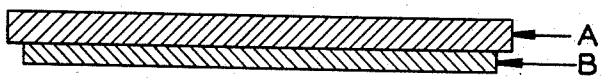
March 1, 1960 C. DAVIS 2,927,040

NON-STAINING TRIARYLMETHANE COLOR BASE AND METHOD OF PRINTING THEREWITH

Filed Aug. 13, 1957



A = BASE WEB

B = COATING CONTAINING NONSTAINING TRIARYLMETHANE COMPOUND

INVENTOR.

CHESTER DAVIS

BY

ATTORNEY

United States Patent Office 2,927,040
Patented Mar. 1, 1960

2,927,040

NON-STAINING TRIARYLMETHANE COLOR BASE AND METHOD OF PRINTING THEREWITH

Chester Davis, Newport, Ky.

Application August 13, 1957, Serial No. 677,837

21 Claims. (Cl. 117—36)

The purpose of this invention is to describe a simple recording system which is nonstaining to skin and clothing. This involves the preparation and use of triphenylmethane dye derivatives which are incapable of chemical adsorption by the normal constituents of skin tissue and textile fibers.

Staining of tissue may be chemical or physical; that is, a chemical compound with tissue may be formed or a colored substance may be physically entrapped by tissue without reacting with the tissue itself. In the case of chemical staining, repeated washing with soap and water usually has little or no effect; but this washing treatment usually removes physically absorbed colors with ease. Chemical staining of skin and clothing is by far the most objectionable feature in recording systems involving the use of triphenylmethane dyes.

For many years the high color intensity of the triphenylmethane dyes (Malachite Green, Crystal Violet, etc.) has prompted their use in business recording systems, especially where multiple copies are desired. A spirit duplicating master sheet containing Crystal Violet Oleate, for example, may give two to five times more satisfactory copies than an azo-dye-forming master sheet; and the requirement that ball point pen inks have high color intensity necessitates the use of Victoria Blue and similar triphenylmethane dyes. Unfortunately, copy fluids and copy papers containing these materials cause permanent chemical staining of skin tissue and clothing fabrics; and workers in the recording field have long sought means of overcoming this basic defect.

The reduction of triphenylmethane dyes to their colorless leuco compounds and the conversion of their dye salts to the colorless carbinol bases by means of strong alkalis has been proposed in one form or another by previous workers in the recording field, but these substances are readily converted back to the intensely colored dye salts by air, sunlight, skin and clothing with consequent strong chemical adsorption. Davis and Thacker (U.S. 2,646,367) have utilized certain colorless triphenylmethane lactones which are nonstaining to skin, but these materials are extraordinarily unstable to light and moisture in the colored form. What is needed for commercial recording systems is a series of triphenylmethane dye compounds which are substantially nonstaining to skin and clothing, cheap, reasonably light-stable in the colored form, and giving on a suitable surface colored characters which are resistant to decoloration by high humidity and adverse atmospheric conditions.

The author of the present invention has chosen to examine the problem from a new theoretical viewpoint as to the exact mechanism of staining by these dyes. The high bactericidal activity of the acridine dyes has been shown by Albert and Goldacre (Nature, 161, 95

(1948)) to be closely related to the disassociation constant of their bases; and it is significant that Gentian Violet Base has a dissociation constant of ($pK \cong 9$) which is very close to the optimum required for maximum adsorption by the living bacterial cell. Michler's Hydrol is a much weaker base ($pK \cong 6$) than Gentian Violet Base and is also much weaker in bactericidal and staining properties. An analysis by the author of the present invention of the available data indicated that the essential factor for a non-staining triphenylmethane color base would appear to be a dissociation constant below 5.0, preferably between approximately $pK \cong 2$ and $pK \cong 4$.

