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PROCESS OF CONVERTING A POLYAMINO-TRIARYLMETHANE DYE COATING ON A BASE FROM A STABILIZED LEUCO FORM TO A COLORED FORM

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This invention relates to a method of converting or developing certain colorless leuco triarylmethanes into their colored forms in a duplication process, such as the hectograph method.

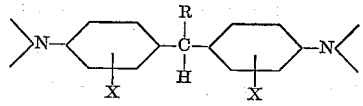
Crystal violet and similar dyes are used to a large extent for the manufacture of "carbon paper" for the spirit hectograph duplication process. This "carbon" is prepared by incorporating the color into a vehicle containing waxes, oils and other special-purpose ingredients. The method of duplication consists first of making a master sheet by typing or writing on glazed paper under which a sheet of the spirit hectograph carbon is placed with the waxed side facing up so that a mirror image of the written matter is formed on the underside of the master sheet. This master sheet is then placed on a rotatable drum in a duplicating machine. Prints are formed on the machine by pressing the master sheet against sheets of copy paper which is moistened with an alcoholic or "spirit" solvent. Only a small portion of the dye is removed when each print is made.

The difficulty of handling the intensely colored crystal violet compositions is well known since even with the greatest care the fingers and clothing become stained with the dye. In the copending application of Balon and Stallmann, Serial No. 456,887, filed on even date herewith, these difficulties are avoided by providing a stabilized leuco base of certain triarylmethanes and incorporating them in a hectograph vehicle which is used for coating the master sheet.

The present invention relates to a new and improved method of developing or converting the stabilized leuco form of the dye into its colored form. This development may be accomplished in various ways although one of the simplest and more convenient methods is to incorporate the developing agent in the alcoholic solvent which is used to moisten the roller of the duplicating machine.

It is an object of the present invention to provide a simple and economical means of converting or developing the leuco form to the colored form of triarylmethane dyes described in the above-mentioned application. Another object is the provision of a developing system which may be incorporated into the alcoholic solvent used in standard spirit duplicating machines. Other objects will be apparent as the description of the invention proceeds.

These and other objects are accomplished by converting from a stabilized leuco form to a color form, a wax formulation containing from about 2% to 60% by weight of a triaryl methane compound selected from the group consisting of the diamino- and triamino- triaryl methanes of the formula:



wherein X designates a member of the group consisting of hydrogen and methyl; wherein R is a radical of the group consisting of phenyl, tolyl, xylyl, mononitrophenyl,

mono- and dichloro-phenyl, aminophenyl, aminotolyl, monoacetylaminophenyl, 1-p-phenylamino-naphthyl, 1-p-monoalkylamino- and dialkylamino-naphthyl, and wherein the N-atoms of said amino-phenyl and aminotolyl radicals and the N-atoms shown in the formula above in para position to the CH group have their second and third valencies satisfied by members of the group consisting of hydrogen, alkyl of less than 5 carbon atoms, 2-hydroxyethyl, 2-cyanoethyl, benzyl and phenyl, said leuco compound being devoid of sulfo, carboxy and phenolic hydroxyl groups and being in a state of purity whereby it is essentially free of color, and being associated with a quaternary ammonium hydroxide in sufficient quantity to stabilize said compound against conversion into color by photochemical oxidation during exposure to the atmosphere. The alkyl groups in each of the above classes should contain fewer than 5 carbon atoms.

The compound is stabilized with about 2% to 10% of a quaternary ammonium hydroxide, i. e., enough to give it a pH of about 8 or higher as measured in a 1% solution or suspension thereof at room temperature in 95% ethanol which normally has a pH of about 7.5. The color of the formulation is developed by contacting it with a developer which is oxidizing and acid relative to the leuco form of the triarylmethane. That is, the nature of the developer is such that when in contact with the leuco, the developer acts as an electron acceptor. Under these conditions, the leuco base acts at the point of contact as an electron donor while it is being converted into its more highly polarized quinonoid conjugated form. Thus the developer oxidizes the leuco to the carbinol form and then converts the carbinol to the dye cation.

