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2,969,015

METHOD OF PRODUCING A SPIRIT MASTER FROM A POSITIVE AND A DUPLICATING PROCESS WITH SAME

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This invention relates to an improvement in a multiple copy process and it relates more particularly to a new and improved process for the preparation of spirit and hectograph type masters by photographic technique and to materials for use in same.

To the present, the only means known to applicants for the preparation of an imaged master for spirit or hectograph duplication has been by processes of imaging the master directly by the application of an imaging composition containing an intense water and alcohol soluble dyestuff, such as crystal violet, in high concentration either in a writing fluid, in a transfer carbon or in a type-writing ribbon, or the like. Photographic means for the production of an image, as in the preparation of a lithographic plate or a stencil has not been adaptable to the preparation of plates for the production of copy by the spirit or hectograph process.

It is desirable to be able to image a spirit master or a hectograph master by a photographic technique to produce the reproductions of an original as embodied in a film positive, penciled or inked vellum or other original on a base penetrable by light for photographic reproduction and it is an object of this invention to provide a method and materials for achieving same.

Another object is to provide a method and materials for producing an image directly on a spirit or hectograph master by an indirect process using light and it is a related object to provide a new and improved copy process which makes use of same.

A further object is to provide a method and materials for imaging a spirit or hectograph type master directly from an original or film positive and it is a related object to provide an imaged master of the type described capable of use to produce a large number of acceptable copies in a large variety of possible colors including black, and to produce such copies with a dyestuff that is substantially insoluble in water and alcohol and thereby to minimize setoff and smearing and to produce copy of a relatively permanent character.

More important, it is an object of this invention to provide a new and improved process for the production of a photo spirit or hectograph master which is substantially free of any dye color and is therefore free of the type of dirtiness and staining characteristic of present spirit duplicating materials but without the loss of the simplicity and ease of operation which is characteristic of the spirit duplicating system.

In the copending application of Klimkowski et al., Ser. No. 287,616, filed on May 13, 1952, now U.S. Patent No. 2,748,024, description is made of a new copy process of the spirit duplicating type which has eliminated the dirtiness and staining characteristic of the present spirit or hectograph system without loss in the simplicity and ease in operation thereof. In the described process, the master is imaged with a composition that is substantially free of any dye color but which contains at least one of the com-

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ponents essential for reaction to form a dyestuff. The component or components in the imaging material is soluble in the fluid with which the impression paper is wet prior to contact with the imaged master so that some of the dye forming component in the image will be leached for transfer from the imaged master to the impression paper where reaction may take place with the remainder of the dye forming components to form a dyestuff as copy in the impression paper.

It will be evident from this brief discussion, that the process described departs from the present system which requires the presence of an intense water and alcohol soluble dye of the type which has been found to be so objectionable when present in the imaging material and which has limited the colors available to purple, blue, red or green. Instead, the described system makes use of an imaging composition containing substantially colorless components which react to form a dyestuff which is relatively water insoluble and permanent when formed in the impression paper and which can be formulated to produce a greater variety of colors including black with relatively low cost materials.

The preferred system in the process of the aforementioned copending application rests upon the reaction of a diazo compound and a coupler to form an azo dyestuff. Either the coupler or the diazo may be contained as the essential dye forming component in the imaging material while the other is provided in the impression paper, as by application onto the surfaces thereof, as a component of the fluid applied to the surface of the impression paper prior to contact with the imaged master, or as a component incorporated in the impression paper by a previous treatment or as an ingredient in the slurry of which the impression paper is formed or by application from a second fluid applied to the surface of the impression paper after contact with the imaged master. When the diazo is stabilized against reaction with the coupler, as by stabilization against reaction in a strongly acidic medium, the two components may be incorporated together in the imaging material in a state which is soluble in alcohol and water for transfer from the imaged master to the impression paper where reaction can take place to form the dyestuff upon adjustment of the pH, as by means of an alkali or base contained in the fluid applied to the impression paper prior to or after contact with the imaged master.

