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2,873,671

COPY PROCESS AND MATERIALS FOR USE IN SAME

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This invention relates to a multiple-copy process and to materials for use in the practice thereof. More particularly, it relates to an improvement in the invention described and claimed in my copending application Serial No. 287,616, filed May 13, 1952, now Patent No. 2,748,024.

It is an object of this invention to provide a new and improved multiple-copy process for use in the field of office copy work, and to provide elements for use in same.

More particularly, it is an object of this invention to provide an improvement in a copy process of the type described in my copending application Serial No. 287,616 wherein a master imaged with a composition containing a water-and-alcohol soluble component of an azo dye is brought into surface contact with copy sheets which have previously been wetted with a solvent for the dye-forming component for leaching some of the dye-forming component for transfer from the imaged portion of the master to corresponding areas of the copy sheet and in which the copy sheet is provided with a component which causes reaction of the dye-forming component upon transfer to form the dyestuffs, and it is a related object to produce new and improved materials for use in same.

In the preferred concept of the invention described and claimed in the aforementioned copending application, a diazo compound and a coupler for reaction therewith are both contained in a non-coupling state in the transfer coating of a carbon sheet or in other compositions for use in the preparation of an imaged master. In the concept described, the diazo compound is stabilized against reaction with the coupler by conversion to a diazonium salt and/or by adjustment to maintain acidic conditions, as below a pH of 3.5 to prevent coupling. The fluid which is used to wet the surfaces of the copy sheets prior to contact with the imaged master is formed of a solvent for the stabilized diazo compound and coupler and contains a basic medium which, upon leaching of the diazo and coupler from the imaged master for transfer to the copy sheets, causes pH adjustment sufficiently for enabling coupling to take place to form the corresponding azo dyestuff in the imaged areas of the copy sheets.

The described process overcomes the dirtiness which constitutes one of the most objectionable characteristics of the spirit duplicating systems heretofore employed for multiple-copy work by reason of the use of a component of a dyestuff which is free of any dye color in the transfer sheet and in the materials with which the image is formed on the master as distinguished from the highly soluble, intense purple dyestuff (crystal violet) employed in the practice of the conventional spirit duplicating proc-

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esses. In the system of the aforementioned copending application, the only time that a dyestuff is formed is in the copy sheets after they have been passed through the duplicating machine, and the dyestuff which is formed at this stage can be an insoluble dyestuff as distinguished from the highly water-and-alcohol soluble dye of which the copy is formed in conventional spirit duplicating systems.

Elimination of the dirtiness characteristic of conventional spirit duplicating or hectograph systems is achieved without sacrifice in the simplicity of the copy process, without sacrifice in the ease of preparation of the imaged master or in the correction or modification of the imaged master, and in the use of the imaged master to produce copies, or in the number of copies of good quality that can be produced.

It has now been found, by way of a still further improvement, that the character of the copy and the stability of the transfer sheet and the master imaged therefrom can be greatly improved when, instead of making use of a coupler and a stabilized diazo compound as separate components in the imaging composition, use is made of a complex compound in the form of a diazo salt of a coupler formed by a non-coupling reaction of the diazo compound with the coupler in acidic medium.

The salt that is formed is sufficiently soluble in the spirit fluids formed of alcohol and/or a mixture of alcohol and water and even more highly soluble in such fluids containing a base, so that upon contact between the imaged master and copy sheets wet with such fluids the salt present in the image on the surface of the master can be leached for transfer from the imaged areas of the master to corresponding areas of the copy sheets. If the fluid applied to the surface of the copy sheets contains a base, such as diethanolamine, monoethanolamine, or other organic base amines, sodium hydroxide, ammonium hydroxide or the like inorganic bases, or if the copy sheets contain a base or alkali incorporated therein, as during manufacture or by application subsequent to manufacture, or if the copy sheets onto which the salt has been leached from the master for transfer to the copy sheets are subsequently wet with a second fluid containing a base or alkali in solution, the adjustment of pH toward the alkaline side is sufficient to initiate coupling reaction between the components of the salt to form the corresponding azo dyestuff or monoazo dye.

