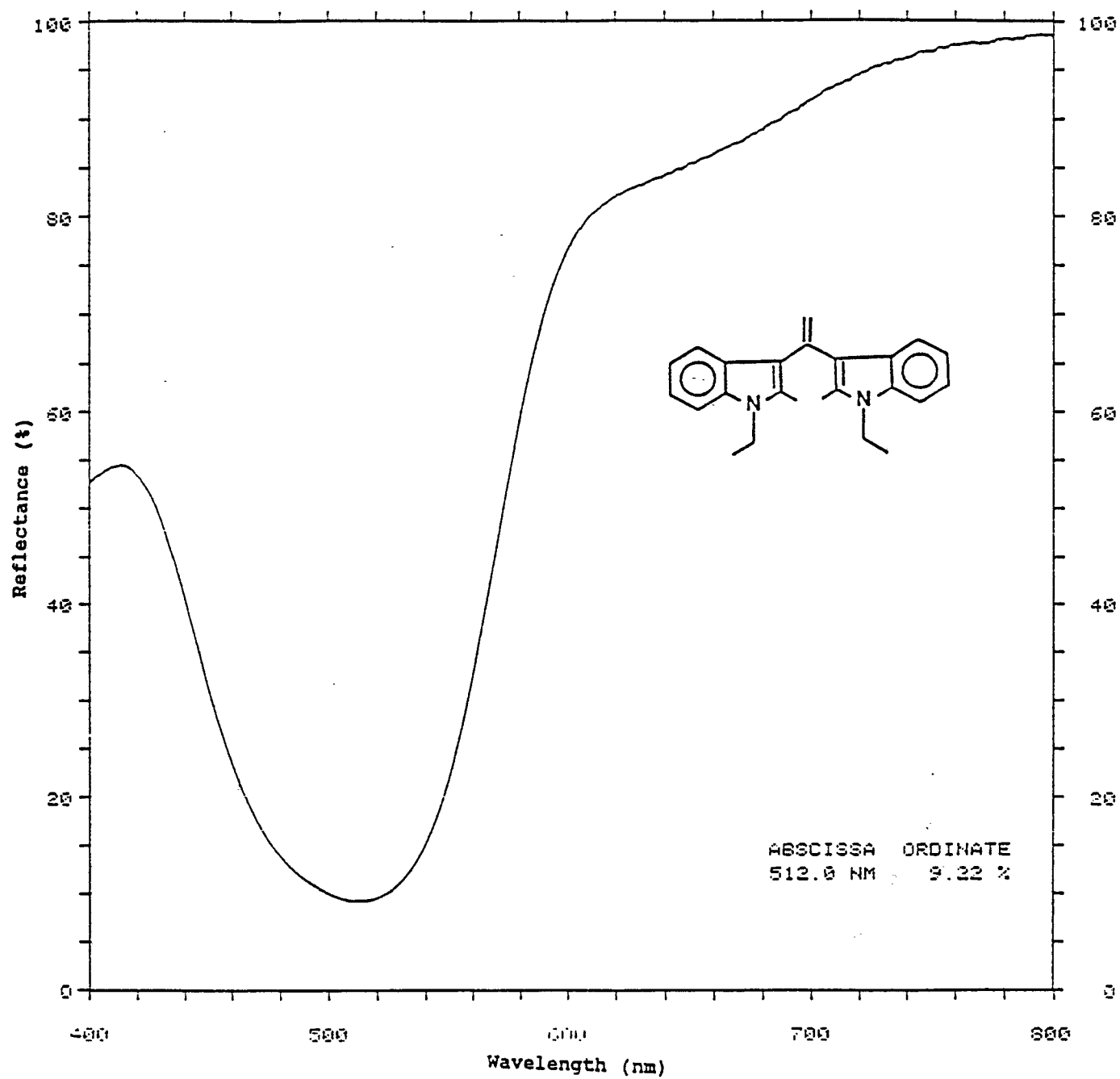


Figure 2. Reflectance spectrum of 1,1-bis(1-ethyl-2-methylindole-3-yl)ethylene on silton-coated paper.