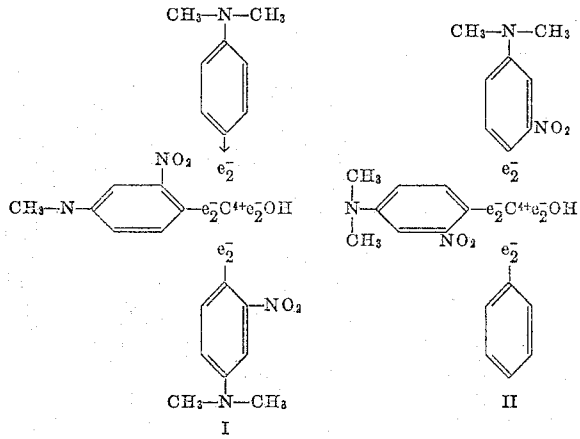
The author of the present invention has discovered that suitable introduction of nitro groups into triphenylmethane dye bases has the effect of lowering their dissociation constants to a level where the resultant dye is too weakly basic to give a stable chemical compound with skin tissue yet is still sufficiently acidic to give intensely colored salts with suitable acids, including the paper coating acid clays and acid silicas which have long been used for preparing coated papers for use in the copy paper field.

The resultant nitrated color bases are yellow to orange-red in color, stable, and readily yield light-stable, intense prints on suitable receiving sheets. Dinitro Crystal Violet Carbinol Base (I) and Dinitro Malachite Green Carbinol Base (II), for example, upon solution in suitable organic solvents give strong yellow solutions which can be freely handled without leaving intense violet or green stains upon the skin. The resultant recording fluids, however, will give intense characters upon transfer to a suitable recording surface.

Previous workers in the recording field have concentrated their investigations on attempts to obtain completely colorless derivatives of the triphenylmethane dyes; these workers failed to realize that the most desirable feature of recording colors is a complete lack of stain and not a complete lack of color, which is a secondary consideration. A colored recording system of high intensity and lacking in chemical staining properties is far more desirable that a colorless system of low tinctorial power or low stability or which stains the skin. It is, therefore, not the purpose of the present invention to claim an absolutely colorless recording system. The point to be emphasized is the lack of permanent chemical stain possessed by compounds of the present invention.

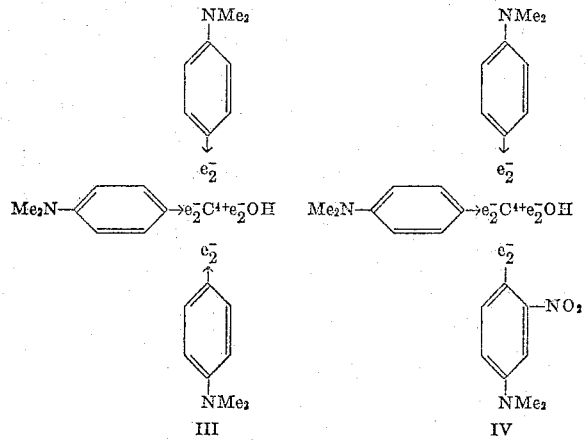
If one examines the structure of Crystal Violet Carbinol Base (III), it is obviously a very strong base due to the high electron density around the central carbon core; and the carbinol hydroxide ion can contribute to the screening of the central carbon core only at very small proton concentrations; i.e., only at high hydroxyl ion concentrations (strongly basic solution). If one forms the mononitro derivative of III, the resultant structure (IV) is stable at a higher proton concentration because here the quanticule of one benzene ring is less free to shield the central carbon atom's charged core and the screening contribution of the hyroxyl quanticule is more strongly needed. Upon dinitration, the resultant structure is such that now two quanticules are less free to shield the central core; and the hydroxyl quanticule is now strongly required for screening the central carbon atom's charged core. In brief, the dissociation constant is decreased and Dinitro Crystal Violet Carbinol Base is a weak base. The Trinitro Crystal Violet Carbinol Base (V) has such a strong screening requirement for the hydroxyl quanticule that dissociation can occur

only at high proton concentrations; and V is a very weak base.