In another copending application of Klimkowski et al., Ser. No. 348,584, filed April 13, 1953, now U.S. Patent No. 2,873,668, description is made of an improvement in the process described embodying the use of a system calling for reaction of a diazotizable amine or salt thereof and an alkali metal nitrite and coupler which may be supplied as an excess of the amine or as a separate coupler, such as phloroglucinol, resorcinol and the like. In this system, when the components are brought together in the impression paper, the nitrite reacts to form nitrous acid in the acidic medium which reacts to diazotize the amine which in turn then reacts with the coupler to form the azo dyestuff. The imaging material may contain the nitrite or the coupler but it is preferred to incorporate the amine as the essential dye forming component in the imaging material, alone or in combination with the nitrite or the coupler for reaction to form the dyestuff upon transfer to the impression medium.

The described system embodying the reaction between a diazotizable amine, nitrite and coupler in acidic medium permits the use of materials which are less expensive than a diazo and coupler used in the process of the earlier filed application and also permits the use of mate-

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rials to form dyestuffs in a wider variety of colors, including intense black.

In a further modification described in the copending application of Klimkowski et al., Ser. No. 348,585, filed on April 13, 1953, now abandoned, use is made of a system embodying the reaction between a coupler and a passive diazo which becomes activated in acidic medium for reaction with the coupler to form the azo dyestuff.

The processes of the type described in the aforementioned copending application as in present spirit duplicating systems have been limited in use for direct imaging of plates, that is where the master is imaged directly by application of the imaging material as by transfer from a carbon sheet in surface contact with the master in response to applied force or by transfer from a typewriter ribbon or liquid ink composition or the like. To the present, none of the spirit duplicating systems have been adaptable for use indirectly for the production of an imaged master as by a photographic process from a film negative or more particularly directly from a film positive.

It has been found that the dye forming systems of the type described in the aforementioned copending applications of Klimkowski et al. may be, with certain modifications, adapted for the first time to make available a photo process for the production of an imaged master of the spirit duplicating type directly from a film positive. The system provided in accordance with the practice of this invention for use in the production of copy by spirit duplicating technique remains free of the objectionable features of staining and dirtiness characteristic of the present spirit duplicating systems, without loss in the simplicity and ease of operation thereof.

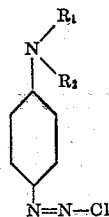
Briefly described, instead of incorporating the essential dye forming component in an imaging material adapted to be applied to form the image on a spirit duplicating master, the dye forming component which is still free of any dye color and which is soluble in the fluid with which the copy sheet is wet prior to contact with the master is embodied as a component in a coating composition which is applied over the entire surface of the duplicating master. While it is possible to make use of any of the ingredients essential to form the dyestuff as a component in the coating composition, it is essential in the practice of this invention that at least one of the dye forming components of the coating constitute a light-sensitive diazo or other essential dye forming component which is capable of being destroyed by light.

In practice, the diazo alone or stabilized for use in combination with the coupler is formulated into a coating composition having a wax or resinous base for application to form a coating on the surface of a suitable base sheet. The film positive, drawing on vellum or other printed or written mater on a base penetrable by light is placed on the coated side of the base sheet and then light of sufficient intensity is directed onto the assembly to destroy the diazo in the non-imaged areas while leaving the diazo in the imaged areas in condition for reaction to form the azo dyestuff upon being leached for transfer from the imaged master to the impression paper.