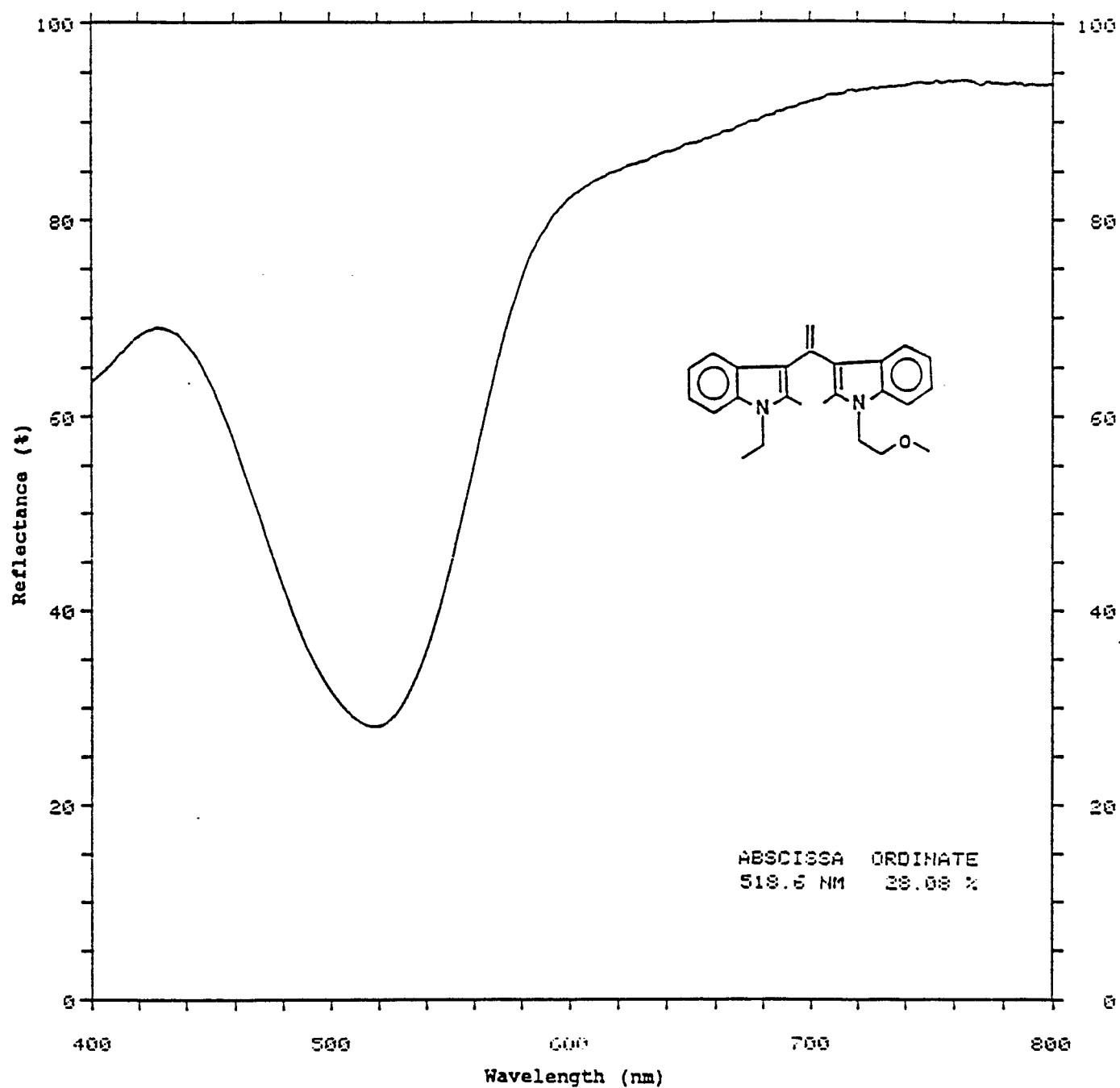


Figure 3. Reflectance spectrum of 1-(1- β -methoxyethyl-2-methyl-indole-3-yl)-1-(1-ethyl-2-methylindole-3-yl)ethylene on resin-coated paper.

