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AZO DYE DUPLICATING PROCESS

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This invention relates to a process for the reproduction of multiple copies and it relates more particularly to the reproduction of copies by a new and improved spirit duplicating system. This application is a division of our copending application Ser. No. 287,616, filed May 13, 1952.

To the present, reproduction processes of the type described have been effected by systems generally referred to in the art as the gelatin system and as the spirit duplicating system. In the gelatin system, a master sheet is imaged by typing, writing or drawing with an ink composition containing a water soluble dye, usually crystal violet. The image is transferred in reverse by absorption during contact into a gelatin compound disposed in a pan or on the surface of a transfer sheet which then forms the printing medium. The water soluble dyestuff transfers from the moist printing medium to form copy upon contact with impression medium.

In the spirit duplicating system, the image is formed in reverse on a master by transfer from a carbon type sheet coated with a composition containing a high proportion of a water soluble dye such as crystal violet, Victoria green, Victoria blue and the like. The image transfers from the master to copy sheets, the surfaces of which have been wetted with an alcohol or alcohol and water combination upon contact, as between a compression cylinder and a printing plate mounted in a rotary duplicating machine. The highly volatile solvents permit the production of a larger number of copies and provide for more rapid drying of the copy sheet to reduce setoff and smear. In the spirit duplicating systems, the dyestuff is preferably contained in a coating such as in a carbon sheet for transfer in mirror image onto the printing master by the application of force or the like.

While hectograph systems of the type described are desirable because of their flexibility in use and simplicity in operation for the production of multiple copies in a rapid and economical manner, there are a number of serious objections which characterize the process as it is presently being practiced. Most of the objectionable characteristics stem from the highly dispersible fine particles characteristic of the dyestuffs and the highly soluble nature thereof in aqueous medium. The fine particle size of the dyestuff leads to objections in their use for the manufacture of the carbon transfer sheet or inking ribbon. In most manufacturing processes, the atmosphere within the formulating and coating room and the atmosphere for miles surround-

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ing the building in which it is being used becomes contaminated with fine particles of the dyestuff whereby the personnel within the buildings and the territory surrounding the buildings acquire a purplish tint which is difficult to remove.

Because of the highly water soluble nature of the dyestuff, moisture on the hands of the operator is sufficient to remove substantial quantities of the dye onto the hands whereby it invariably spreads to other parts of the body and clothing. It is difficult to operate a hectograph system embodying such dyestuffs without staining one's hands and clothing.

The limitations with respect to the use of dyestuffs highly soluble in water and in spirit solvents has to the present limited color of copy reproduced to the dye colors formed of such compositions as crystal violet, rhodamine (red), Victoria blue or Victoria green. It is impossible to produce intense black copy or copy in any other color than the four defined or shades thereof. Attempts have been made to formulate a black by combining the various usable dyestuffs but the best that such combinations have been able to produce is gray copy and the differences in solubility of the various dyes causes differential leaching and gradual toning off of one color relative the other to produce copy of variable color quality from start to finish.

Important also is the inability to produce permanent copy because of the instability of the water soluble basic dyes especially upon exposure to light.

Finally it is difficult to control the solvency of the dye or the effect of the medium in which it is contained with sufficient regularity to produce copy of uniform quality and often the number of copies of readable quality vary from time to time depending upon the conditions existing during reproduction.

It is an object of this invention to provide a hectograph system which is substantially free of the objectionable features of the prior art processes of the types described.

Another object is to provide a spirit duplicating system free of compounds capable of coloring or dirtying one's hands, clothing, the atmosphere or the environment during the manufacture and use of the elements employed.

A further object is to provide a spirit duplicating system in which permanent copy of good quality is produced.

A still further object is to provide a new and improved spirit duplicating process including compositions and elements used therein.

Another object is to provide a spirit duplicating system in which the color of the copy can be varied over a fairly wide range and includes the production of intense black copy of good quality.

A further object is to provide a spirit duplicating system wherein the copy is formed of a water and alcohol insoluble coloring compound incapable of removal, smearing or smudging even under high humidity conditions.

A still further object is to provide a new and improved hectograph duplicating system capable of producing copy of various colors from a single prepared master.

