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SUBSTITUTED DIALKYLAMINO-(PHTHAL(YL/AN) ACRIDAN COMPOUNDS

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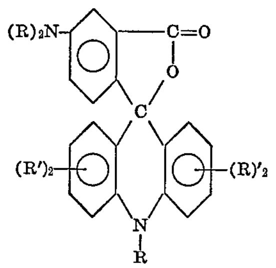
U.S. Cl. 260—279 R 4 Claims

ABSTRACT OF THE DISCLOSURE

Colorless, but colorable acridan compounds are disclosed, which are represented by the formula:



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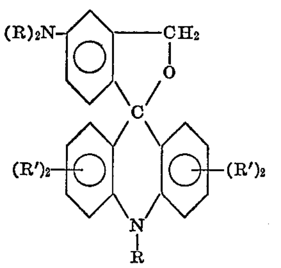


wherein each R is an alkyl radical having 1 to 5 carbon atoms and each R′ is hydrogen, an alkyl radical having 1 to 5 carbon atoms, an alkoxy radical having 1 to 5 carbon atoms, a dialkylamino radical wherein each alkyl radical has 1 to 5 carbon atoms, an amino radical, a nitro radical or a halogen. These compounds are used in pressure-sensitive record material and in mark-forming manifold systems.

This invention relates to colorless, but colorable compounds. More specifically, this invention relates to certain acridan compounds.

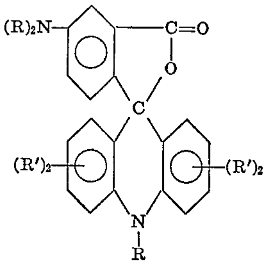
These compounds are colorless or substantially colorless when in liquid solution, but are converted to dark-colored forms upon reactive contact with an acidic material. In pressure-sensitive mark-forming systems, the unreacted mark-forming components (the colorless, but colorable compound and the acidic material) and a liquid solvent in which each of the mark-forming components is soluble is disposed on or within a sheet support material. The liquid solvent is present in such form that is maintained isolated by a pressure-rupturable barrier from at least one of the mark-forming components until the application of pressure causes a breach of the barrier in the area delineated by the pressure pattern. The application of pressure brings the mark-forming components into reactive contact, thereby producing a distinctive mark.

Certain colorless, but colorable acridan compounds now have been invented.

Accordingly, an object of this invention is to provide colorless, but colorable acridan compounds.

Other objects, aspects and advantages of this invention will be apparent to one skilled in the art from the following disclosure and appended claims.

The colorless, but colorable acridans of this invention are represented by the formula:



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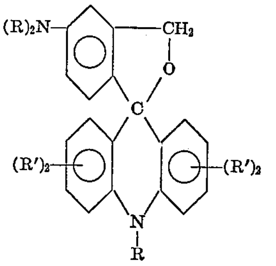
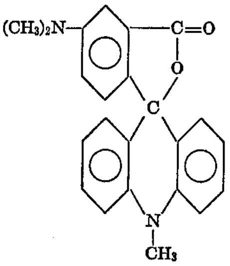
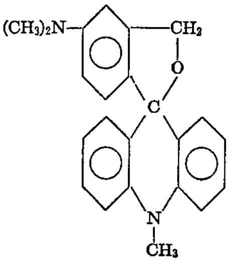


wherein each R is an alkyl radical having 1 to 5 carbon atoms and each R′ is hydrogen, an alkyl radical having 1 to 5 carbon atoms, an alkoxy radical having 1 to 5 carbon atoms, a dialkylamino radical wherein each alkyl radical has 1 to 5 carbon atoms, an amino radical, a nitro radical or a halogen. Preferably, each R is an alkyl radical having 1 to 3 carbon atoms and each R′ is hydrogen or an alkyl having 1 to 3 carbon atoms.

Specific examples of these acridan compounds are: (a) 9-(p-dimethylaminophthalyl-3)-10-methylacridan:



and (b) 9-(p-dimethylaminophthalan-3)-10-methylacridan:



Both of these acridan compounds are stable in their colorless form and develop a neutral (black) color upon reactive contact with an acidic material.

In a preferred embodiment of this invention, the acridan and liquid solvent are encapsulated in microscopic capsules which are coated on base sheet record material. In close contact with the base sheet record material is a sensitized undersheet. The base sheet yields the acridan under pressure of writing against the sensitized undersheet in a pattern of droplets corresponding to the written matter, in accordance with the disclosure of such a capsule-bearing sheet in U.S. Pat. No. 2,712,507, which issued July 5, 1955, on the application of Barrett K. Green. U.S. Pat. No. 2,712,507 also discloses a preferred method of forming the capsules. Other preferred methods for preparing solvent-containing microscopic capsules are disclosed in U.S. Pat. No. 2,800,457, which issued on July 23, 1957, on the application of Barrett K. Green and Lowell Schleicher and in U.S. Pat. No. 3,041,289, which issued on June 26, 1962, on the application of Bernard Katchem and Robert E. Miller.