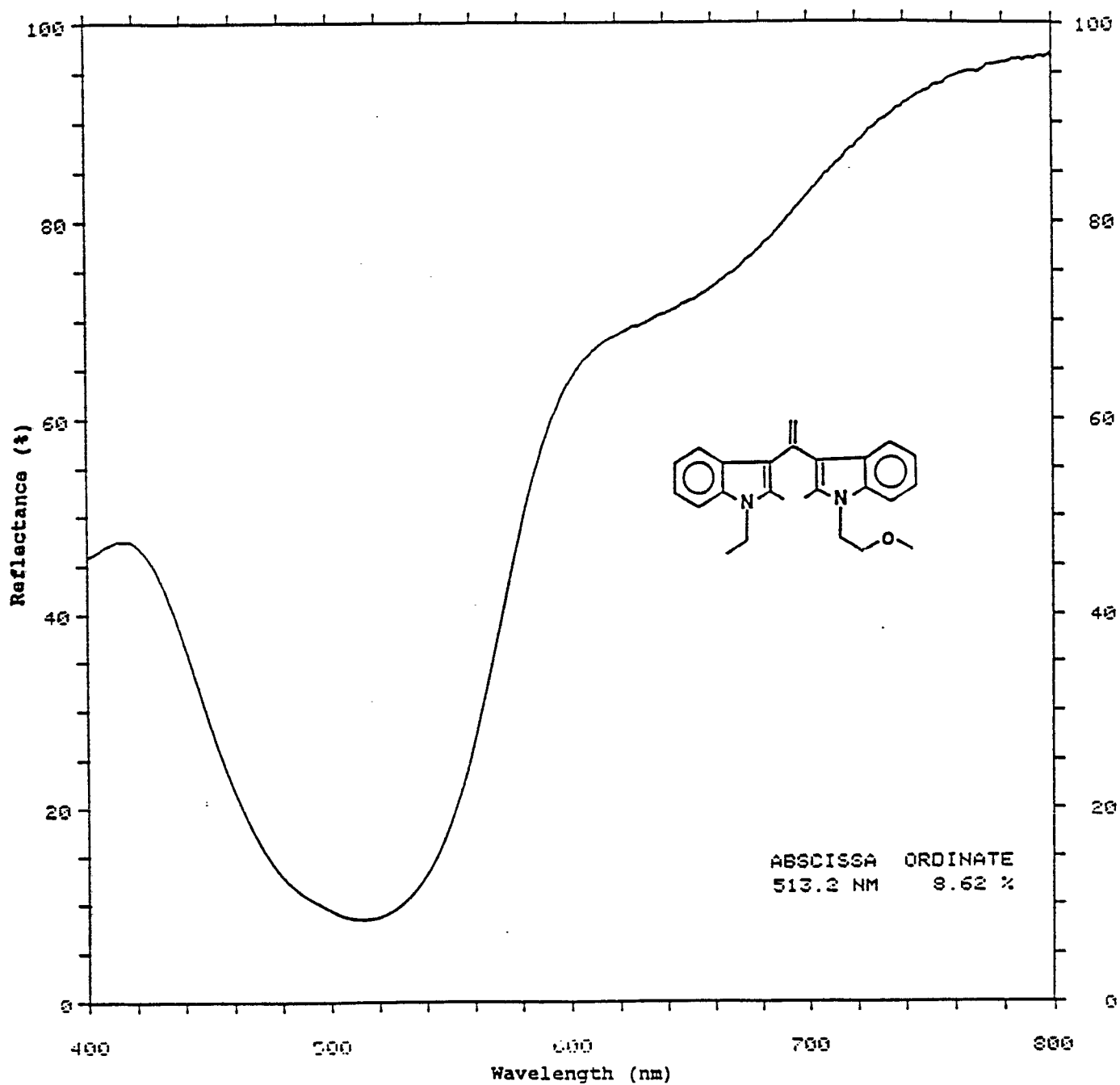


Figure 4. Reflectance spectrum of 1-(1- β -methoxyethyl-2-methyl-indole-3-yl)-1-(1-ethyl-2-methylindole-3-yl)ethylene on silton-coated paper.