More specifically, it is an object of this invention to provide a new and improved spirit duplicating system and materials for use in same wherein the materials involved in the manufacture and use are incapable of transferring color and wherein the copy is developed in the copy sheet itself thereby to permit the production of copy with insoluble dyestuffs incapable of use in systems heretofore employed and which are sufficiently stable and insoluble to remain permanently in the copy sheet.

Briefly described, instead of forming the image on the master of a basic aniline dye highly soluble in water or spirit solvents, as in processes heretofore employed in gelatin or in spirit duplicating systems, the image herein, preferably in reverse, is formed on the master of a water or alcohol soluble component of a water insoluble dye and which has no objectionable color transfer value in the state in which it exists in the master or in the ink composition, inking ribbon or carbon sheet with which the master is formed but which upon transfer to the copy sheet forms a water insoluble dye by chemical reaction with other dye forming components contained in non-reactive state in the imaged master, or contained in the fluid with which the copy sheet is wetted for effecting transfer of the imaging component upon contact, or in the copy sheet or contained in a fluid applied to the copy sheet subsequent to transfer of the imaging material from the master.

The concepts of this invention are capable of a number of modifications which will hereinafter be described in greater detail and for purposes of illustration, but not of limitation, examples will now be given of one mode for carrying out the inventive concepts embodied herein.

Example 1

A carbon type transfer sheet is formed by coating a thin fibrous sheet with a composition compounded of the following materials:

- 8 parts by weight carnauba wax
- 11 parts by weight oxidized microwax (Cardis 262)
- 3 parts by weight polybutene (Oronite 128)
- 6 parts by weight petrolatum
- 17 parts by weight mineral oil (100 seconds)
- 55 parts by weight paradiazo diethyl aniline zinc chloride

The composition is reduced to molten state at a temperature of about 80-85° C. for application as a hot melt onto the surface of the base sheet in concentrations ranging from 15-20 pounds per 3000 square feet.

Example 2

For preparation of the imaged master, the coated sheet manufactured in accordance with Example 1 is positioned with the coated side in surface contact with the prepared surface of a suitable

master sheet whereby material is displaced from the coating to the surface of the master to form the mirror image of forces applied against the uncoated side of the coated sheet as by a stylus, writing pen or pencil, typewriter key, die impression or the like.

To the present, the active ingredient in the coating composition for development of the image in the copy sheet comprises the paradiazo diethyl aniline zinc chloride which is a water and alcohol soluble component of an azo dye and which has no objectionable color transfer value thereby to provide for a clean process in the manufacture of the coated sheet and the imaged master. In the event that it is desirable to introduce some color for inspection of the imaged master, it is possible to compound the coating composition or the imaging composition with a minute amount of some coloring component selected of any one of the common pigments, dyestuffs or other coloring agents.

Example 3

For the production of multiple copies, the imaged master prepared in accordance with Example 2 is mounted on a cylinder of a rotary duplicating machine of the conventional type for hectograph duplication. The fluid applied to the surface of the copy sheet in advance of contact with the master may be formulated to contain the following:

- 0.5 percent phloroglucinol
- 5.0 percent b-naphthol
- 2.0 percent diethanolamine
- 92.5 percent methanol

As the wetted surface of the copy sheet moves into surface contact with the imaged master between the impression roller and the cylinder mounting the master, some of the diazo dye forming component is dissolved from the surface portion of the image whereupon coupling takes place between the phloroglucinol and the p-diazo diethyl aniline zinc chloride at pH levels adjusted by the diethanolamine to form a water insoluble and permanent deep purple diazo dyestuff in direct image in the copy sheet.

It will be significant that the dyestuff is formed only in the copy sheet when it is observed that upon emergence of the copy sheet from between the impression roller and master cylinder very faint if any copy is visible. Color development rather quickly takes place once the dye component and coupler have been combined in the copy sheet in the presence of the alkaline medium to form the dyestuff. The copy sheet is capable of being handled almost immediately without fear of setoff or smear and the color produced is permanent in character.

The number of copies secured depends greatly upon the thickness of the coating of which the image is formed, the amount of dye forming component contained in the coating composition and the character and quantity of solvent applied to the copy sheet for effecting transfer of the dye component from the imaged master for coupling reaction to develop color. It will be apparent, however, that the intensity of color capable of being developed by azo dye systems of the type described permits the production of readable copy with minimum concentration of dye forming component with the result that by proper control, up to 100 to 500 copies may easily be secured from a single master.