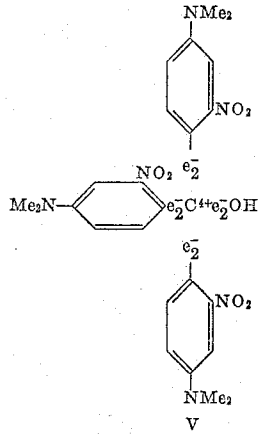


I

II



III IV



V

In place of a proton, one may use a Lewis acid for removing a quanticule (electron pair) from the screening electrons around the central carbon core. The most suitable Lewis acids for commercial purposes are the acid silicates, such as clays, fuller's earth, activated slica, and similar materials which have an acid strength equivalent to a pH below 5, preferably from 1 to 4. These solid acids are sufficiently strong that they form stable colored salts with the nonstaining color bases of the present invention.

For certain applications, the use of performed dye salts of the nonstaining color bases would be preferable to the use of the free bases themselves; this removes the need for a specially coated receiving sheet and permits the use of standard paper as a receiving sheet. The use of oleic acid and organic acids such as trichloracetic and tannic acid is ideal for these applications. Any colored salts which accidentally contact fibers can be easily removed by treatment with a mild alkali (soap, ammonium hyroxide solutions, triethanolamine solutions, etc.) and subsequent washing with water or a wool-cleaning solvent such as carbon tetrachloride.

All that is essential for the purpose of the present invention is a reduction of the dye base dissociation constant to a value sufficiently below pK 7 that reaction with constituents of skin tissue and textile fibers is negligible. The best results are obtained with materials of dissociation constant between pK 2 and 5. This is accomplished by the suitable introduction of nitro groups into the triphenylmethane aromatic rings. While the products from Crystal Violet and Malachite Green are of special interest because of the fundamental simplicity of these structures and their low cost, the process is generally applicable to the entire field of the triphenylmethane dyes and their closed ring analogues.

Description

Because the triphenylmethane dyes and most of their mononitro derivatives stain the skin, it is essential that the starting materials and intermediate nitration products be absent from the nonstaining derivatives obtained by controlled nitration. This is best achieved by careful control of the amounts of nitric acid used and the temperature at which the reaction is carried out.

100 gms. (0.257 mol) of Crystal Violet Carbinol Base or a corresponding amount of the colored dye salt is dissolved in 1500 gms. of concentrated sulfuric acid; and the resultant solution is cooled to 0–3° C. To the cold dye solution is added with stirring a cold solution of 51.7 gms. (0.517 mol) of 63% concentration nitric acid in 400 gms. concentrated sulfuric acid, maintaining the reaction temperature below 8° C., usually around 3–5° C. The solution is allowed to stand for one hour at 3–5° C. and then slowly warmed to 25° C. After one hour at 25° C., the sulfuric acid is poured onto a large amount of crushed ice and water. The resulting sulfuric acid solution is neutralized with a suitable base, usually ammonium hydroxide solution or caustic soda solution to precipitate out 2,2'-dinitro-4,4',4''-tris (dimethylamino)-triphenylcarbinol (Dinitro Crystal Violet Carbinol Base). This is thoroughly washed with water and dried to give a yellow-green powder which is pure enough for most purposes; however, the slightly impure product can be further purified by recrystallization from acetone-water or by resolution in dilute mineral acids followed by reprecipitation by base at a pH of 6–7.

100 gms. (0.257 mol) of Crystal Violet Carbinol Base or a corresponding amount of the dye salt is dissolved in 1500 gms. of concentrated sulfuric acid; and the resultant solution is cooled to 0–3° C. To the cold dye solution is added with stirring a cold solution of 76.9 gms. (0.785 mol) of 63% concentration nitric acid in 400 gms. of concentrated sulfuric acid, maintaining the reaction temperature below 10° C., usually between 3–5° C. After one hour at 5° C., the temperature of the reaction mixture is slowly raised to 25° C. and maintained at 25° C. for one hour. The reaction mixture is then poured onto a large amount of crushed ice and water; and the resulting acid solution is then neutralized with base to precipitate out 2,2',2''-trinitro-4,4',4''-tris (dimethylamino)-triphenylcarbinol (Trinitro Crystal Violet Carbinol Base). This is filtered off, thoroughly washed with water, and dried to yield a light green powder. The product may be further purified by resolution in mineral acids and reprecipitation with base at a pH of 6.