The diazo dye forming component substantially free of color transfer value and soluble in fluid with which the impression paper is wet prior to contact with the formed master may be selected of the light-sensitive diazo compounds described in the copending application of Klimkowski et al., Ser. No. 316,948, filed on October 25, 1952, now U.S. Patent No. 2,795,504. As described therein, such diazo compounds may include (1) the diazo compounds which are stable as the corresponding diazonium sulfates or chlorides, such as p-diazo diphenylamine sulfate, (2) diazo compounds which are stabilized as the corresponding zinc chloride or other metallic chloride salt complexes, or (3) diazo compounds which are stabilized as salts of sulfonic acids or aryl sulfonic acids. The following structural formulae are representative of

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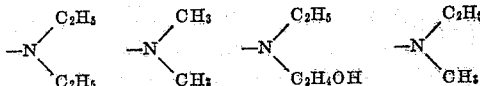
the general types of diazo compounds which may be used:



wherein the



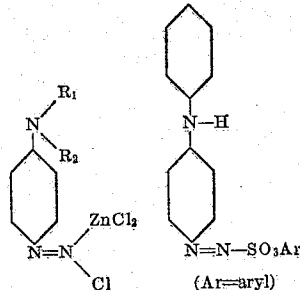
group comprises



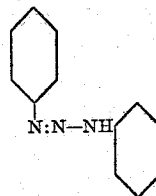
and



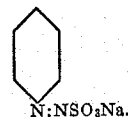
The corresponding stabilized zinc chloride complex or sulfonates of groups 2 and 3 above may be represented by the following typical formulae:



In the alternative, the diazo compounds may be of the passive type which are light-sensitive but which are activated only in acidic medium for reaction with a coupler to form an azo dyestuff. These include diazo compounds of the type described in the copending application Ser. No. 316,948 such as the metallic salts of the acid isomeric forms of the diazo compounds, including the isodiazotates or nitrosoamines or the diazo amino or diazo imino compounds represented by the formula



or diazo sulfonates such as



Couplers suitable for use with either of the diazo dye forming materials may be selected of the organic aromatic compounds such as aromatic amines of the type aniline or substituted aniline, such as dimethyl aniline, phenolic compounds such as phenol, resorcinol, phloroglucinol, 2,3-dihydroxy naphthalene 6-sulfonic acid and

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water soluble salts thereof, 6-amino 1-naphthol 3-sulfonic acid, 8-amino 1-naphthol 3,6-di-sulfonic acid monosodium salts, thio compounds, such as thio-barbituric acid, or cyano compounds, such as cyanoacetamide, or pyrazolone or derivatives thereof.

When the diazo is of the passive type or stabilized against reaction with the coupler in strongly acidic medium, the coupler may be and preferably is incorporated as a component with the diazo in the coating formed on the surface of the photo spirit master. Otherwise, the coupler is supplied for reaction as a component in the fluid with which the surface of the impression medium is wet prior to contact with the formed master, or incorporated as a component of the impression paper by prior treatment, or applied as from a second solution with which the impression paper is wet subsequent to contact with the formed master.

When the diazo is contained alone as the component in the coating on the master, and when the coupler is supplied in the fluid or as a constituent of the impression medium, a diazo capable of coupling reaction without adjustment of pH may be used. If the diazo is stabilized against reaction with the coupler in strongly acidic medium such as a pH below 3.5 so as to enable the coupler to be incorporated in combination with the diazo in the coating on the master, or separate and apart therefrom for application as described, the base for adjustment of the pH for coupling may be supplied as a component in the fluid applied to the surface of the impression medium prior to contact with the formed master or in a second fluid applied subsequent thereto.

A base of the type described may be selected of such materials as organic amines of the type monoethanolamine, triethanolamine, or ammonium hydroxide or inorganic bases such as sodium hydroxide, potassium hydroxide, or other metal salts formed of a strong base and a weak acid.

If the light-sensitive diazo is of the passive type, the coupler may be incorporated in the coating in combination with the diazo or separate and apart thereof, in the fluid or in the impression paper, or in a second fluid applied to the impression paper after contact with the formed master. The acidic medium for activating the diazo for reaction with the coupler may also be contained as a component in the fluid or in the impression paper or in the second fluid, either together or separate and apart from the coupler. When the coupler is supplied in a medium other than a coating on the master, the acidic medium may also be embodied with the dye as a component of the coating on the master.