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It is believed that the amount of spirit solvent present on the copy sheet during contact with the master is sufficient to cause transfer of an infinitesimal proportion of the azo dye forming component present and that a minute portion of the carrier or wax base in which the dye component is contained is also removed to the copy sheet, otherwise the dye forming component in the master sheet would be converted into a water insoluble dyestuff incapable of being transferred to form copy in accordance with the concepts of this invention. In this respect, the invention herein differs basically from the gelatin or the spirit processes which have heretofore been employed in the reproduction of copy.

Example 4

In the event that it is desired to produce red copy instead of purple from the master prepared in accordance with Example 2, the copy sheet is wetted with a solution formulated of the following:

5.0 percent phenylmethyl pyrazolone
2.0 percent diethanolamine
93.0 percent methanol

Upon contact between the imaged master and the surface of the copy sheet wetted with the above composition, some of the diazo dye forming component transfers to the copy sheet to form a red diazo dye upon coupling with the phenylmethyl pyrazolone in the presence of the base. As described before, drying occurs almost immediately so that, although the intensity of the color continues to increase upon standing, the copy produced is incapable of setoff or smear.

Example 5

For the production of blue copy from the master prepared in accordance with Example 2, the copy sheet may be wetted in conventional manner with the following composition:

5.0 percent 2,3-dihydroxy naphthalene, 6, sulfonic acid
8.0 percent diethanolamine
10.0 percent water
77.0 percent methanol

Example 6

By way of a still further example, a suitable transfer sheet or a suitable imaging composition in aqueous dispersion or solvent solution for use in the practice of this invention may be compounded of the following composition:

8.5 percent carnauba wax
14.0 percent oxidized microcrystalline wax
12.0 percent dark petrolatum
15.5 percent mineral oil (100 seconds viscosity)
50.0 percent paradiazo-ethyl-hydroxy ethylamine zinc chloride

In the preparation of a transfer sheet, coatings having a weight of about 20 pounds per 3000 square feet of surface area are made from a hot melt onto a suitable base sheet by conventional coating technique, such as by a roller coater, knife coater, spray coater, dip-squeeze process or the like. The coating composition is incapable of free flow when cooled to room conditions but is capable of transfer responsive to applied force from the opposite side of the base sheet to form the mirror image on the surface of a suitable master sheet positioned in surface contact therewith.

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Example 7

Dark purple copy may be produced from the master sheet imaged in accordance with Example 6 by use of a fluid corresponding to the composition of Example 3 for wetting out the surface of the copy sheet in advance of contact with the master. As many as 100 to 500 copies can be made before the dye forming diazo component is exhausted from the imaged master sheet. Red copy can be produced by use of the fluid of Example 4 for wetting out the surface of the copy sheet and the same master can be used to produce blue copy when the copy sheets are wetted with a fluid of Example 5.

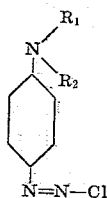
The composition of the base in which the diazo dye forming component is embodied in the manufacture of a coated carbon sheet is unimportant and other conventional compositions used in the manufacture of coated carbons may be used. Generally such compositions are formulated of waxy materials in various combinations including carnauba wax, microcrystalline wax, paraffin wax, ozokerite and the like, alone or in combination with softening agents such as mineral oils, fatty acids and the like. Modification to improve strength and film forming characteristics may include the addition of small amounts of polyethylene, polybutylene and other polymeric compounds formed of unsaturated aliphatics and other materials capable of compatibility with the waxy substances to form a stable composition. The composition of the base in which the dye component is contained should provide for a continuous layer capable of transfer to surfaces in contact therewith upon impression but it is preferred to formulate the composition of materials which have slight solubility in the spirit solvents so as continuously to cleanse the surface of the imaged master during production of copy.

While it is preferred to apply the carbon type coating composition as a hot melt in the manner described in Examples 1 and 6, it is possible to achieve the desired coating of the base sheet by application of the materials from solvent solutions or aqueous emulsions. However more than one coating will usually be required to achieve the desired coating weights on the base sheet. For example, the compositions of Example 1 or 6 may be dissolved in ethyl acetate, trichloroethylene and the like alone or in combination with toluene or benzene diluents to form a 20-40 percent solution or the compositions of the type described may be dispersed in aqueous medium with a small amount of surface active agent to form a 40-60 percent aqueous emulsion. From the solvent solution of lower solids content more than one coating will be necessary to achieve the desired coating weight but generally one, or at most two coatings will be sufficient when coatings are prepared by the high solids content dispersions of the type described. Where high temperatures are not used to eliminate the diluents, almost any stable diazo dye forming component may be used, but where temperatures in excess of 80° C. are used for drying, the diazo component is limited because the great majority are unstable at such temperature levels.