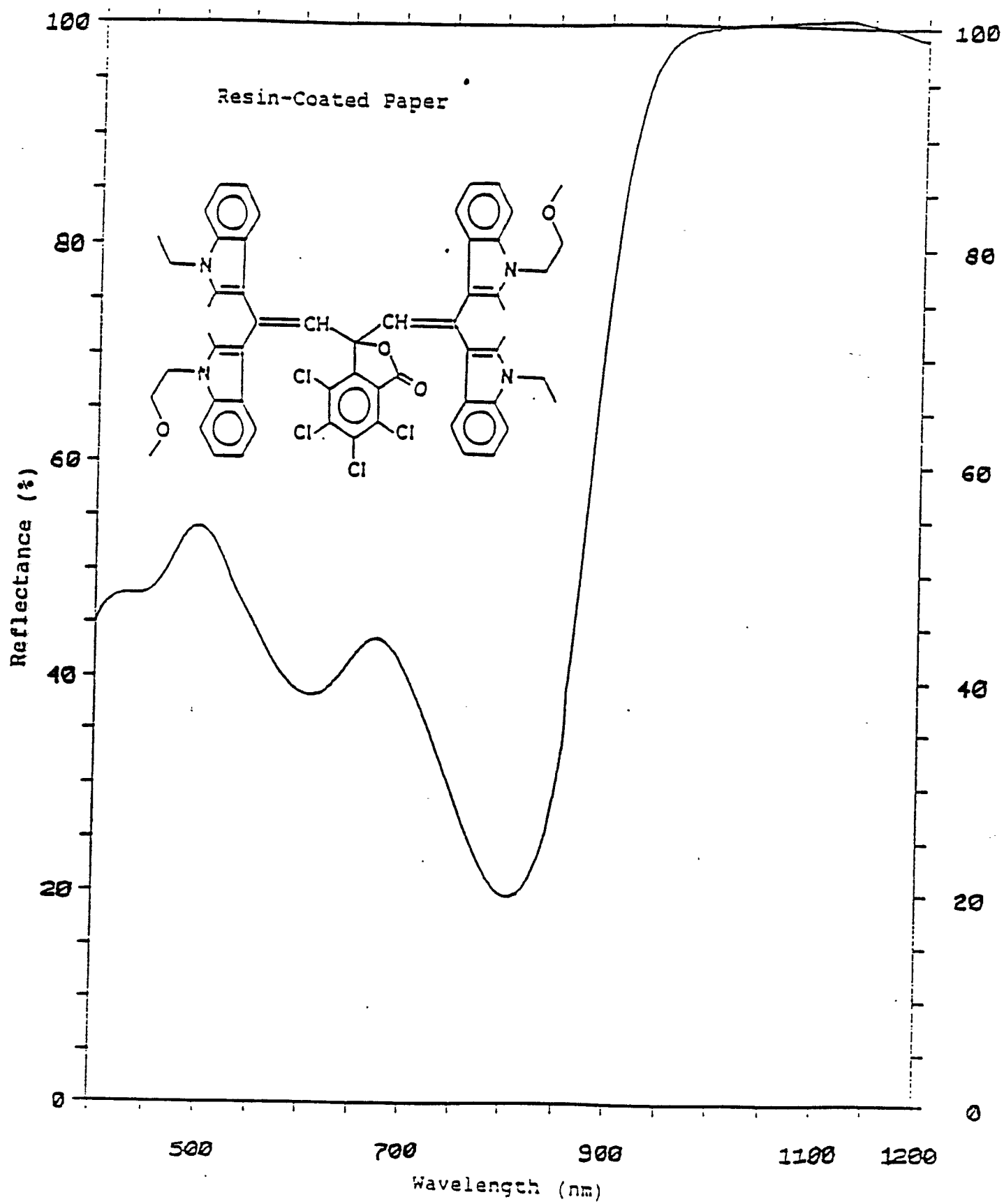