It is preferred to embody the light-sensitive diazo dye forming component in a coating having a base which is film forming and slightly soluble or swellable in a fluid such as alcohol or water and preferably mixtures thereof. The film forming base may be selected of cellulose ethers and esters or of resinous materials such as cellulose acetate-propionate, cellulose acetate-butyrate, cellulose acetate, methyl cellulose, benzyl cellulose, polymethyl methacrylate, Beckacite P-720, or polyvinyl chloride (Geon 101), or wax materials such as the polyethylene glycols marketed under the trade name "Carbowax" having a molecular weight range from 2,000 to about 9,000, or wax and resin combinations such as the combination of a cellulose ether or ester of the type previously described with one or more of the waxes such as polyethylene glycol having a molecular weight ranging from 1500-9000, or diethylene glycol esters, such as polyethylene glycol stearate, mono-oleates and the like.

For the production of the maximum number of copies, it is desirable to incorporate as high a concentration of the essential dye forming components as possible in the coating formed on the surface of the spirit master. When the diazo and coupler are both contained in the coating composition, it is desirable to have an amount of diazo

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at least equivalent to the amount of coupler but it is preferred that the amount of diazo be in excess thereof, such as in proportions greater than 2 to 1. When a carrier is used to form the coating containing the light-sensitive diazo dye forming components, it is desirable, if possible, to incorporate the dye forming components in amounts as high as 75 percent by weight of the coating composition. It is sometimes difficult to formulate a coating of the desired character when more than 75 percent of diazo or diazo and coupler are contained therein. However, in order to secure copy of good quality and to secure a desired number of copies, it is desirable to embody the dye forming component in the coating composition in amounts to form at least 20 percent by weight thereof.

The following will represent compositions which may be used to form coatings on the surface of a spirit master:

Example 1

	Grams
Carbowax 6000	20
Diglycol stearate S	5
Citric acid	5
8-amino 1-naphthol 3,6-disulfonic acid monosodium salt	25
p-Diazo diethyl aniline zinc chloride	20
H ₂ O	50

Example 2

	Grams
Carbowax 6000	20
Diglycol stearate S	5
Citric acid	5
8-amino 1-naphthol 3,6-disulfonic acid monosodium salt	25
p-Diazo diethyl aniline zinc chloride	20
H ₂ O	25
10% cellulose acetate in acetone	50

Example 3

	Grams
Carbowax 6000	5
p-Diazo diethyl aniline zinc chloride	27
6-amino 1-naphthol 3-sulfonic acid	18
Acetone	45

Example 4

	Grams
10% cellulose acetate in acetone	50
p-Diazo diethyl aniline zinc chloride	17
6-amino 1-naphthol 3-sulfonic acid	18

Example 5

	Grams
10% cellulose acetate in acetone	50
p-Diazo diethyl aniline zinc chloride	27
6-amino 1-naphthol 3-sulfonic acid	18
Dimethyl phthalate	4

Coating compositions of Examples 1-5 are representative of coatings formulated with bases embodying waxes, resins and resinous wax combinations, with or without plasticizers and softeners of the type dimethyl phthalate, tributyl stearate and the like. These coating compositions may be formulated in solutions in solvent or dispersed in water or a non-aqueous medium for application to form the coating on the surface of the spirit master. For such use the formulations of Examples 1-5 may be diluted in solvent solution or dispersed in aqueous medium to provide concentrations ranging from 10 up to 60 percent by weight. In preparing the master, the compositions are applied in one or more coatings to produce coating weights in amounts of about 10-30 pounds per 3000 square feet of surface area.