100 gms. (0.289 mol) of Malachite Green Carbinol Base or a corresponding molar equivalent of the dye salt is dissolved in 1500 gms. of concentrated sulfuric acid; and the resultant solution is cooled to 0° C. To the cold dye solution is added with stirring a cold solution of 58.1 gms. (0.581 mol) of 63% concentration nitric acid in 400 gms. concentrated sulfuric acid, maintaining the reaction mixture below 8° C., usually between 2–5° C. After one

hour at 5° C., the temperature of the reaction mixture is slowly raised to 25° C. and maintained at 25° C. for one hour. The reaction mixture is then poured onto a large amount of crushed ice and water, and the resulting acid solution is neutralized with base to precipitate out 2,2'-dinitro-4,4'-bis (dimethylamino) triphenylcarbinol. This is filtered off and washed thoroughly with water to yield a yellow-green powder. The product may be purified by resolution in dilute mineral acids and reprecipitation with base at a pH of 6.

The mononitration product, 2-nitro-4,4'-bis (dimethylamino)triphenylcarbinol, can be obtained by the use of one equivalent of nitric acid; this has very slight staining properties and is suitable for certain uses. The mononitro compound, 2''-nitro-4,4'-bis (dimethylamino) triphenylcarbinol, which is obtainable by the condensation of ortho-nitrobenzaldehyde with dimethylaniline, possesses strong staining properties.

100 gms. (0.267 mol) of Methyl Violet Carbinol Base or a corresponding amount of the dye salt is dissolved in 1500 gms. of concentrated sulfuric acid; and the resultant solution is cooled to 3–5° C. To the cold dye solution is added with stirring a cold solution of 53.3 gms. (0.534 mol) of 63% concentration nitric acid in 400 gms. of concentrated sulfuric acid, maintaining the reaction temperature below 8° C., usually between 3–5° C. The reaction mixture is allowed to stand for one hour at 3–5° C. and then slowly warmed to 25° C. After one hour at 25° C., the sulfuric acid reaction mixture is poured onto a large amount of crushed ice and water. The resulting acid solution is neutralized with ammonium hydroxide solution to precipitate out 2,2'-dinitro-N,N',N''-pentamethyl-4,4',4''-triaminotriphenylcarbinol (Dinitro Methyl Violet Carbinol Base). This is thoroughly washed with water and dried to give a yellow-green powder which is pure enough for most purposes; the slightly impure product can be further purified by resolution in dilute mineral acids followed by reprecipitation with base at a pH of 6–7.

A general rule is that the triaminotriphenyl methane dyes require at least two nitro groups for adequate reduction of basicity and diaminotriphenylmethane dyes require at least one and preferably two nitro groups. The nitro group must be attached to the aromatic nucleus containing the basic substituent in order to reduce the quanticule-donating effect of the amino aromatic system. The principle can be applied to all types of basic triphenylmethane dyes and their closed ring analogues; and variations are readily obvious to one skilled in the art, once the fundamental principle is known.

An example of a recording fluid containing a nonstaining color base is a 3% solution of 2,2'-dinitro 4,4'4''-tris (dimethylamino)-triphenylcarbinol (Dinitro Crystal Violet Carbinol Base) in toluene. This gives an intense dark violet (almost blue-black) coloration on a receiving sheet covered with an activated silica coating.

Another example of this invention is a 3% solution of 2,2',2''-trinitro-4,4'4''-tris(dimethylamino) triphenylcarbinol (Trinitro Crystal Violet Carbinol Base) in alcohol. This gives an intense dark violet (almost blue-black) coloration on a receiving sheet coated with a colloidal silicate acid (kaolin, etc.).

Still another example of this invention is a 2.5% solution of 2-Nitro Malachite Green Carbinol Base in chlorinated diphenyl of 42% chlorine content. This gives an intense green coloration on a receiving sheet coated with calcium silicate.