A number of very important and distinct advantages and improvements are achieved by the use of the coupler-stabilized salt instead of the coupler and stabilized diazo compound as separate components, as in the process described in the copending application. From the standpoint of shelf life, and conditions of use in storage, the coupler-stabilized diazo salt employed in the practice of this invention enjoys considerably greater stability as compared to the system wherein use is made of a stabilized diazo compound as a component separate and apart from the coupler. As a result, the coupler-stabilized diazo salt or the diazo salt of the coupler is capable of storage over extended periods of time and under differing atmospheric conditions without destruction or decomposition, and its resistance to decomposition and light is also greatly improved thereby markedly to enhance the service conditions and life of the imaging composition, the transfer sheets formed thereof, and the imaged master.

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More important from the standpoint of the copy process itself, it has been found that the presence of the diazo and coupler in a single compound in the ratio in which they react to form the dyestuff insures intimate contact and immediate availability of the components necessary for reaction to form the dyestuff in the copy sheets. As a result, reaction takes place more quickly and more completely, and full use is made of all the diazo and coupler in dye formation to produce copy.

Still more important from the standpoint of the character of the copy and the intensity of the copy produced, as well as the number of copies available, is the fact that the presence of the diazo and coupler in a single compound militates against the extraction of one component in greater amounts than the other. In the system wherein the diazo is present in an imaging composition as a compound separate and apart from the coupler, the more soluble component, such as the coupler, is usually extracted in greater amounts than the other with the result that less copy is produced, and the copy is of inferior quality. By way of illustration, it may be assumed in a process of the type described in the aforementioned copending application that the coupler is more soluble in the fluid than the diazo compound. If the coupler and diazo are present in substantially equal proportions in the imaging material, then the fluid on the surface of the copy sheets brought into contact with the imaged master will tend to leach larger amounts of coupler than diazo from the image. While this may result in the production of copy of high intensity at the start, soon the image, or at least the surface portion thereof, will become exhausted or depleted of coupler, with the result that the intensity of copy produced will diminish greatly before all or even a good part of the diazo compound has been employed. As a result, any fraction of the diazo compound will be used, and an equally large fraction of the coupler will be wasted. The number of copies of good quality produced will be less than the amount that should have been produced in proportion to the fraction of diazo which remains unused or inadequately used in the imaged master.

If, on the other hand, the ratio of coupler to diazo is increased in the imaging material to compensate for the greater solubility and preferential extraction of the coupler, the concentration of the essential dye-forming components in the imaged master will of necessity be reduced. This will result not only in reduction in the number of copies that can be made available, but the intensity of the copies produced throughout the run will be similarly diminished.

When, however, in accordance with the practice of this invention, the diazo and coupler are present as a single stabilized soluble compound, one equivalent weight of diazo will be removed with one equivalent weight of coupler. As a result, a maximum amount of the dye-forming components may be embodied in the imaging material. Only the amount of coupler necessary for reaction with the diazo will be leached with the diazo from the imaged master for use in production of the dyestuff.

Relatively little, if any, unused diazo will remain in the imaging material without an equivalent amount of coupler present for reaction therewith to form the monoazo dye. As long as the rate of solution is controlled and remains substantially uniform, the intensity of copy will have very little variation from beginning of the run to the end. Full utilization can be made of the dye-forming components formulated in higher concentrations in the imaging material thereby greatly to increase the number of copies of good quality that can be produced. As previously pointed out, the coupler and diazo are so intimately associated together in the compound that the coupling reaction takes place sub-

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stantially completely and immediately upon adjustment of the pH to form the dyestuff in the copy sheets. These and other advantages are available in the practice of this invention.