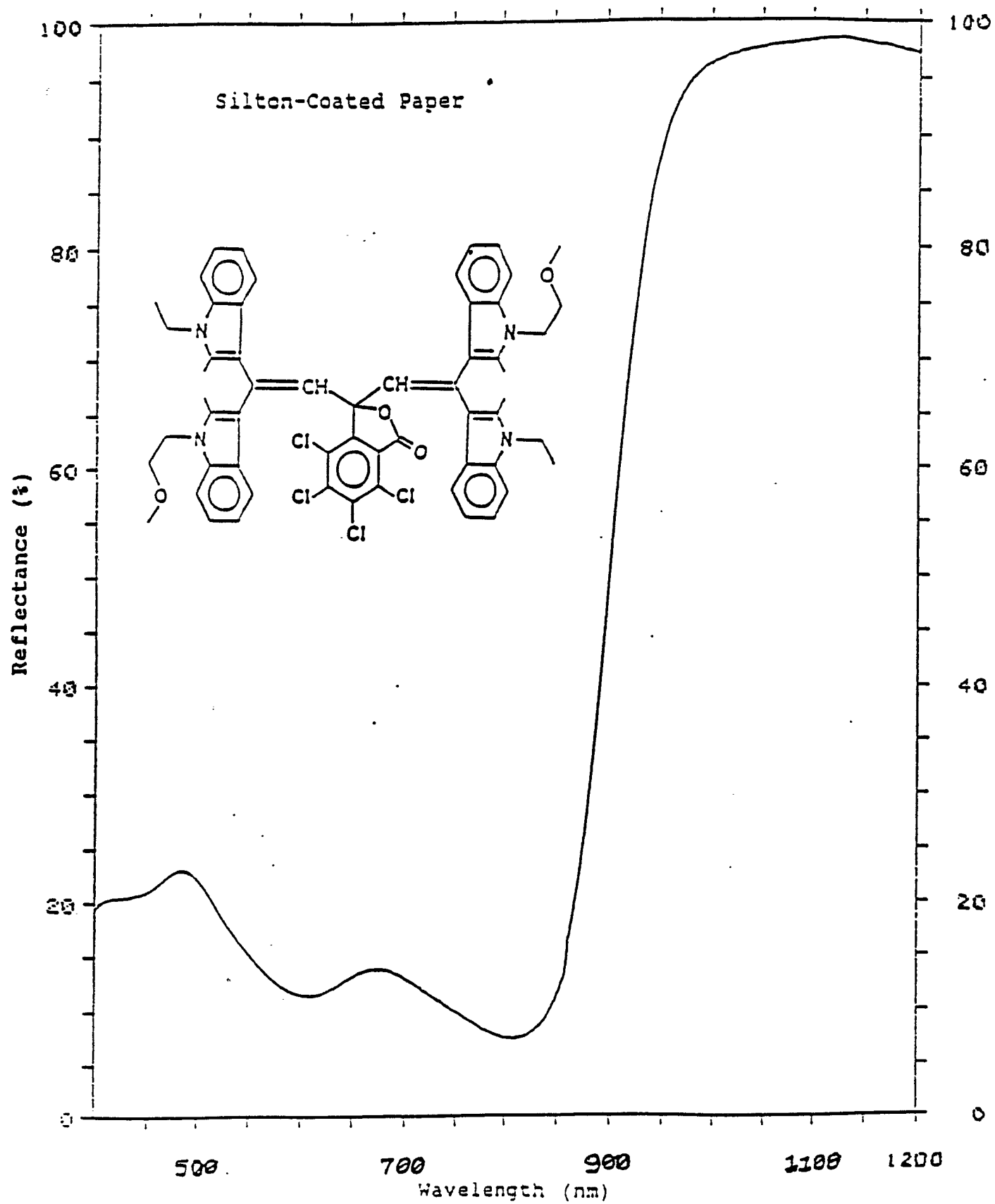


FIGURE 5