Still another example of this invention is a 4% solution in alcohol of the colored dye salt from Dinitro Crystal Violet Carbinol Base and benzenesulfonic acid. This gives an intense violet coloration on an ordinary paper receiving sheet.

It should be clearly understood that the invention is not limited to the examples set forth but is generally applicable to the entire family of basic triphenylmethane dyes and their closed ring analogues (notably the xanthines) which may undergo suitable nitration to form weak bases incapable of reacting chemically with skin tissue and textile fbers yet are capable of reacting with stronger acids to form stable colored salts.

The drawing is a cross-sectional view illustrative of a typical base web (A) coated with a composition containing nonstaining triarylmethane compound (B).

It is also to be understood that the nonstaining color bases of the present invention may be used to make recordings on appropriate surfaces by any desired conventional method or technique. For instance, the nonstaining color base or a derivative thereof may be used for direct printing on appropriately coated paper or the nonstaining color base or a derivative thereof may be utilized as a component of the coating of a transfer sheet. In other words, the recording media of this invention may be used in a great variety of recording, printing, and manifolding systems. The utilization of my invention by means of a transfer sheet is particularly disclosed in my co-pending application Serial No. 677,838, filed August 13, 1957, for "Nonstaining Transfer Sheet."

Having described my invention, I claim:

1. The method of printing which comprises applying to a surface characterized by high acid strength a substantially nonstaining liquid which comprises a nonstaining triarylmethane color base containing at least two dialkylamino-substituted aryl groups having as a substituent a nitro group and characterized by a logarithmic dissociation constant between 2 and 5, said nonstaining triarylmethane color base being structurally adapted to react with the acid surface to form an intensely colored salt.

2. The method of printing which comprises applying to a surface characterized by high acid strength a substantially nonstaining liquid which comprises a nonstaining triarylmethane color base containing at least dialkylamino-substituted aryl groups having as a substituent ortho to the central carbon atom a nitro group and characterized by a logarithmic dissociation constant between 2 and 5, said nonstaining triarylmethane color base being structurally adapted to react with the acid surface to form an intensely colored salt.

3. The method of claim 1 wherein the nonstaining triarylmethane color base is a member of the group consisting of N,N',N''-alkylated-2,2'-dinitro-4,4'4''-triaminotriphenylcarbinols and their carbinol ethers.

4. The method of claim 1 wherein the nonstaining triarylmethane color base is a member of the group consisting of N,N',N''-alkylated-2,2',2''-trinitro-4,4',4''-triaminotriphenylcarbinols and their carbinol ethers.

5. The method of claim 1 wherein the nonstaining triarylmethane color base is a member of the group consisting of N,N'-alkylated-2,2'-dinitro-4,4'-diaminotriphenylcarbinols and their carbinol ethers.

6. The method of printing which comprises applying to a surface having thereon a silicate coating of high acid strength a substantially nonstaining liquid which comprises a nonstaining triarylmethane color base containing at least two dialkylamino-substituted aryl groups having as a substituent a nitro group and characterized by a logarithmic dissociation constant between 2 and 5, whereby contact of the nonstaining triarylmethane color base and the acid silicate causes the formation of an intensely colored triarylmethane colored salt to form a colored print.

7. The method of printing which comprises applying to a surface having thereon a silicate coating of high acid strength a substantially nonstaining liquid which comprises a nonstaining triarylmethane color base containing at least two dialkylamino-substituted aryl groups having as a substituent ortho to the central carbon atom a nitro group and characterized by a logarithmic dissociation constant between 2 and 5, whereby contact of the nonstaining triarylmethane color base and the acid silicate

causes the formation of an intensely colored triarylmethane colored salt to form a colored print.

8. The method of claim 7 wherein the nonstaining triarylmethane color base is a member of the group consisting of N,N',N''-alkylated-2,2'-dinitro-4,4',4''-triaminotriphenylcarbinols and their carbinol ethers.

9. The method of claim 7 wherein the nonstaining triarylmethane color base is a member of the group consisting of N,N',N''-alkylated-2,2',2''-trinitro-4,4',4''-triaminotriphenylcarbinols and their carbinol ethers.