The coupler-stabilized diazo compound can be prepared by combining an alkaline solution of the sulfonic acid coupler compound with an acid solution of the diazo in which sufficient free acid is available to more than neutralize the free alkali in the solution of the coupler to form a mixture having a weakly acid pH, such as in the range of 6.0-6.5. By way of example, 1-naphthol-8 amino-3,6 disulfonic acid (mono sodium salt) in alkaline solution can be added slowly to p-diazo dimethyl aniline to form the p-diazo dimethyl aniline salt of 1-naphthol-8 amino-3,6 disulfonic acid. 2,3 dihydroxy naphthalene-6 sulfonic acid in alkaline solution can be combined with p-diazo diethyl aniline to form the p-diazo diethyl aniline salt of the 2,3 dihydroxy naphthalene-6 sulfonic acid.

The 2,3 dihydroxy naphthalene-6 sulfonic in alkaline solution can be combined with an acid solution of p-diazo-N ethyl-N hydroxy ethyl aniline to form the p-diazo-N ethyl-N hydroxy ethyl aniline salt of 2,3 dihydroxy naphthalene-6 sulfonic acid. 1-naphthol-8 amino-3,6 disulfonic acid sodium salt in alkaline solution can be combined with p-diazo diethyl aniline in acid solution to form the corresponding p-diazo diethyl aniline salt of 1-naphthol-8 amino-3,6 disulfonic acid. 1-naphthol-6 amino-3 sulfonic acid in alkaline solution may be combined with o-anisidine diazo in acid solution to form the corresponding o-anisidine diazo salt of 1-naphthol-6 amino-3 sulfonic acid. 1-naphthol-5 sulfonic acid in alkaline solution can be combined with o-anisidine diazo in acid solution to form the corresponding o-anisidine diazo salt of 1-naphthol-5 sulfonic acid.

As an example of the formation of a coupler-diazo salt, one molecular weight of a sulfonic acid coupler is dissolved in water at an alkaline pH. A separate acid pH solution is formed of an equivalent molecular weight of the diazo compound. The alkaline solution is added slowly to the acid solution with vigorous stirring to maintain a uniform mixture. The free acid content in the second solution is preferably greater than the free alkaline content of the first by about ten percent. The volume of the two solutions can vary widely without changing the course of the reaction. The pH of the final solution will usually be below 7 and preferably within the range of 6-6.5 for best results, and the temperature should be held at about room temperature or lower. For a more detailed description of the reaction to form a corresponding salt, reference may be had to the U. S. Patent No. 2,525,751.

By way of illustration, but not by way of limitation, description will now be made of the preparation of a transfer sheet which makes use of the coupler-stabilized diazo compound and the use of the transfer sheet in the preparation of an imaged master and in the production of copy therefrom.

Example I

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

- 11% by weight carnauba wax
- 15% by weight oxidized microcrystalline wax
- 15% by weight heavy mineral oil
- 13% by weight light mineral oil
- 1.5% by weight sodium oleate
- 44.5% by weight coupler-stabilized diazo complex compound

The composition is heated to a temperature of about 80° to 90° C. for application as a hot melt onto the surface of the base sheet in concentrations ranging from 15 to 20 pounds per 3,000 square feet of surface area.

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When applied as a hot melt, the composition applied as a coating to the surface of the base sheet remains as a substantially separated layer on the surface to form a transfer coating capable of displacement onto materials in surface contact therewith responsive to the application of force. Instead of applying the coating materials as a hot melt, the composition may be applied from solvent solution or aqueous dispersion by other conventional coating techniques, such as spray-coating, roller-coating, flow-coating, and the like. When applied from solvent solution or aqueous dispersion, limitations with respect to the heat stability of the diazo complex compound presents no problem.