It is desirable to embody as high concentration of the dye component as possible in the carbon coating consistent with the ability of the coating to maintain the desired film characteristics and strength. Generally the amount of the dye forming component introduced as an in-

gradient in the coating composition depends on the ability to maintain sufficient fluidity under the condition of coating to achieve the desired application and coverage. For the production of a number of copies of sufficient intensity, it is advisable to maintain the concentration of dye component in excess of 20 percent by weight and preferably in excess of 50 percent by weight. In general, fluidity of the desired character falls off when the concentration reaches 75 percent by weight but more may be used with the introduction of fluidizing agents.

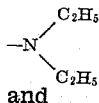
With reference particularly to the preferred diazo dye forming system heretofore described, it has been found that very few dye components are capable of use in the manufacture of a transfer sheet by coating with a hot melt. To the present, use has been limited to diazo compounds of the type described characterized by the formula



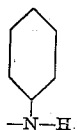
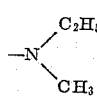
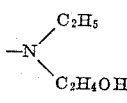
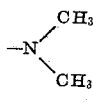
wherein the



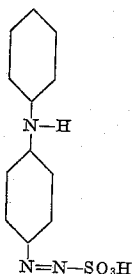
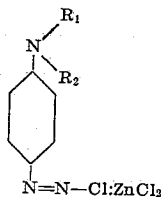
group comprises



and



It has been found that the stability of the diazo dye forming components is vastly improved when embodied in the treating composition as their corresponding zinc chloride or sulfonic acid salts such as



Compounds capable of use as couplers with the diazo dye forming components in accordance with the practice of this invention are limited in character. In general, such couplers should be capable of removal of a hydrogen ion for combination with the chloride ion of the diazo compound for dye formation. Such compounds are limited to aromatics in the form of amines, such as aniline and substituted anilines like dimethyl aniline, phenolic compounds such as phenol, resorcinol, phloroglucinol, 2,3-dihydroxy naphthalene, 6-sulfonic acid or water soluble salts thereof, and the like, thio compounds such as

thio-barbituric acid and cyano compounds such as cyanoacetamide. When the coupler is embodied in the fluid or as a component in the copy sheet, as will hereinafter be illustrated, it is desirable that the coupler be stable and incapable of developing background color because of the presence thereof over the entire surface of the copy sheet. It is also desirable to make use of a coupler which is readily available and inexpensive. Where the coupler is combined as a component of the carbon sheet or imaging composition, such limitations as to color development and cost are minimized.

For coupling to form the dye by reaction between the coupling agent and the diazo dye forming component in the copy sheet, it is necessary to provide for a pH in excess of 3.5 and preferably a pH above 7. By maintaining a pH less than 3.5 and preferably as low as 1.5, as by acidification with boric acid, tartaric acid, citric acid and acid salts such as aluminum sulphate or zinc chloride, coupling can be prevented thereby to permit the diazo dye forming component and the coupler to be arranged in the same composition without dye formation but with means for adjusting the pH above 3.5 upon transfer to the copy sheet for coupling to form the colored diazo dyestuff.

Compounds preferably dissolved in the fluid for adjusting the pH to a level for coupling may include the organic amines such as described in Examples 3-5, amongst others including monoethanol amine, triethanol amine and other organic amines, ammonium hydroxide, ammonia gas, or inorganic bases such as sodium hydroxide, potassium hydroxide, zinc hydroxide or other water soluble hydroxides or salts formed of strong bases and weak acids.