The vehicles used in the formulations may be conventional or special but usually are composed of oils and waxes either of animal or vegetable origin. Other agents are usually added to improve the transferring properties of the formulation and may include plasticizers, hygroscopic control substances, and similar agents. The percentage of leuco in the formulation is relatively immaterial provided sufficient developing agent is present to develop the color on the copy sheet, whether a small amount of leuco, such as 5% to 20%, is present as in the coating for one-time "carbon" papers, or up to 60% as is commonly used in spirit hectograph paper.

The leuco triarylmethanes used in duplicating systems incorporating the present invention are those described in the above-mentioned copending application and its parent application, preferably the stabilized leuco ethyl violet and stabilized p - chlorophenyl - bis(p - dimethylaminophenyl) methane. Among the dyes which may be used in addition to these compounds may be mentioned the stabilized form of the following:

Crystal Violet, C. I. 681, leuco derivative
3,3'-dimethyl derivative of leuco ethyl violet
p - Diethylaminophenyl - bis(benzylethylaminophenyl) methane
p - Diethylaminophenyl - bis(3 - methyl - 4 - ethyl - β - hydroxy ethylaminophenyl) methane
p - Diethylaminophenyl - bis(p - methyl - β cyanoethyl - aminophenyl) methane
p - Dimethylaminophenyl - bis(p - methyl - β - cyano - ethylaminophenyl) methane
p - Diethylaminophenyl - bis(p - dimethylamino - phenyl) methane
Tris(p-di-n-butylaminophenyl) methane
p - Diethylaminophenyl - bis(p - di - n - butylamino - phenyl) methane
p - Ethyl - methylaminophenyl - bis(p - di - n - butyl - aminophenyl) methane
p - Methyl - β - cyanoethylaminophenyl - bis(p - di - n - butylaminophenyl) methane
Victoria pure blue BO, U. S. 2,422,445, leuco derivative

Phenyl-bis(p-ethyl-benzylaminophenyl) methane
o-Chlorophenyl-bis(p-diethylaminophenyl) methane
p-Chlorophenyl - bis(p-ethyl-benzylaminophenyl) methane
Brilliant Green, C. I. 662, leuco derivative
New Fuchsine, C. I. 678, leuco derivative
Paraleucaniline
Fuchsine, C. I. 677, leuco derivative
2-methyl leuco crystal violet
2-methyl leuco ethyl violet
5-methyl - 2-dimethylaminophenyl-bis(p-dimethylaminophenyl) methane
2,2'-dimethyl leuco crystal violet
Pentamethyl-paraleucaniline (main component in leuco methyl violet, the reduction product of the commercial dye of C. I. 680)
p-Ethyl-sec. butylaminophenyl-bis(dimethylaminophenyl) methane
Tris(p-benzylaminophenyl) methane
Diphenylated paraleucaniline (the reduction product of Spirit Blue 2B, C. I. 689)
p-Aminophenyl-bis(diethylaminophenyl) methane
p-Acetylaminophenyl-bis(p-dimethylaminophenyl) methane
p-Methylacetylaminophenyl-bis(p-dimethylaminophenyl) methane
2-methylphenyl-bis(p-dimethylaminophenyl) methane
4 - methyl - 3 - dimethylaminophenyl-bis(p-dimethylaminophenyl) methane
p-Nitrophenyl-bis(p-diethylaminophenyl) methane
Victoria Blue R, C. I. 728, leuco derivative
Victoria Blue B, C. I. 729, leuco derivative
1-p-dimethylaminonaphthyl-bis(p-dimethylaminophenyl) methane

The ethyl analogues of the N-methylated leuco Victoria blue dyes may also be used with advantage in many cases since they have lower melting points and are more compatible in waxy vehicles.

In addition to the above dyes, it is to be understood that shading dyes such as oil yellow N, C. I. 19, phthaloperinone, safranine T base, C. I. 841, oil scarlet C. I. 73 (Sudan II), oil red, C. I. 258, and other similar yellow, red, and brown dyes may be used as shading dyes to produce black shades from the above-listed stabilized dyes. Useful shading components must retain their original shades during development with chloranil and similar developing and oxidizing agents, they must be soluble in solvents such as alcohol or dioxane, and must be compatible with the oily or waxy vehicle used in the transfer medium. These shading compounds and their preparation and use are disclosed more fully in the above-mentioned application of Balon and Stallmann.