The encapsulated droplets are released by the rupture of capsules in writing operations. The acridan liquid droplets are transferred in the pattern of the data configuration to the top of the underlying sheet. The top of the underlying sheet is coated or impregnated with at least one material which is an acid reactant with respect to the acridan and produces color with any such component that is reactive therewith. Representative acidic coating materials are, on one hand, oil-insoluble minerals or inorganic particulate solid material, represented by kaolin, attapulgite, silica gel, zeolites, and the like, and, on the other hand, organic polymeric acidic materials, such as acid-reacting phenolic resins of oil-soluble characteristics.

The record member consists of a base sheet or web member either of fibrous construction, such as paper, or of continuous structure, such as films of organic polymer material, carrying the color reactant in an exposed state with respect to applied liquid. The acid reactant, when of particulate nature, is arranged in intimate juxtaposition to form an apparently unbroken liquid receptive surface, yet substantially each particle individually is available for contact with applied liquid.

Polymeric materials of sufficient activity in an acid sense and suitable for use in this invention because they are oil-soluble are disclosed in U.S. Letters Patent No. 3,672,935, issued June 27, 1972, on application Ser. No. 44,805, filed June 9, 1970, which was a continuation application for U.S. Letters Patent, Ser. No. 744,601, filed June 17, 1968, based on application for U.S. Letters Patent Ser. No. 392,404, filed Aug. 27, 1964, by Robert E. Miller and Paul S. Phillips, Jr.

Among the oil-soluble organic polymeric materials suitable for use in this invention together with appropriate solvents to be used therewith, acid-reaction phenol-aldehyde and phenol-acetylene polymers, maleic acid-rosin resins partially or wholly hydrolyzed styrene-maleic anhydride copolymers and ethylene-maleic anhydride copolymers, carboxy polymethylene (Carbopol 934), and wholly or partially hydrolyzed vinyl methyl ether-maleic anhydride copolymer are specified as typical of the reactive acidic polymeric materials.

Among the phenol-aldehyde polymers found useful are members of the type commonly referred to as novolaks, which are characterized by solubility in common organic solvents and which are, in the absence of cross-linking agents, permanently fusible. Another group of useful phenol polymeric materials are alkylphenol-acetylene resins, likewise soluble in common organic solvents and possessing permanent fusibility in the absence of being treated by cross-linking materials. Generally, the phenolic polymer materials useful in practicing this invention are characterized by the presence of free hydroxyl groups and by the absence of groups, such as methylol, which tend to promote infusibility or cross-linking of the polymer, and by their solubility in organic solvents and relative insolubility in aqueous media.

A laboratory method useful in the selection of suitable phenolic resins is a determination of the infrared radiation absorption pattern of a candidate material. It has been found that phenolic resins showing an absorption in the 3200–3500 cm.$^{-1}$ region (which is indicative of the free hydroxyl groups) and not having an absorption in the 1600–1700 cm.$^{-1}$ region are suitable. The latter absorption region is indicative of the desensitization of the hydroxyl groups and consequently makes such groups unavailable for reaction with the chromogenic material to be specified.

The liquid solvent portion of this invention is capable of dissolving the mark-forming components. The solvent can be volatile or nonvolatile, and a single or multiple component solvent which is wholly or partly volatile can be used. Examples of volatile solvents useful with the acridan and acidic polymer mark-forming components specified are toluene, petroleum distillate, perchloroethylene, and xylene. Examples of nonvolatile solvents are high-boiling-point petroleum fractions and chlorinated diphenyls.

Generally, the solvent forming the vehicle to a large extent should be chosen so as to be capable of dissolving at least 1%, on a weight basis, of the acridan, preferably in excess of 2%, and a larger amount of polymeric material—up to, say 15% or more—to form an efficient reaction. However, in the preferred system, the solvent should be capable of dissolving an excess of the polymeric material, so as to provide every opportunity for maximum reaction utilization of the acridan and thus to assure the maximum coloration at a reaction site.

A further criterion of the selected solvent is that it must not interfere with the mark-forming reaction. In some instances, the presence of the solvent may interfere with the mark-forming reaction or diminish the intensity of the mark, in which case the solvent chosen should be sufficiently vaporizable to assure its leaving the reaction site after having, through solution, brought the mark-forming components into intimate admixture, so that the mark-forming reaction proceeds.

In the base-acid color system, as stated above, the polymeric mark-forming component(s) chosen must be acidic relative to the acridan compound and reactive with the acridan material to effect the distinctive color formation or color range.

Kaolin is generally known and used in the papermaking industry as "china clay" and is outstandingly preferable as a particulate oil-insoluble and water-insoluble mineral material of acid characteristics necessary to color the acridan of this invention. A white kaolin is used, and, because of its whiteness, its plate-like particle form, which gives it unparalleled coating properties in aqueous slurries, its universal abundance in supply, its historical general usage in the papermaking and paperconverting industries, and its low cost, it is an ideal material. Other types of particulate and substantially colorless water-and oil-insoluble minerals of the necessary acid properties are deemed equivalents of kaolin, some being bentonites.

