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METHODS OF COPY REPRODUCTION

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This invention deals with improved methods of producing copies by typewriting, handwriting or printing and with means of reproducing copies from an original; it relates in particular to hectographic reproducing processes.

It has previously been proposed to use a variation of the spirit-reproduction process in which, instead of using a dyestuff in the formulation of the transfer coating on the base sheet, a dye intermediate is used which, when brought into contact with copy paper damped with a liquid containing a coupling agent, will combine to form the dye. This process has a great advantage in that the transfer sheet is perfectly clean to handle. A disadvantage is that the dye intermediates disclosed are in general of the azo type and consequently are much less brilliant and do not produce as many copies in the finished state as the triphenylmethane dyes.

It is an object of the present invention to provide a method of producing copy on paper employing an improved form of transfer paper which obviates the above disadvantage.

We have now found it possible to produce an improved transfer paper having as the transfer coating colour-reactive complexes formed by a combination of certain dyes or reduced dyes or dye intermediates with higher alkylamines. These novel colour-reactive complexes are far more stable than previously known non-staining materials and can be oxidised by the use of mild reagents. Such reagents include derivatives of succinic acid and hydroquinone with high oxidation potentials.

These new colour-reactive complexes are not liable to oxidise under normal atmospheric conditions or under light and heat.

According to the present invention there is provided a method of producing copy on paper which method comprises bringing into superimposed relationship a sheet of paper having impressions thereon of a composition consisting of or comprising a colourless or substantially colourless complex formed by the combination of a dye, reduced dye or dye intermediate with a non-ionising salt-free surface active agent and a second sheet of paper coated with or having incorporated therein an oxidising agent capable of reacting with the aforesaid complex to produce a colour product, and thereafter applying pressure to the superimposed sheets to develop a coloration on the sheet containing or coated with the oxidising agent at those points corresponding with the impressions on the complex-coated sheet.

By the expression "non-ionising salt-free surface active agent" as used herein we mean a surface active agent which does not dissociate to yield a free acid radical.

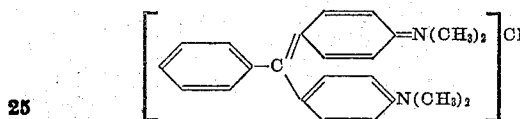
When the present invention is to be applied to the hectographic reproduction process the colour reactive complex is incorporated with suitable waxes and/or wax-like materials to form the transfer coating of the uncoloured carbon paper and when the master copy is typed a mirror image impression is obtained, which is substantially non-staining. The oxidising agent is incorporated

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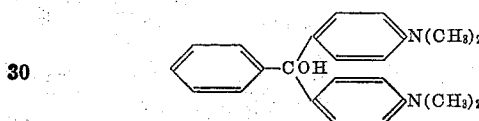
in the liquid used in the reproduction process. When solid oxidising agents dissolved in the liquid are used it is advisable to employ spirit-reproducing machines which deliver the liquid by means of pumps or gravity feed, and apply the liquid to the copy paper by means of damping rollers to which the liquid is fed by a system of intermediate rollers or sprays. When liquid oxidising agents are used it is possible to employ the older types of spirit-process machines depending on the delivery of the liquid to the paper by capillary action through pads or wicks.

Dyes suitable for use in connection with the invention are the triphenylmethane and diphenylmethane dyes, e.g. Crystal Violet, Victoria Blue and Malachite Green, in their leuco base form. Since these dyes exist in several forms other than the leuco base, the following structural formulae, using Malachite Green as an example, will serve to distinguish these forms and to clarify the nature of the dye material from which the stable complex is prepared:

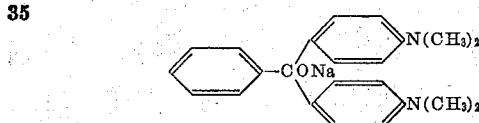
(a) The dyestuff or dyesalt itself (a hydrochloride):



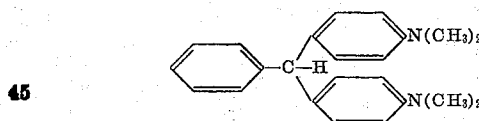
(b) The dyebase or carbinol form:



(c) The sodium salt of the dyebase (color base) or carbinol form:



(d) The leuco base:



Where the term "leuco" is used herein, the last of these forms is intended.

According to the present invention, the leuco base form of the particular dyestuff is reacted with a higher alkylamine to form a stable color-reactive complex. As a preliminary step, the leuco form may be reacted with a strongly basic compound such as primary amine or an alkali metal or alkaline-earth metal base to produce a dye intermediate, after which the complexing reaction with the higher alkyl amine is carried out. The structure of the alkaline salt of the leuco base form is extremely difficult to establish and it is not possible herein to illustrate that structure. Nor is it possible to readily explain the theory underlying the present discovery. All that can be said is that the complex product of the reaction of a higher alkylamine with the leuco base form as such, or with the salt of the leuco base form with a strongly basic compound, there is obtained a highly stable material that is particularly adapted for use in a transfer coating in connection with hectographic reproduction processes.