By way of further illustration, the following compositions may be used for preparing a carbon sheet or imaging composition containing the diazo dye forming component for coupling on the copy sheet to develop the visible image:

Example 8

- 12.5 percent carnauba wax
- 10.5 percent microcrystalline wax
- 12.0 percent petrolatum
- 15.0 percent mineral oil
- 50.0 percent p-diazo dimethyl aniline zinc chloride

Example 9

- 19.0 percent carnauba wax
- 25.0 percent cetyl alcohol
- 14.0 percent mineral oil
- 42.0 percent p-diazo diethyl toluidine zinc salt

The following are further illustrations of fluid compositions containing a coupler and base substance for adjusting the pH above the level to effect dye formation in the copy sheet:

Example 10

- 3.0 percent phloroglucinol
- 2.0 percent resorcinol
- 1.0 percent sodium hydroxide
- 94.0 percent ethyl alcohol

Example 11

- 5.0 percent 2,3-dihydroxy naphthalene, 6-sulfonic acid sodium salt
- 0.8 percent sodium hydroxide
- 94.2 percent methyl alcohol

While it is most economical to place the expensive diazo dye forming component in the car-

bon sheet or imaging composition whereby limited use is made thereof in the production of copy, it will be evident that the concepts of this invention may be achieved when the coupler is compounded as a component of the carbon coating or imaging composition and the diazo dye forming component is contained in the wetting out fluid in combination with the base substance for adjusting the pH, or else in the copy sheet wetted out with the solution of the base for adjusting the pH to the point where coupling can take place.

Example 12

A coating composition for the preparation of a transfer sheet may be formulated of the following:

8.5 percent carnauba wax
14.0 percent oxidized micro wax
12.0 percent petrolatum
15.5 percent mineral oil
50.0 percent phloroglucinol

Application onto a suitable base sheet may be made in weights of about 20 pounds per 3000 square feet from a hot melt raised to a temperature of about 80-90° C.

When the coating composition is formulated to contain the coupler as described in Example 12, the fluid for wetting out the copy sheet for purposes of extracting a proportion of the phloroglucinol from the imaged master whereby the dyestuff is developed by reaction in the copy sheet may be formulated of the following:

Example 13

2.0 percent ammonium hydroxide
98.0 percent methanol

In operation of the process, the copy sheet is adapted to have been treated to contain a diazo dye intermediate such as p-diazo benzyl aniline sulfonate for reaction with the coupler transferred from the imaged master.

By way of further modification, the coupler and the alkali may be compounded in the carbon sheet and the diazo dye forming component placed in the fluid, as illustrated by the following examples:

Example 14

Carbon coating composition:

5.0 percent carnauba wax
20.0 percent micro wax
15.0 percent paraffin wax
15.0 percent petrolatum
35.0 percent phloroglucinol
10.0 percent triethanol amine

Example 15

Fluid containing the diazo component:

2.0 percent p-diazo diethyl aniline zinc chloride
98.0 percent methanol

The combination described may be processed in the usual manner for spirit duplication to form a dark purple water insoluble dye in the imaged areas of the copy sheet. When the diazo component is provided as an ingredient in the fluid or as a component of the copy sheet introduced, as by impregnation, it is imperative that the dye intermediate be relatively free of color and sufficiently stable to prevent the development of background color in the copy sheet.

By way of still further modification, it is possible in accordance with the practice of this in-

vention to place both the diazo intermediate and the coupler in the coating composition thereby to conserve on the amounts thereof employed in the preparation of copy. Under such circumstances, the fluid is formulated to contain the solvent for transfer of the colorless materials from the imaged master and also to contain the alkali for adjusting the pH to the level where coupling reaction can take place on the copy sheet between the components in the imaged master to form the insoluble dye on the copy sheet. This mode of practice may be illustrated by the following examples:

Example 16

Carbon coating composition:

5.0 percent carnauba wax
20.0 percent micro wax
15.0 percent paraffin wax
20.0 percent petrolatum
20.0 percent p-diazo diethyl aniline zinc chloride
20.0 percent 1-amino-8-naphthol-4-sulfonic acid

Example 17

Fluid composition: A fluid for use with an imaged master prepared with the composition of Example 16 may be formulated of the following:

2.0 percent potassium hydroxide
98.0 percent methanol

The use of these compositions in the practice of this invention produces blue copy.

Example 18

Carbon coating composition:

15.0 percent micro wax
15.0 percent paraffin
30.0 percent petrolatum
30.0 percent p-diazo diethyl aniline zinc chloride
10.0 percent 2,4-diamino toluene dihydrochloride

In the absence of a solvent, the coupler and the diazo intermediate in the coating composition remain separate sufficiently to prevent coupling reaction to form the color dyestuff. With a composition of the type described it becomes unnecessary to make use of an alkali to adjust the pH to the level desired for coupling heretofore described so that the fluid with which the copy sheets are wetted out to effect transfer of the components from the imaged master to the copy sheet for development of the image thereon may be composed essentially of pure solvents such as methanol, ethanol, or combinations thereof. With compositions of the type described, a water insoluble permanent clean dye is formed in the imaged areas of the copy sheet.