The materials embodying the features of this invention may be formulated into a coating adapted to be applied

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as a hot melt to produce the desired coating weights as represented by the following formulations:

Example 6

	Grams
Carbowax 1500	10
Carbowax 4000	40
Carbowax 6000	5
p-Diazo diethyl aniline zinc chloride	25
6-amino 1-naphthol 3-sulfonic acid	20

Example 7

	Grams
"Carbowax 6000"	25
Flexol 3GH	30
p-Diazo diethyl aniline zinc chloride	25
6-amino 1-naphthol 3-sulfonic acid	20

Instead of making use of carriers or bases which are slightly soluble in the fluid with which the impression medium is wet prior to contact with the formed master, coating may be formulated of a base which is substantially insoluble in the aqueous medium and which may be applied to form the coating on the imaged master in weights of 10-30 pounds per 3000 square feet of surface area by means of a hot melt, as in the following formula:

Example 8

	Grams
Carnauba wax	11
Cardis 262	15
Mineral oil	28
Dispersing agent	1
p-Diazo diethyl aniline zinc chloride	20
8-amino 1-naphthol 3,6-disulfonic acid monosodium salt	25

In use, the coated master is positioned in surface contact with a film positive, with an inked vellum or with another original through which light is capable of penetration. The coated master having the film positive in surface contact therewith is then exposed to ultra-violet light with the result that the diazo in the non-imaged areas is destroyed and the diazo in the imaged areas remains unchanged.

The formed master is then separated from the original and mounted in a standard spirit duplicating machine. When the imaged paper wet with a fluid is brought in surface contact with the formed master, the diazo which has not been destroyed in the imaged areas is leached for transfer to the impression medium. The fluid is adapted to contain a base for adjustment of the pH to enable reaction to take place between the diazo and coupler to form the azo dyestuff in the impression medium.

As previously pointed out, various permutations are possible, such as formulation of the coating to contain only the light-sensitive diazo dye forming component while the fluid is formulated to contain the coupler in addition to the other means, when necessary, for pH adjustment to activate the undestroyed diazo for reaction for dye formation. A system illustrative of a coating containing the diazo only may be illustrated by the following examples:

Example 9

	Grams
Carbowax 6000	20
Diglycol stearate S	5
Citric acid	5
p-Diazo diethyl aniline zinc chloride	20
H ₂ O	50

Example 10

	Grams
Carbowax 1500	10
Carbowax 4000	40
Carbowax 6000	5
p-Diazo diethyl aniline zinc chloride	25

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When a light-sensitive master of the type illustrated by Examples 9 and 10 is used to produce copy, the fluid with which the surface of the impression medium is wet may be formulated to contain from 1-5 percent by weight of a coupler such as resorcinol, 6-amino 1-naphthol 3-sulfonic acid, or the like, alone or in combination with a base, such as from 1-3 percent by weight monoethanolamine, triethanolamine, ammonium hydroxide or the like.

When the dye forming compounds are embodied in a carrier of the type described, it is preferred to make use of a carrier which is slightly soluble in the fluid medium with which the surface of the copy sheet is wet so as to cause gradual solution of the coating with the result that the dye forming components contained in the coated master will not be leached therefrom at a substantially greater rate than the base in which it is contained with the result that the dye forming components remain available on the surface of the master for transfer by leaching from the formed master to the copy sheets. When the base of the coating on the imaged master is wholly insoluble in the fluid, the light-sensitive dye forming components in the coated master will have to be leached through greater depths as a number of copies are produced thereby to cause more rapid weakening of the intensity of the copy as the number of copies are formed or else the rate of production is necessarily decreased.