While the invention is not restricted to any special formulations used to coat the master sheet, it has been found that the above leuco compounds retain their stability if certain basic compounds are aded to the formulation, such as quaternary ammonium hydroxides, tertiary amine oxides, such as dimethylstearylamine oxides and aliphatic amines. These formulations are also improved if certain gasoline or rubber-anti-oxidants are incorporated to prevent or retard the discoloration of the leuco compound due to oxidation prior to the color development step.

In general, the color development on the final copy sheets in spirit hectograph work is achieved by bringing the transferred leuco in close contact with an oxidizing agent in the presence of an acid or with a compound which acts like an acid in the presence of moistening medium, such as alcohol, dioxane, or other polar solvents. A preferred developer is, in most cases, a compound in which both of these essential functions for color development are combined in the same compound. Many oxidizing agents perform these dual functions. Chloranil and

related halogenated benzoquinone or toluquinone compounds, including their haloimide derivatives, such as 2,6-dichlorobenzoquinone chlorimide, and benzoyl peroxide (or aliphatic acid peroxides) are examples of such preferred compounds which have good solubility in the above solvents. Triphenylchloromethane type compounds also serve well as developers when radiatnt heat is applied to the surface of the final copy sheet. I have found that under these conditions triarylchloromethane type developers oxidize the leuco and at the same time produce in situ the standard chloride salt of the color while the developer itself is reduced simultaneously to the corresponding triarylmethane compound according to the following probable reaction:

$$(RR'N\cdot C_6H_4)_3CH+(C_6H_5)_3CCl\rightarrow (RR'N\cdot C_6H_4)_3CCl+(C_6H_5)_3CH$$

For either one-time "carbon" paper or spirit hectograph duplication, the above-mentioned and other types of solid developers can also be incorporated in the paper, or deposited on the surface of the paper sheets, which are to be used for producing the final copies. This can conveniently be done by adding the compounds in the form of water-dispersible pastes or powders (made by viscous milling an aqueous slurry or paste of the original compound with a large amount of dispersing agents) to the pulp in the manufacture of such paper sheets which, with the conventional duplicating devices and techniques, give directly the developed color on the final copies.

Certain inorganic developers, such as iodine monochloride and other readily available iodohalides which are volatile liquids at room temperature, and which are very highly soluble in organic solvents, also are very effective developers. Some gaseous developers such as nitrous acid or NO_2 gas, and compounds which furnish oxidizing and acidic gases in a nascent state, such as the alkylnitriles, also are useful developers for these leuco compounds when they are used in specially designed duplication devices.

In some cases satisfactory color development can be achieved by the use of an acid producing agent alone without a special oxidizing agent incorporated in the copy sheets. In this case use may also be made of a local photo-oxidation of the leuco by exposure to light and air oxygen. This color development (without the use of special oxidizing agents in the system) can be greatly accelerated by exposing for a few seconds the transferred leuco on the copy sheets to a source of radiant heat, or by incorporating, either in the solvent or in the coating composition or in the paper itself, catalytic amounts of a phenolic accelerator, such as p-t-butyl phenol.

As a consequence, the novel, leuco-base compositions of the mentioned colors are ideally adapted for the purposes hereinabove discussed, that is, production of non-staining coatings on transfer media for spirit duplication processes and impact printing.

There is no limitation placed on the method of making the leuco-base compositions to be developed by the present invention. Any of the methods and formulations described in the above-mentioned copending applications are satisfactory.