As the coupler-stabilized diazo salt in the foregoing composition, use can be made of p-diazo dimethyl aniline-1 naphthol-8 amino-3,6 disulfonic acid; p-diazo diethyl aniline-2,3 dihydroxy naphthalene-6 sulfonic acid; p-diazo-N ethyl-N hydroxy ethyl aniline-2,3 dihydroxy naphthalene-6 sulfonic acid; p-diazo diethyl aniline-1 naphthol-8 amino-3,6 disulfonic acid; o-anisidine diazo-1 naphthol-5 sulfonic acid; o-anisidine diazo-1 naphthol-6 amino-3 sulfonic acid; 6 benzoyl amino-4 methoxy toluene-3 diazo salt of 1-naphthol-6 amino-3 sulfonic acid, or the like coupler-stabilized diazo complex compounds which are soluble in alcohol and water.

Example II

For preparation of the imaged master, the coated carbon sheet manufactured in accordance with Example I, is positioned with the coated side at surface contact with the prepared surface of a suitable master, and the coating is displaced from the carbon sheet to the master to form the mirror image in response to forces applied against the uncoated side of the carbon sheet, as by means of a stylus or other writing tool, typewriter key, die impression, or the like.

Instead of forming the image on the master sheet by transfer of portions of the coating from the described carbon sheet, the image may be formed on the master sheet directly by printing or by the application of a composition containing the coupler-stabilized diazo complex in a suitable carrier, such as when contained in a writing crayon, in a typewriter ribbon, or in a writing fluid or ink.

Example III

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

12% by weight diethanolamine
3% by weight Cellosolve
10% by weight water
75% by weight methanol

As the wetted surfaces of the copy sheets are brought into surface contact with the imaged master between the impression roller and the cylinder, some of the coupler-stabilized diazo complex is dissolved from the surface portion of the image and is transferred to the corresponding areas of the copy sheet where the diethanolamine functions to adjust the pH level for effecting the coupling reaction to form a water-insoluble monoazo dyestuff in direct image in the copy sheets.

From observation, it will become evident that the dyestuff is formed in the copy sheets as distinguished from the imaged master, otherwise transfer of the coupled reaction product would be more difficult to achieve under the conditions described and very faint, if any, copy would result. Color development takes place rather quickly once the coupler-stabilized diazo compound has been adjusted toward the alkaline side by the alkali me-

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dium to form the dyestuff. The copy sheets are capable of being handled almost immediately without fear of set-off or smear, because the color produced is rather permanent and substantially insoluble in character.

The number of copies secured depends in part upon the thickness of the coating of which the image is formed and the amount of coupler-stabilized diazo compound contained in the coating composition, as well as the character and quantity of fluid applied to the copy sheets for effecting transfer of the dye components from the imaged master for coupling to form the dyestuff. It will be apparent, as previously described, that the intensity of the color developed by the azo dye will remain substantially uniform throughout the run as long as the amount of coupler-stabilized diazo compound that is transferred remains substantially the same. Under normal conditions, the number of copies produced by the practice of this invention is greater than that heretofore secured by the process described in the aforementioned copending application. From 100 to 500 copies may be secured from a single master.

It is desirable to embody as high a concentration of the coupler-stabilized diazo compound as possible in the imaging composition consistent with the ability of the coating to remain as a film for forming the image. Generally, the amount of dye-forming components introduced as an ingredient in the coating composition depends upon the ability to maintain sufficient fluidity under the conditions existing in applying the coating to achieve the desired coverage. For the production of a number of copies of sufficient intensity, it is desirable to maintain the concentration of the coupler-stabilized diazo compound in amounts in excess of 40% by weight, and preferably in amounts in excess of 60% by weight. When the concentration reaches as much as 80% by weight, the film-forming characteristics of the imaging material are reduced unless modification is made by the addition of fluidizing agents.

When applied as a hot melt, or when applied from solvent solution or aqueous emulsion, it is desirable to secure a coating on the transfer sheet having a coating weight within the range of 10 to 30 pounds per 3,000 square feet of surface area. When applied in solvent solution with ethyl acetate, tri-chloroethylene, and the like, alone or in combination with diluents such as toluene or benzene, application may be made of the coating composition present in amounts ranging from 20% to 40% solids by weight, or the composition may be formulated into an aqueous dispersion containing 40% to 60% by weight solids.