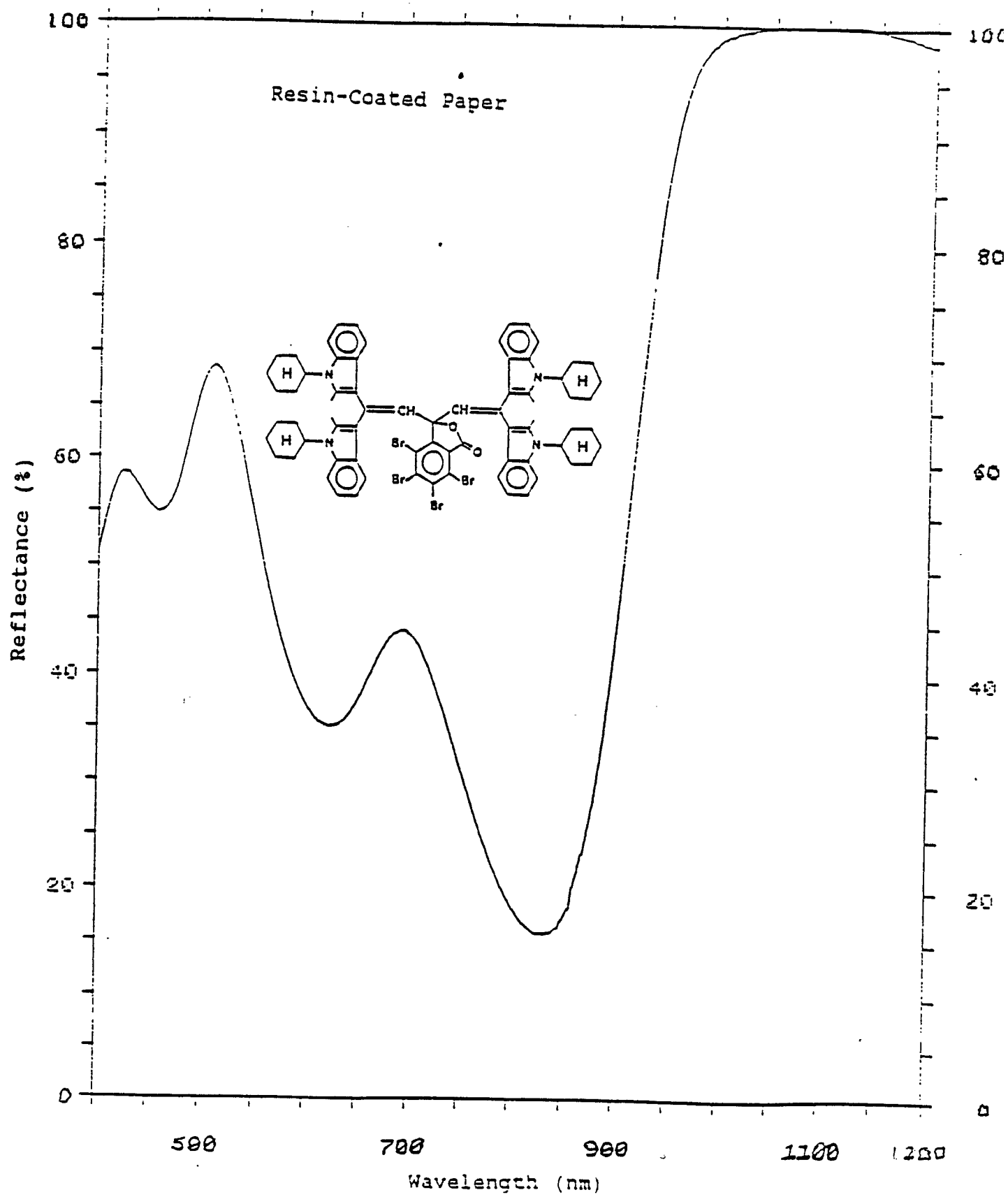


FIGURE 7