As previously pointed out, the coupler or the diazo dye forming compound may be contained in the carbon coating composition, as illustrated in Examples 1 and 6, or in Example 11, and the coupler for use with compositions of the type set forth in Examples 1 and 6 or the diazo component for use with compositions of Examples 11 and 12 may be disposed in the base sheet, but, in any event, at least one of the components for developing the dye must be contained in the imaging material transferred by carbon or by typewriter or by writing ink to the master. When embodied in the base sheet, such dye forming components may be incorporated by conventional coating or impregnating systems or by incorporating the component as an ingredient in the fiber containing slurry from which the copy

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sheet is formed. Under these circumstances and under circumstances where the component is applied as a part of the fluid over the entire surface of the copy sheet, it is desirable that the components in combination with the alkali be sufficiently stable to avoid the development of background color on the copy sheet.

By way of still further modification, it is possible to embody one of the water or alcohol soluble dye forming components substantially free of color in the imaging material and then produce copy in the impression material by first wetting out the copy sheet with the solvent or diluent to effect transfer of some of the dye forming component from the imaged master to the copy sheet and subsequently wetting the copy sheet with a second fluid containing the coupler, in the event that the imaging material contains diazo, or else with a diazo intermediate in the event that the coupler is embodied as an ingredient in the imaging material or else with a base in the event that the diazo and coupler are applied one from the imaged master and the other with the first fluid for transfer of material from the master to the copy sheet.

It will be obvious from this description that various combinations are possible such as placing the diazo, the coupler and the alkali in the carbon sheet, master paper, fluid or impression paper except that the diazo intermediate and alkali should be placed in separate systems.

The concepts of this invention may also be adapted for use in a gelatin process wherein the imaging composition is formulated of the following:

Example 19

- 12.5 percent carnauba wax
- 12.0 percent microcrystalline wax
- 12.0 percent petrolatum
- 15.5 percent mineral oil
- 48.0 percent p-diazo ethyl hydroxyethyl aniline zinc chloride

Example 20

The coating solution is formulated of the following:

- 3.0 percent phloroglucinol
- 2.0 percent resorcinol
- 1.0 percent sodium hydroxide
- 94.0 percent ethyl alcohol

In operation, the master imaged with the diazo containing composition is placed and impressed on a gelatin bed. When a deposit of the diazo compound is transferred into the gelatin, the moist master sheet is then removed. Then a copy sheet previously coated with the solution of Example 20 is pressed into surface contact with the imaged gelatin bed. Coupling results in the copy sheet to form the water insoluble diazo dyestuff.

While description herein has been confined chiefly to the use of a water and alcohol soluble diazo dye forming component and water and alcohol soluble couplers by which a water insoluble dyestuff is formed in the presence of alkali to adjust the pH to 3.5 or above, it will be apparent that the components for the formation of the diazo may be themselves arranged in separate elements to form the diazo by reaction in acid medium for coupling with an amine or the like to form the dyestuff.

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Example 21

Carbon coating composition;

- 33 percent polyethylene glycol (MW about 6000) (Carbowax 6000)
- 33 percent polyethylene glycol (MW about 1500) (Carbowax 1500)
- 34 percent sodium nitrite

Example 22

Fluid composition:

- 10 percent N-N-dimethyl aniline in 1 N hydrochloric acid
- 90 percent ethyl alcohol

When the nitrite in the imaged master transfers to the copy sheet wetted with fluid of Example 22, the sodium nitrite reacts with the amine in the presence of acid to form a diazo compound which may then couple with agents of the type previously described or with the amine when present in excess to form the water insoluble dyestuff in the copy sheet.