Instead of the fluid employed in Example III, use may be made of other fluids embodying the following compositions.

Example IV

1.0% by weight sodium hydroxide
90.0% by weight ethyl alcohol
5.0% by weight methyl alcohol
5.0% by weight water

Example V

2.0% by weight ammonium hydroxide
98.0% by weight methanol

The following example provides for the production of red copy from an imaged duplicating master:

Example VI.—Transfer sheet composition

44.5% by weight 6 benzoyl amino-4 methoxy toluene-3 diazo salt of 1-naphthol-6 amino-3 sulfonic acid (coupler-stabilized diazo complex)
11.0% by weight carnauba wax
15.0% by weight oxidized microcrystalline wax
28.0% by weight light mineral oil
1.5% by weight sodium oleate

The above composition is reduced to a fluid state by heating to a temperature of about 80–85° C. and then applied by a hot melt coating process in weights of about 20–30 pounds per 3,000 square feet of surface area onto a suitable base sheet whereby the applied coating composition remains concentrated on the surface of the base sheet for easy transfer therefrom upon cooling.

A master imaged with a transfer sheet prepared in accordance with Example VI may be used to produce red copy when the fluid applied to the surface of the copy sheets contains a base such as diethanolamine, monoethanolamine or the like.

It will be understood that the coupler-stabilized diazo complexes may be embodied in other suitable carriers such as combinations of oils in waxes wherein the oil components are present in higher concentrations to provide a liquid composition which may be inscribed to form the image on a suitable master sheet. Instead, the coupler-stabilized diazo complex may be embodied in a waxy system of the type which is applied on typewriter ribbons for transfer directly to the master to provide the image thereon from which copy may be produced.

It will be understood that changes may be made in the method of formulation and application in preparation of the imaging material to form the transfer coating on the carbon sheet or the image on the master, and that changes may also be made in the techniques for effecting transfer of some of the imaging material from the master to the copy sheets for the production of copy without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. A transfer medium for use in the preparation of an image duplicating master which is substantially free of color transfer value, comprising a base fabric and a composition present in transfer relation on said base fabric containing a coupler-stabilized diazo compound.

2. A transfer sheet for use in the preparation of an imaged duplicating master which is substantially free of color transfer value, comprising a paper base sheet and a continuous coating concentrated on the surface of the base sheet and capable of substantially complete displacement therefrom containing a stabilized diazo salt of a coupler which is soluble in a medium selected from the group consisting of water and alcohol and containing a base.

3. A transfer sheet for use in the preparation of an imaged duplicating master which is substantially free of color transfer value, comprising a paper base sheet and a continuous coating concentrated on the surface of the base sheet and capable of substantially complete displacement therefrom formed of a wax base and containing a coupler-stabilized diazo compound.

4. A transfer sheet as claimed in claim 2 in which the stabilized diazo salt of the coupler is present in amounts ranging from 40–80 percent by weight in the coating composition.

5. A transfer sheet as claimed in claim 2 in which the stabilized diazo salt of the coupler comprises a diazo salt of a sulfonic acid coupler.

6. A transfer sheet as claimed in claim 2 in which the stabilized diazo salt of the coupler is a stabilized compound selected from the group consisting of p-diazo dimethyl aniline-1 naphthol-8 amino 3,6 disulfonic acid; p-diazo diethyl aniline-2,3 dihydroxy naphthalene-6 sulfonic acid; p-diazo-N ethyl-N hydroxy ethyl aniline-2,3 dihydroxy naphthalene-6 sulfonic acid; p-diazo diethyl aniline-1 naphthol-8 amino-3,6 disulfonic acid; o-anisidine diazo-1 naphthol-5 sulfonic acid; o-anisidine diazo-1 naphthol-6 amino-3 sulfonic acid, and 6 benzoyl amino-4 methoxy toluene-3 diazo salt of 1 naphthol-6 amino-3 sulfonic acid.