10. The method of claim 7 wherein the nonstaining triarylmethane color base is a member of the group of N,N'-alkylated 2,2'-dinitro-4,4'-diaminotriphenylcarbinols and their carbinol ethers.

11. The method of printing which comprises applying to a receptive surface a substantially nonstaining liquid which comprises a substantially nonstaining colored salt of a nonstaining triarylmethane color base containing at least two dialkylamino-substituted aryl groups having as a substituent a nitro group and characterized by a logarithmic dissociation constant between 2 and 5, said colored salt having too low an ionization constant to undergo a permanent chemical reaction with the constituents of human skin.

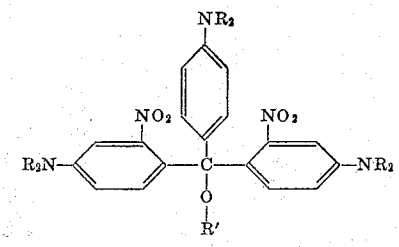
12. The method of printing which comprises applying to a receptive surface a substantially nonstaining colored salt of a nonstaining triarylmethane color base containing at least two dialkylamino-substituted aryl groups having as a substituent ortho to the central carbon atom a nitro group and characterized by a logarithmic dissociation constant between 2 and 5, said colored salt having too low an ionization constant to undergo a permanent chemical reaction with human skin.

13. A printing medium comprising a substantially nonstaining triarylmethane color base containing at least two dialkylamino-substituted aryl groups having as a substituent a nitro group and characterized by a logarithmic dissociation constant between 2 and 5, said compound dissolved in a solvent therefor, said compound being structurally adapted to form an intensely colored salt upon contact with a surface characterized high acid strength.

14. A printing medium comprising the colored salt of a nonstaining triarylmethane color base containing at least two dialkylamino-substituted aryl groups having as a substituent a nitro group and characterized by a logarithmic dissociation constant between 2 and 5, said colored salt dissolved in a solvent therefor, said colored salt having too low an ionization constant to undergo a permanent chemical reaction with human skin.

15. A new composition of matter comprising a substantially nonstaining triarylmethane color base containing at least two dialkylamino-substituted aryl groups having as a substituent a nitro group, the logarithmic dissociation constant of which is within the range 2 to 5, whereby said nonstaining triarylmethane color base becomes chemically unreactive towards human skin but reacts with strong acids to form an intensely colored salt.

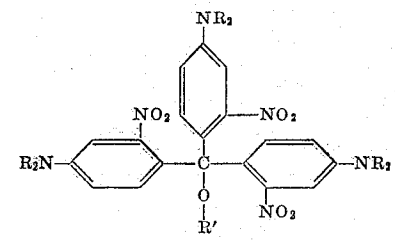
16. A new composition of matter represented by the following formula:



wherein R is a lower alkyl group and R' is chosen from the group consisting of hydrogen and lower alkyl.

17. A new composition of matter comprising the intensely colored salts obtained by the reaction of the nonstaining color base of claim 16 with a strong acid.

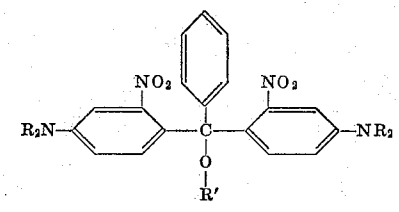
18. A new composition of matter represented by the following formula:



wherein R is a lower alkyl group and R' is chosen from the group consisting of hydrogen and lower alkyl.

19. A new composition of matter comprising the intensely colored salts obtained by the reaction of the nonstaining color base of claim 18 with a strong acid.

20. A new composition of matter represented by the following formula:



wherein R is a lower alkyl group and R' is chosen from the group consisting of hydrogen and lower alkyl.

21. A new composition of matter comprising the intensely colored salts obtained by the reaction of the nonstaining color base of claim 20 with a strong acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,755,201	Webber	July 17, 1956
2,755,202	Balon	July 17, 1956
2,755,203	Stallman	July 17, 1956