It will be understood that other dye systems, such as the leuco dyes separable into substantially colorless dye forming components which are water and alcohol soluble and one of which may be embodied as a component in the imaging or carbon coating material to form the imaged master and the other in the fluid or in the copy sheet for reaction with the component in the imaging material may be used to form the dye upon transfer in the copy sheet. The following will illustrate the practice of this invention with other dye systems:

Example 23

- 12.0 percent carnauba wax
- 10.0 percent microcrystalline wax
- 12.0 percent petrolatum
- 15.0 percent mineral oil
- 51.0 percent leuco base of malachite green

A fluid for use in combination with the above to develop the malachite green dye in the copy sheet may be formulated of the following:

Example 24

- 4 percent potassium dichromate
- 1 percent nitric acid
- 45 percent ethanol
- 50 percent methanol

Example 25

Carbon coating composition:

- 33 percent carboxwax 6000
- 33 percent carbowax 1500
- 34 percent phenolphthalein

A fluid for use in combination with the composition of Example 25 and with which the copy sheet may be wetted to form the dye color therein is formulated of the following:

Example 26

- 1 percent sodium hydroxide
- 99 percent ethyl alcohol

Example 27

Carbon coating composition:

- 33 percent polyethylene glycol (MW about 6000) (Carboxwax 6000)
- 33 percent polyethylene glycol (MW about 1500) (Carbowax 1500)
- 17 percent sodium sulphate ($\text{Na}_2\text{S}_2\text{O}_8$)
- 17 percent para-phenylenediamine

A fluid composition for use in wetting a copy

sheet to develop a dye therein by reaction with the active ingredient in the imaging composition of Example 27 may contain the following:

Example 28

20 percent aniline
80 percent glacial acetic acid

It will be further understood that the concepts of this invention may be practiced by the use of imaging materials in the form of typewriter ribbons, writing ink, drawing crayon or the like embodying one or more of the substantially colorless dye forming components of the type described for preparation of the imaged master and that other components for completing the reaction to form the dyestuff may be placed in the fluid or in the copy sheet for reaction to develop the dyestuff as an incidence to the transfer of the dye forming component from the imaged master to the copy sheet. The composition of such inking materials or crayons may be formulated with a conventional base containing the dye forming component in relatively high proportion.

It will be apparent from this description that a completely new and improved duplicating process is provided herein capable of use in conventional hectograph duplicating machines to produce copy of improved quality formed of a water insoluble dyestuff. Until the dye is formed in the copy sheets, the elements involved in the preparation of the master or in the manufacture of imaging compositions and the elements present in materials used to produce the imaged master or the imaged master itself remain wholly free of color transfer value and therefore avoids one of the most objectionable features of processes which have heretofore been employed. In addition, black copy or copy of various colors unlimited in their range may be produced and such copies of different colors may be produced from a single master depending upon the coupling agent employed or the dye components employed.

It will be evident also that the master sheet, being free of color, may be handled in the normal manner without dirtying one's hands or clothing and that it may be filed away for subsequent use to produce additional copies without loss of definition or quality of the copy produced.

As used in the claims, the term "hectograph" is intended to include gelatin systems and spirit duplicating systems of the types described.

It will be further understood that changes may be made in the details of composition, arrangement and method of use without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. The method of producing copy comprising the steps of imaging a master with a composition substantially free of any dye color and containing a high proportion of a stabilized diazo dye intermediate and a coupler both of which are soluble in a medium selected from the group consisting of water, alcohol and mixtures thereof capable of reaction with the diazo dye intermediate to form a substantially water insoluble azo dyestuff, the imaging composition being maintained at a pH below that at which coupling takes place to prevent reaction between the intermediate and the coupler, wetting the surface of a copy sheet with a fluid containing a solvent for the diazo dye intermediate and coupler and

containing a base for adjusting the pH to permit reaction between the diazo dye intermediate and coupler to form the azo dyestuff, contacting the wetted copy sheet with the imaged surface of the master to effect transfer of some of the imaging material to the copy sheet whereby reaction takes place to form the azo dyestuff therein.

2. The method of producing copy by spirit duplication with a master imaged with a material containing a large proportion of a stabilized water and alcohol soluble diazo dye intermediate lacking in color transfer value and a large proportion of a water or alcohol soluble coupler capable of reaction with the diazo dye intermediate at pH levels above 3.5 to form an azo dyestuff, comprising contacting the imaged surface of the master with a copy sheet wetted with a fluid containing a solvent for the diazo dye intermediate and coupler and containing an alkali for adjusting the pH above the level where coupling may take place to form the azo dyestuff whereby some of the diazo dye intermediate and coupler transfers from the imaged areas of the master sheet to the copy sheet where reaction takes place to form the azo dyestuff.