7. A composition for imaging a spirit duplicating master comprising a wax-oil base containing a coupler-sta-

bilized diazo compound in the form of a diazo salt of a sulfonic acid coupler stabilized against reaction in acidic medium and which is soluble in a medium selected from the group consisting of water and alcohol.

8. A duplicating master comprising a master sheet comprising a waxy carrier and an image on the surface of the master sheet containing a coupler-stabilized diazo complex compound which is soluble in a medium selected from the group consisting of water and alcohol and containing a base.

9. A duplicating master as claimed in claim 8 in which the coupler-stabilized diazo complex compound is present in the imaging material in amounts ranging from 40–80 percent by weight.

10. A duplicating master as claimed in claim 8 in which the coupler-stabilized diazo complex compound is a diazo salt of a sulfonic acid coupler stabilized by formation in an acidic medium.

11. A duplicating master as claimed in claim 8 in which the coupler-stabilized diazo complex compound is a coupler-stabilized diazo salt selected from the group consisting of p-diazo dimethyl aniline-1 naphthol-8 amino-3,6 disulfonic acid; p-diazo diethyl aniline-2,3 dihydroxy naphthalene-6 sulfonic acid; p-diazo-N ethyl-N hydroxy ethyl aniline-2,3 dihydroxy naphthalene-6 sulfonic acid; p-diazo diethyl aniline-1 naphthol-8 amino-3,6 disulfonic acid; o-anisidine diazo-1 naphthol-5 sulfonic acid; o-anisidine diazo-1 naphthol-6 amino-3 sulfonic acid, and 6 benzoyl amino-4 methoxy toluene-3 diazo salt of 1 naphthol-6 amino-3 sulfonic acid.

12. The method of producing copy by spirit duplication with a master imaged with a material containing a large proportion of a coupler-stabilized diazo complex compound lacking in color transfer value and which is incapable of coupling reaction without adjustment of pH, comprising contacting the imaged surface of the master with copy sheets wetted with a fluid containing a solvent for the coupler-stabilized diazo complex compound and a compound for adjustment of the pH to a level where reaction can take place between the coupler and diazo components of the compound to form the corresponding azo dyestuff whereby some of the coupler-stabilized diazo complex compound transfers from the imaged areas of the master to the copy sheet upon contact where reaction takes place to form the azo dyestuff.

13. The method of producing copy by spirit duplication with a master imaged with a composition containing a large proportion of a coupler-stabilized diazo complex compound substantially free of any color transfer value and which remains non-coupling until adjustment of pH to a higher pH level, comprising contacting the imaged master with a copy sheet wetted with a fluid containing a solvent for the coupler-stabilized diazo complex compound and a base for adjustment of the pH to a level where coupling reaction can take place between the diazo and coupler components of the compound to form the azo dyestuff whereby some of the coupler-stabilized diazo complex compound transfers from the imaged areas of the master to the copy sheet where reaction takes place to form the azo dyestuff.

14. 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 coupler-stabilized diazo complex compound soluble in a medium selected from the group consisting of alcohol and water, wetting the surface of a copy sheet with a fluid containing a solvent for the coupler and a base for adjusting the pH to permit coupling reaction between the diazo and coupler components of the compound, contacting the wetting copy sheet with the imaged surface of the master to effect transfer of some of the imaging material from the copy sheet where reaction takes place to form the azo dyestuff.

15. The method of producing copy, comprising the steps of imaging a master with a composition substan-

tially free of any dye color and containing a high proportion of a coupler-stabilized diazo complex compound which is non-coupling until adjustment of the pH, wetting the surface of a copy sheet with a fluid containing a solvent for the coupler-stabilized diazo complex compound and a medium for adjusting the pH to permit coupling reaction between the diazo and coupler components of the compound to form the corresponding azo dyestuff, contacting the wetted copy sheet with the imaged surface of the master to leach some of the coupler-stabilized diazo complex compound for transfer from the imaged master to the copy sheet where reaction takes place upon pH adjustment to form the azo dyestuff therein.

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