Instead of embodying the light-sensitive components of the dyestuff in a carrier of wax or resinous materials of the type described to minimize penetration into the base sheet and to retain the dye forming components in the desired concentration to be available on the surfaces, it has been found that a master capable of use in the production of a suitable number of copies of acceptable quality can be formed without the use of a carrier when the dye forming components are present in sufficient concentration on a non-absorbent base sheet. In a sense, a master formed in accordance with this further concept of this invention is somewhat similar to that of a conventional diazotype sheet used in single copy work except that instead of the requirement for anchorage of the diazo dye forming components as by impregnation of the base sheet of a diazotype paper, impregnation to anchor the coating would be undesirable in a master embodying the features of this invention. Similarly, transferability which is a requirement of a light-sensitive master embodying the features of this invention for use in the production of multiple copies by spirit duplication would be contrary to the characteristics desired of the materials in a diazotype sheet and such transferability would render the diazotype sheet unfit for its intended purpose. Marked differences also exist in the concentrations of the diazo dye forming components which are present in the coating of a master sheet embodying the features of this invention in amounts twenty to one hundred times greater than that which is present in a similar area of a diazotype sheet.

The following will illustrate the preparation of a master formed without a carrier in the light-sensitive coating:

Coating composition:

50 parts by weight methyl alcohol.
20 parts by weight 6-amino 1-naphthol 3-sulfonic acid.
20 parts by weight p-diazo diethyl aniline zinc chloride.

The composition is applied by a roller coater or the like onto an enamelled surface of the base sheet in amounts to provide ¾-3 pounds of diazo and coupler per 3000 square feet of surface area. The coating is allowed to dry at room or at slightly elevated temperature and then the coated material is sheeted to form plates or master sheets for use in the production of an imaged master by the technique previously described.

When the diazo is applied without coupler to the surface $\frac{1}{2}$ -2 pounds per 3000 square feet of surface area is sufficient.

In order to provide readability of the image formed on the master sheet in response to exposure to a film positive in the manner described, a small amount of a light-sensitive dyestuff may be incorporated into the coating composition so that the dyestuff as well as the diazo dye forming components will be destroyed in the non-imaged areas by reaction to ultra-violet light which penetrates through the film positive. The dyestuff will remain in the imaged areas to impart visibility of the imaged portion.

Instead of incorporating a light-sensitive dyestuff as an additional component in the coating composition, visibility of the non-imaged portion may be brought out after exposure by subjecting the surface of the plate to ammonia vapors, or by wetting the surface of the plate with a solution of ammonia or an amine or other suitable base for initiating coupling in an amount sufficient to react a minute portion of the coating to form the dye color. It has been found that when the surface of the imaged master is exposed to ammonia vapors or solutions of ammonium hydroxide or of other amine compounds prior to mounting in the press for the production of copies, immediate copy of good quality will be secured even after the master has been stored for some time or even upon reruns after earlier use. The phenomenon which provides this result is not for the present known but it is believed that the ammonia or other equivalent materials tend to increase the solubility of the coupler in the fluid medium and make it more immediately available in sufficient quantities for coupling to form a desired concentration of dyestuff by reaction in the copy sheet.

It will be apparent from the description that the system described and claimed herein for the first time provides a means for the production of an imaged master directly from an original by a light or photographic technique so as to enable the production of copies which are an exact reproduction of an original. The dye forming components may be selected to produce dye colors of a large variety and the dye substance produced in the impression paper may be substantially insoluble in aqueous medium or the solids since transfer thereafter is unnecessary and, in fact, undesirable.

It will be apparent from the description that a process of the type described which provides for a type of spirit duplication enables the production of a coated master and the use thereof to produce copy without the existence of any dye color in any of the materials being handled thereby to avoid the objectionable characteristics of staining and dirtiness in manufacture and use which is characteristic of present spirit systems. Yet the process enables the production of copy of acceptable quality without loss of the simplicity and ease which constitute some of the desirable features in present spirit systems.

Concepts somewhat similar to those described may be adapted for the production of an imaged master directly from a negative by thermal reaction when the diazo or other dye forming components contained in the coating on the surface of the master are heat-sensitive instead of or as well as light-sensitive. A heat pattern for destruction of the dye forming components in the coating of the master in the non-imaged areas may be generated from a negative in surface contact with the coated surface of the master by radiation with infrared in accordance with the teaching embodied in the copending application of Roshkind, Ser. No. 273,530, filed on February 26, 1952, now U.S. Patent No. 2,808,777, wherein the infrared rays are absorbed in the non-imaged areas of the negative and converted into heat to form a heat pattern which destroys the dye forming components in the coating of the master in surface contact therewith.