Attapulgite can be used in this invention as an efficient colorless mineral reactant material to color the benzopyrans of this invention that react on contact in an electron-donor-acceptor reaction, and, by reason of its high oil absorbency, is doubly useful as an absorbent reactant coating on paper to form color with such compounds dissolved in oil as may be applied to it.

Various methods known to the prior art and disclosed in the aforementioned application Ser. No. 392,404 to Miller et al. and U.S. patent application Ser. No. 420,193 to Phillips et al. can be employed in coating compositions of the mark-forming materials into their supporting sheets. An example of the compositions which can be coated onto the surface of an underlying sheet of a two-sheet system to react with the capsule coating of the underside of an overlying sheet is as follows.

Coating composition:	Percent by weight
Phenolic polymer mixture	17
Paper coating kaolin (white)	57
Calcium carbonate	12
Styrene butadiene latex	4
Ethylated starch	8
Gum arabic	2
	100

All of the above-described materials, solvents, systems and the like, except for the acridans of this invention, are further described in U.S. Pat. 3,491,117.

The advantages of this invention are further illustrated by the following examples. The reactants and the proportions and other specific conditions are presented as being typical and should not be constructed to limit the invention unduly.

EXAMPLE 1

Preparation of 9-(p-dimethylaminophthalyl-3)-10 methylacridan

A mixture of 4.18 g. (0.02 mole) of N-methylacridone and 12.24 g. (0.04 mole) of phosphorus oxychloride was heated one hour at 80–90° C. The excess phosphorus oxychloride was removed under reduced pressure and 6.88 g. (0.044 mole) of methyl-p-dimethylaminobenzoate added. After three hours at 90–100° C. the reaction solution was dissolved in water, made basic and extracted with benzene. Partial concentration of the benzene solution gave recovery of some unreacted N-methylacridone. Subsequent treatment of the remaining benzene filtrate with hexane gave crystallized colorless product, M.P. 270–271° C. The compound had lactone type carbonyl absorption in the infrared at 1740 cm.$^{-1}$.

Analysis.—Calcd. for $C_{23}H_{20}N_2O_2$ (percent): C, 77.50; H, 5.66; N, 7.86. Mol. wt., 360. Found (percent): C, 77.23; H, 5.62; N, 8.17. Mol. wt. 345.

When this compound is dissolved in an organic solvent such as benzene the colorless solution yields a neutral (black) color response on application to an acidic surface such as a phenolic resin. The color has reflectants minima at 420 mμ and 564 mμ and a dominant reflectance maximum at 476 mμ.

EXAMPLE 2

Preparation of 9-(p-dimethylaminophthalan-3)-10-methylacridan

The reaction was carried out as in Example 1 using N-methylacridone, phosphorus oxychloride and M-dimethylaminobenzyl alcohol. The same isolation procedure was employed and the product finally recrystallized from ethyl ether-petroleum ether (30–60° C.) as faintly colored prismatic crystals, M.P. 179–181° C.

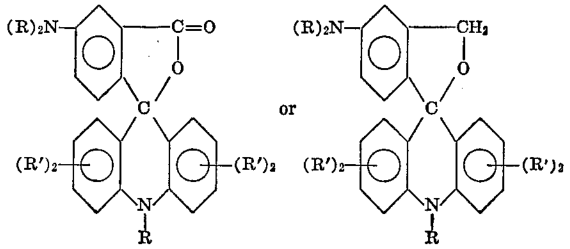
Analysis.—Calcd. for $C_{23}H_{22}NO$ (percent): C, 80.67; H, 6.48; 8.18; O, 4.67. Mol. wt., 342. Found (percent): C, 80.91; H, 6.59; N, 8.01; O, 4.49. Mol. wt., 341,

When this compound is dissolved in an organic solvent such as benzene the colorless solution yields a neutral (black) color response to an acidic surface such as phenolic resin. The color has minima at 424 mμ and 470 mμ and a dominant reflectance maximum at 480 mμ.

Although this invention has been described in considerable detail, it must be understood that such detail is for the purposes of illustration only and that many variations and modifications can be made by one skilled in the art without departing from the scope and spirit thereof.

What is claimed is:

1. A colorless, but colorable acridan compound represented by the formula:



wherein each R is an alkyl having 1 to 5 carbon atoms and each R' is hydrogen, an alkyl having 1 to 5 carbon atoms, an alkoxy having 1 to 5 carbon atoms, a dialkylamino wherein each alkyl has 1 to 5 carbon atoms, an amino, a nitro or a halogen.

2. The compound according to claim 1 wherein each R is an alkyl having 1 to 3 carbon atoms and each R' is hydrogen or an alkyl having 1 to 3 carbon atoms.

3. The compound according to claim 1 wherein said compound is 9-(p-dimethylaminophthalyl-3)-10-methylacridan.

4. The compound according to claim 1 wherein said compound is 9-(p-dimethylaminophthalan-3)-10-methylacridan.

References Cited

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DONALD G. DAUS, Primary Examiner

U.S. Cl. X.R.

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