One preferred form of the dye intermediate is the amino salt of the leuco dye obtained by reacting the leuco dye with a strongly basic primary amine for example a diamine such as stearyl diamine or lauryl diamine. Thus the leuco compound may be dispersed in water at 90° to

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100° C. and stearyl diamine added with stirring when reaction takes place to give a stable salt. This salt may also be prepared in the oil/wax vehicle of a normal hectographic coating composition.

Alternatively the dye intermediate is that obtained by reacting the leuco compound with an alkali metal or alkaline-earth metal base to form the alkali metal or alkaline earth metal leuco form of the dye. Thus the leuco compound may be reacted with a strong base such as sodium hydroxide thereby forming the sodium leuco form of the dye. The strong base may be dissolved in the least possible quantity of water and added to a boiling solution of the leuco form of the dye in dioxane, an off-white product being obtained which is stable in air and light up to a temperature of 70° C. The sodium leuco form of the dye may also be prepared by boiling the leuco in a concentrated aqueous solution of caustic soda.

The complex formation is carried out by heating the dry components together, at a temperature of approximately 90° C. in the case of the amino-leuco salt, with stearylamine and, at a temperature of about 100° C. in the case of the alkali-metal or alkaline earth metal base salt, with stearylamine or alternatively in the oil/wax hectographic coating composition.

Suitable non-ionising salt-free surface active agents are higher alkylamines such as stearylamine.

Examples of suitable oxidising agents include derivatives of quinone e.g. tetrachloroquinone and derivatives of succinic acid e.g. N-bromosuccinimide.

In an alternative form of the present invention the oxidising agent comprises a two component system, one component being combined in the transfer coating and the other incorporated in the liquid with which the copy sheet is wetted. Some of these oxidation systems are purely organic in nature, some are inorganic while the preferred are a combination of both.

Examples of such systems are:

(a) Potassium permanganate in the coating with chloranil contained in a liquid comprising a ketone and a chlorinated solvent.

(b) Potassium permanganate combined in the coating with chloranil contained in liquid comprising a ketone and nitrobenzene.

(c) Potassium permanganate combined in the coating with N-bromosuccinimide in a liquid comprising a ketone and a chlorinated solvent.

(d) Potassium permanganate combined in the coating with chloranil contained in a liquid comprising a ketone and a 0.5% surface active quaternary ammonium compound.

The transfer coatings which incorporate the colour-reactive complexes (other than those including inorganic oxidising agents) are almost white or are very pale, depending to a large extent on the colour of the waxes or wax-like materials used in their composition. It may be found useful to incorporate in the complex-coating a small proportion of a corresponding partially reacted and therefore faintly coloured complex sufficient to give a slight indicative colour to the coating without causing any stain. This procedure has the advantage that a transfer paper with such slightly coloured coating denotes the colour which can be produced from the transfer paper during the liquid reproducing process. The addition of partially reacted complexes to the transfer coating, serves another purpose inasmuch as this colour effect will make the master copy more legible, which is of value for mirror-printed master sets when the printer finds it useful to get a fairly dark imprint when making ready.

Papers coated with the complexes are stable and do not discolour under atmospheric conditions or under light and heat, and can therefore be used without any overlying protective coating or the use of any other protective measures within the transfer coating or base paper. Such a super-coating may, however, be applied to the complex coating, if desired, e.g. to indicate the colour of the

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reproductions obtainable from the transfer paper. In this case it will be found useful to incorporate into the super-coating a coloured impalpable fine grade of aluminum powder in the desired colour. The addition of this aluminum powder has also the advantage that it makes the super-coating more friable, and this effect can be improved by adding other impalpable fillers such as china clay, asbestos powder, mica powder, talcum or silica gel.

In one form of the invention the oxidising material may be incorporated in the copy paper by mixing in the pulp.

The complexes of the present invention are substantially water insoluble and may be used in hydrophilic coatings. For example, the transfer coating may consist of a dispersion of colour reactive material dispersed in film forming hydrophilic materials such as starch, casein, gelatine or synthetic polymeric materials such as methyl cellulose. Inert fillers such as china clay and alumina may also be incorporated both to assist transfer and intermingling of the coatings when copy is being produced.

Following is a description by way of example of methods of carrying the present invention into effect in a hectographic spirit duplicating process.

Example I

Eight to ten parts by weight of amino leuco crystal violet salt such as the stearyldiamine, phenylenediamine, diphenylamine, diethanolamine, ethylene diamine or spermine salts are reacted with one part of stearylamine at 80° C. until the reaction is complete giving a white product. The complex is then incorporated with wax and filler to form a normal hectographic coating. This is applied to the transfer sheet.