When the process of this application is applied to hectograph duplication to produce a violet copy, it is important that the shade of the regenerated color appearing on the final copies does not deviate substantially from the violet shade which has become firmly established in the trade by many years of using crystal violet in duplicating devices. Spectrophotometric measurements have confirmed that many of the leuco compounds to which the process of this invention is applicable and the dyes regenerated therefrom by the process of this invention have the same significant light absorption peaks as leuco crystal violet

and crystal violet itself. The supporting data are as follows:

Main light absorption peaks

No. and Nature of Alkyl Groups	Example No. from Balon and Stallmann App.	Leuco U. V. (A.)	Visible (A.)[b]
Hexamethyl	2	2,625	6,000
Hexaethyl	13	2,725	6,060
Tetramethyl-diethyl	5	2,650	6,050
Hexa-n-butyl	6	2,620	6,120
Diethyl-tetra-n-butyl	7	2,720	6,150
Methylethyl-tetra-n-butyl	8	2,710	6,150
Diethyl-di(ethyl-β-hydroxyethyl)[a]	9		5,900
Diethyl-di(methyl-β-cyanoethyl)	10	2,625	5,900
Dimethyl-di(methyl-β-cyanoethyl)	11	2,650	5,900
Tetra-n-butyl-methyl-β-cyanoethyl	12	2,550	6,100

[a] Also contains a methyl group o- to each N bearing a hydroxyethyl group.
[b] Satisfactory violets in range of about 5850–6200.

The following examples are given by way of illustration and no limitation is placed thereon since it will be apparent that any dye falling within the above class may be substituted in like amount for this given in the examples.

Example I

A hectograph paper coating mass was prepared by adding the required amount of the stabilized leuco ethyl violet, which may be made according to Example 1 of the above-mentioned application Serial No. 456,887, to the molten mixture of the other ingredients in a beaker while the mass was kept at approximately 100° C. The highly fluid and colorless coating formulation so produced had the following composition:

30 parts high-melting stearylamine wax sold as AM–1180 by Armour & Company
20 parts petrolatum No. 5 (a commercial "hard" paraffin)
10 parts aluminum stearate
40 parts leuco compound

A hectograph paper sheet was then coated with this formulation at 100° C. and a "master copy" was prepared in the conventional manner on a typewriter. The colorless "master sheet" was then placed over the cylinder in a spirit duplicating machine in which the regular liquor had been replaced by a special developer prepared by diluting 25 parts of a 1% solution of chloranil in dioxane with 75 parts of ethanol. A total of 650 copies were then run off on the machine in the usual manner. Each copy was initially colorless but developed, almost immediately and without any further treatment, easily readable reproductions of the original type in a color similar to that produced from standard crystal violet. The last copy was as strong as the first copies.

When the amounts of stearylamine and petrolatum were reduced by 5 parts each, and 10 parts of triethanolamine were substituted for them, a thinner but equally useful hectograph formulation resulted.

Example II

Satisfactory spirit hectograph duplication also resulted when the following developer solutions were substituted for the dioxane-ethanol solution of chloranil in the procedure of Example 1 and with many other stabilized triphenylmethane dyes falling within the above formula:

(*a*) 1.0% chloranil, 49.5% dioxane, 49.5% 95% ethanol
(*b*) 1.0% chloranil, 62.0% dioxane, 37.0% 95% ethanol
(*c*) 1.2% chloranil, 82.3% tetrahydrofuran, 16.5% Cellosolve
(*d*) 1.0% benzoyl peroxide, 99.0% 95% ethanol
(*e*) 1.0% benzoyl peroxide, 99.0% isopropanol
(*f*) 1.0% benzoyl peroxide, 99.0% t-butanol
(*g*) 0.5% 2,4-dichlorobenzoyl peroxide, 99.5% t-butanol
(*h*) 1.0% 2,5-dichloro-p-quinone, 49.5% dioxane, 49.5% 95% ethanol
(*i*) 2.0% 2,6-dichloro-p-quinone chlorimide, 49.0% dioxane, 49.0% 95% ethanol
(*j*) 1.0% iodine monochloride, 49.5% dioxane, 49.5% ethanol
(*k*) 1.0% 2,6-dichloro-p-quinone, 49.5% dioxane, 49.5% ethanol

Example III

A one-time paper for impact copy printing was prepared by coating a sheet of high-quality tissue paper with the following formulation:

1 part by weight of stabilized leuco crystal violet
4 parts by weight of a molten vehicle consisting of three parts of carnauba wax and 1 part of a commercial stearylamine wax known by the trade-name AM–1180 and marketed by Armour and Company.