3. The method of producing copy by a duplicating process comprising the steps of positioning the surface of a duplicating master in contact with the coated side of a transfer sheet having a transfer coating substantially free of any dye color and containing a water and alcohol soluble diazo dye intermediate stabilized against reaction in strongly acidic medium, and a water and alcohol soluble coupler, imaging the master by transfer of coating from the transfer sheet in response to applied force, wetting the surface of the copy sheets with a solvent for the coupler and diazo and a base for adjusting the pH concentration to a range wherein reaction can take place between the diazo and coupler to form the corresponding azo dyestuff, contacting the imaged master with the wetted side of the copy sheets whereby sufficient of the diazo and coupler transfer from the imaged areas for reaction to form an azo dye in corresponding areas of the copy sheets.

4. The method of producing copy by a duplicating process comprising the steps of positioning the surface of a duplicating master in contact with the coated side of a transfer sheet having a transfer coating substantially free of any dye color and containing a stabilized water and alcohol soluble diazo dye intermediate, a water and alcohol soluble coupler and an acidic medium to prevent formation of an azo dyestuff therebetween, imaging the master by causing transfer of coating from the transfer sheet in response to applied force, wetting the surface of the copy sheets with a solution containing a solvent for the coupler and diazo and a base for raising the pH to a range which permits reaction between the diazo and coupler to form an azo dyestuff, and contacting the imaged master with the wetted copy sheets whereby sufficient of the diazo and coupler transfers from the imaged areas for reaction in the copy sheets to form an azo dye.

5. The method of producing copy by a duplicating process comprising the steps of positioning the surface of a duplicating master in contact with the coated side of a transfer sheet having a transfer coating substantially free of any dye color and containing a high concentration of a coupler and diazo dye intermediate stabilized against reaction with the coupler in strongly acidic medium, imaging the master by transfer

of coating from the transfer sheet in response to applied force, wetting the surface of the copy sheets with a solvent for the coupler and diazo and a base for adjusting the pH concentration to a range where coupling reaction can take place between the diazo and coupler to form the corresponding azo dyestuff, contacting the imaged master with the wetted side of the copy sheets whereby sufficient of the diazo and coupler transfers from the imaged areas for reaction to form an azo dye in corresponding areas of the copy sheet.

6. The method of producing copy by a duplicating process comprising the steps of positioning the surface of a duplicating master in contact with the coated side of a transfer sheet having a transfer coating substantially free of any dye color and containing a high concentration of a coupler and diazo dye intermediate stabilized against reaction to produce a dyestuff without adjustment of pH, imaging the master by transfer of coating from the transfer sheet in response to applied force, wetting the surface of the copy sheet with a solvent for the coupler and diazo and a compound for adjusting the pH concentration to a range where coupling reaction can take place between the diazo and coupler to form the corresponding dyestuff, contacting the imaged master with the wetted side of the copy sheets whereby sufficient of the diazo and coupler transfers from the imaged areas for reaction to form an azo dye in corresponding areas of the copy sheets.

7. The method of producing copy by spirit duplication using a master imaged with a material containing a large proportion of a coupler and a diazo dye intermediate lacking in color transfer value and stabilized against reaction in strongly acidic medium, comprising contacting the imaged surface of the master with copy sheets wetted with a fluid containing a solvent for the diazo dye intermediate and coupler and an alkali for adjusting the pH above the level where cou-

pling reaction can take place to form the azo dyestuff whereby some of the diazo dye intermediate and coupler transfers from the imaged areas of the master to the copy sheet on contact where reaction takes place to form the azo dyestuff.

8. The method of producing copy by spirit duplication with a master imaged with a composition containing a large proportion of a coupler and diazo dye intermediate stabilized against coupling reaction to produce an azo dyestuff until adjustment of the pH and both of which are soluble in a medium selected from the group consisting of alcohol and water, comprising contacting the imaged surface of the master with a copy sheet wetted with a fluid containing a solvent for the diazo dye intermediate and coupler and a medium for adjustment of the pH to the level where coupling reaction between the diazo and the coupler can take place to form the azo dyestuff whereby some of the diazo dye intermediate and coupler transfers from the imaged areas of the master to the copy sheet where reaction takes place to form the azo dyestuff.

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