Example II

In this example the amino leuco crystal violet salt and the stearylamine of Example I are heated together in the presence of the principal wax constituent or constituents, e.g. carnauba wax or microcrystalline wax to form the basis of the hectographic transfer coating compositions.

There may be incorporated in the coating composition an auxiliary oxidising agent, e.g. potassium permanganate.

Example III

Equivalent proportions of leuco crystal violet and a C₁₈ alkylamine are reacted together at 100° C. until the mixture changes colour. The complex is incorporated with wax and filler to form a normal hectographic transfer coating composition. This is applied to the transfer sheet.

Example IV

In this example the leuco crystal violet and the alkylamine are heated together in the presence of the principal wax constituent or constituents e.g. carnauba wax or microcrystalline wax to form the basis of the hectographic transfer coating composition.

Example V

Eight parts by weight of an alkaline metal leuco crystal violet salt such as the sodium, potassium or barium salt, are reacted with one part of stearylamine at 80° C. until the reaction is complete giving a white product. The complex is then incorporated with wax and filler and inorganic oxidising agent such as potassium permanganate to form a normal hectographic coating.

Example VI

In this example the alkaline metal leuco crystal violet salt and the stearylamine of Example V are heated together in the presence of the principal wax constituent or constituents, e.g. carnauba wax or microcrystalline wax to form the basis of the hectographic transfer coating composition.

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A master is made from the transfer sheets of any one of the specific examples and copy obtained from this master by a hectographic reproducing process in which the copy paper is damped with a liquid of which the following are examples:

	Percent
A	
Methylethylketone -----	99
Chloranil -----	1
B	
Methylethylketone -----	90
Tetrachloroethylene -----	9.5
Chloranil -----	0.5
C	
Methylethylketone -----	80
Tetrachloroethylene -----	9.5
Dioxane -----	10
Chloranil -----	0.5
D	
Methylethylketone -----	90
Perchloroethylene -----	9.5
N-bromosuccinimide -----	0.5
E	
Acetone -----	80
Dioxane -----	10
Trichloroethylene -----	9.5
Chloranil -----	0.5
F	
Methylethylketone -----	90
Tetrachloroethylene -----	9
p-Nitrophenyl iso-cyanate -----	0.5
Chloranil -----	0.5
G	
Methylethylketone -----	99
Chloranil -----	0.5
p-Nitrophenyl iso-cyanate -----	0.5

The transfer sheet is produced by any of the conventional coating procedures, viz. roller coating (with or without doctor blades), fountain coating or spray coating. The coating is applied either as a hot melt mix at a temperature of the order of 130° C. or in the form of a true or colloidal solution with a suitable solvent at a temperature of the order of 50° C. Suitable solvents include petroleum distillates, esters and ketones admixed with the solids in the proportion of 1 of solids to 1 of solvents by weight. The solvents are completely removed by evaporation over hot rollers or in drying tunnels subsequent to the coating operation. When using a solution it is desirable to use a body paper which is very hard or alternatively, is sized, waxed, printed or treated with a thin plastic film to stop undue penetration.

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I claim:

1. A method of producing copy by a hectographic reproducing process comprising imaging a master sheet from a transfer sheet having a transfer coating consisting essentially of wax in admixture with a substantially colorless complex formed by the combination of (a) the leuco form of a dye selected from the group consisting of a triphenylmethane dye and a diphenyl-naphthyl methane dye with (b) a non-ionising surface active agent consisting of a higher alkylamine, and transferring some of the complex to a copy sheet brought into superimposed contacting relationship with the master sheet, the coloration being developed by oxidation of the complex by means of an oxidizing agent therefor present on the surface of said copy sheet.

2. A method of producing copy by a hectographic reproducing process comprising imaging a master sheet from a transfer sheet having a transfer coating consisting essentially of wax in admixture with a substantially colorless complex formed by the combination of (a) the salt of a strong base selected from the group consisting of the primary amines, alkali metal bases, and alkaline-earth metal base with the leuco form of a dye selected from the group consisting of a triphenylmethane dye and a diphenyl-naphthylmethane dye with (b) a non-ionising surface active agent consisting of a higher alkylamine, wetting the surface of a copy sheet with a liquid containing a compound selected from the group consisting of tetrachloroquinone and N-bromo-succinimide, and contacting the wetted copy sheet with the imaged surface of the master sheet in order to effect transfer of some of the complex to the copy sheet to develop a coloration on the copy sheet to develop to the imaged master.

3. A transfer sheet for use in a hectographic reproducing process which sheet comprises a base sheet having a transfer coating thereon consisting essentially of wax in admixture with a substantially colorless complex formed by the combination of (a) the leuco form of a dye selected from the group consisting of a triphenylmethane dye and a diphenyl-naphthylmethane dye with (b) a non-ionising surface active agent consisting of a higher alkylamine.

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