The coating composition thus obtained showed good fluidity at steam bath temperature. A sheet of ordinary paper was then coated with this mass and used in the same manner as ordinary carbon paper. It showed excellent transfer properties, producing on a typewriter or with a stylus or pencil colorless carbon copies which were readily developed in situ to a very strong crystal violet shade when the surface of the originally colorless copy sheet was slightly wetted with 1% solution of chloranil in dioxane.

Example IV

One part by weight of the dry stabilized leuco crystal violet of Example III was thoroughly mixed with 0.5 part of triphenylchloromethane to give a colorless powder with which the surface of a paper sheet was coated by working some of the powder with a spatula into the pores of the paper surface. The excess powder was then removed by turning the paper upside down and a metal stencil was placed over the coated paper. Exposure of this system to a source of radiant heat (holding it over an electrically heated hot plate or under an infrarad heating bulb) produced instantaneously a permanently fixed, very strong and sharp pattern in which the shielded areas (underneath the metal) had remained white while all the directly exposed area showed a deep violet-blue coloration.

The powders mentioned in Example IV may be incorporated in a binder such as gelatin, casein, albumin, starch, and dextrin.

It is to be understood that any of the above disclosed stabilized leuco compounds may be used in combination. If a black or shade approaching black is desired, a mixture of a green with a violet or blue together with a yellow, orange, brown, or red shading color should be selected. Some mixtures of this type are disclosed and illustrated in the above-mentioned copending application.

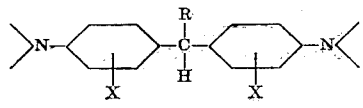
The present invention offers many advantages over the prior art. The final color of the dye is rapidly and completely developed on the copy paper. The present invention offers a method which makes the compositions containing stabilized leuco triarylmethane dyes practical. Another advantage is that as many as 650 readable copies may be made from one master sheet.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. In the process of converting a triarylmethane dye from a stabilized leuco to a colored form in which the triarylmethane compound is selected from the group con-

sisting of the spirit soluble polyamino-triarylmethanes of the formula:



wherein X designates a member of the group consisting of hydrogen and methyl; wherein R is a radical of the group consisting of phenyl, tolyl, xylyl, mononitrophenyl, mono- and dichloro-phenyl, aminophenyl, aminotolyl, mono-acetylaminophenyl, 1-p-phenylamino-naphthyl, and 1-p-monoalkylamino- and dialkylamino-naphthyl, and wherein the N-atoms of said aminophenyl and aminotolyl radicals and the N-atoms shown in the formula above in para position to the CH group have their second and third valencies satisfied by members of the group consisting of hydrogen, alkyl of less than 5 carbon atoms, 2-hydroxyethyl, 2-cyanoethyl, benzyl and phenyl, said leuco compound being devoid of sulfo, carboxy and phenolic hydroxy groups and being in a state of purity whereby it is essentially free of color, and said leuco compound being contained within the bounds of a symbol imprinted upon a supporting sheet and having incorporated therewith a quaternary ammonium hydroxide in quantity amounting to from 0.2% to 10% by weight of said leuco compound, the improvement which comprises contacting the said symbol with an oxidizing developer selected from the group consisting of halogenated monocyclic quinones, the corresponding haloimides, carboxylic acid peroxides, triaryl chlormethanes, alkyl nitriles, volatile liquid iodohalides, and nitrogen oxides.

2. The process of claim 1 in which the developing agent is chloranil.

3. The process of claim 1 in which the developing agent is a halogenated benzoquinone compound.

4. The process of claim 1 in which the developing agent is a halogenated toluquinone compound.

5. The process of claim 1 in which the developing agent is an acid peroxide.

6. The process of claim 1 in which the developing agent is a triphenylchloromethane.

7. The process of claim 1 in which the developing agent is carried in an alcohol.

8. The process of claim 7 in which the developing agent contains dioxane.

No references cited.