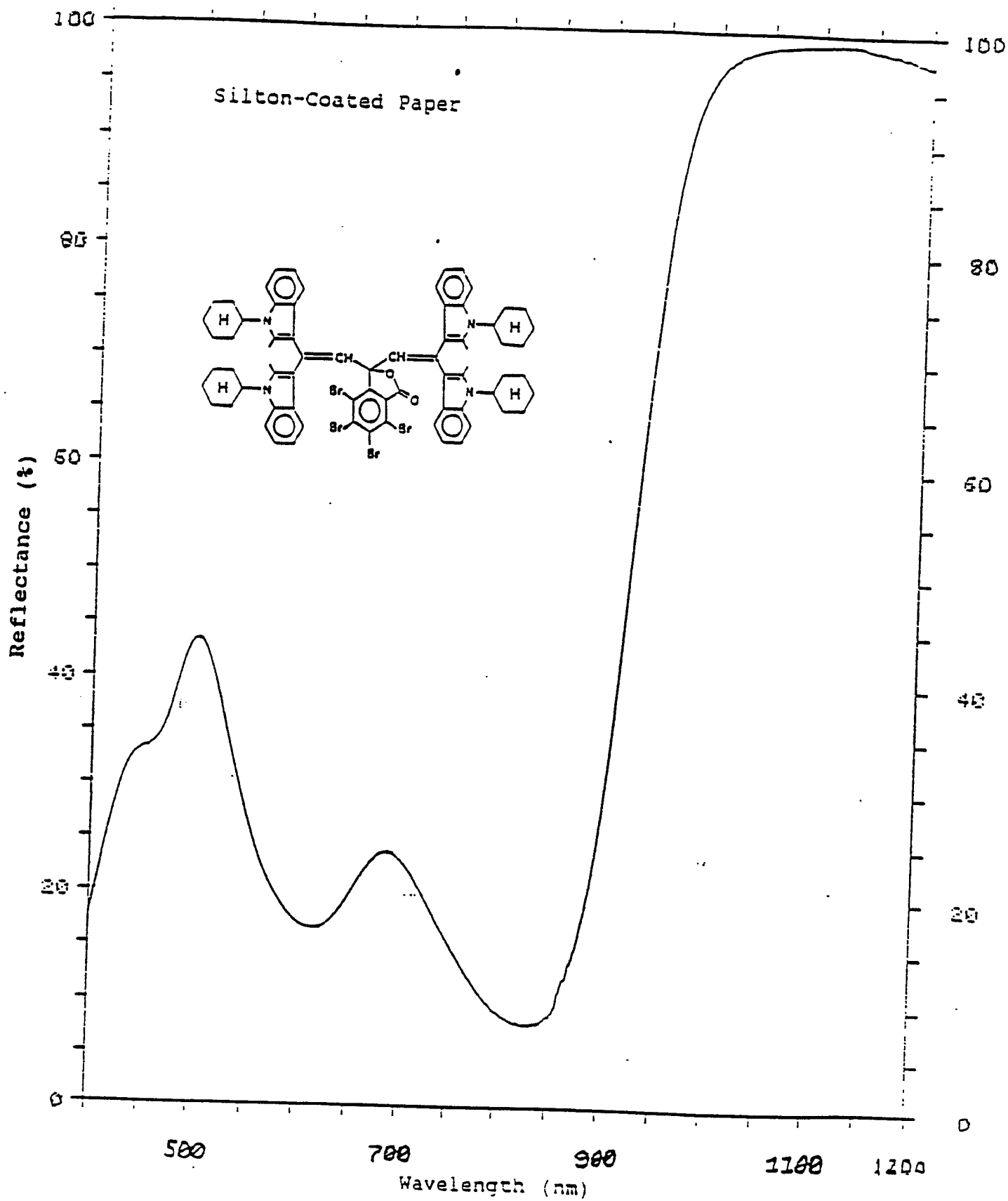


FIGURE 8