It will be understood that the coated master constitutes

a new article of manufacture since coated masters of the type described even with the present spirit duplicating materials have never been produced and have never had any utility since photographic means for the inactivation of the dye components contained therein have not been available.

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

We claim:

1. In the method of producing copy from a positive having an opaque image on a light-transmitting background, the steps of exposing to light through the positive, a master sheet having a substantially continuous coating concentrated on the surface portion thereof formed of a composition containing a high proportion of a soluble azo dye forming component which is sensitive to light and which is soluble in the fluid applied to the surface of the copy sheets prior to contact with the coated side of the master whereby the azo dye forming component in the coating on the master sheet is destroyed in the exposed portions and retained in the imaged portions to form an imaged plate, contacting the imaged surface of the master with copy sheets wetted with a fluid containing a solvent for the azo dye forming component and the other components for reaction therewith to form the azo dyestuff in the copy sheets whereby some of the azo dye forming component is transferred from the imaged master to the copy sheets upon contact where reaction takes place to form the azo dyestuff.

2. In the method of producing copy from a positive having an opaque image on a light-transmitting background, the steps of exposing to light through the positive, a master sheet having a non-displaceable coating extending continuously over the surface thereof containing a high concentration of a light sensitive azo dye forming component which is soluble in the fluid applied to wet the surface of the copy sheets prior to contact with the coated side of the master whereby the azo dye forming component is destroyed in the non-imaged portions and retained in the imaged portions to form an imaged plate, contacting the imaged surface of the master with a copy sheet wetted with a fluid containing a solvent for the azo dye forming component and a coupler whereby some of the azo dye forming component transfers from the imaged areas of the master to the copy sheets where reaction can take place to form the azo dyestuff.

3. In the method of producing copy from a positive having an opaque image on a light-transmitting background, the steps of exposing to light through the positive, a master sheet having a coating concentrated as a continuous layer over the surface thereof containing a high concentration of an azo dye forming component which is destroyed by light and which is soluble in a medium selected from the group consisting of alcohol and water, contacting the imaged surface of the master with a copy sheet wetted with a fluid containing a solvent for the azo dye forming component and the other components necessary for reaction therewith to form the azo dyestuff whereby some of the azo dye forming component transfers from the imaged areas of the master to the copy sheet where reaction takes place with the other components to form the azo dyestuff.

4. In the method of producing copy from a positive having an opaque image on a light-transmitting background, the steps of exposing to light through the positive, a master having a non-displaceable coating extending substantially continuously over a surface thereof containing a high concentration of a light sensitive azo dye forming component which is substantially free of any color transfer value and which is soluble in a medium selected from the group consisting of alcohol and water whereby the azo dye component is destroyed in the non-imaged areas and retained in the imaged areas to form

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an imaged plate, contacting the imaged surface of the master with a copy sheet wetted with a fluid containing a solvent for the azo dye component and a coupler for reaction therewith to form an azo dyestuff whereby some of the azo dye component transfers from the imaged areas of the master to the copy sheet where reaction takes place with the coupler to form an azo dyestuff.

5 In the method of producing copy from a positive having an opaque image on a light-transmitting background, the steps of exposing to light through the positive, a master having a coating extending substantially continuously over the surface thereof containing a high concentration of a coupler and a diazo dye intermediate stabilized against coupling reaction to produce an azo dyestuff until adjustment of the pH and both of which are soluble in the fluid applied to wet the surface of the copy sheets prior to contact with the coated side of the master whereby the diazo dye intermediate is destroyed in the non-imaged areas and retained in the imaged areas to form an imaged plate, 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 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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6. The method as claimed in claim 5 in which the diazo dye forming compound and coupler is present on the surface of the master in amounts ranging from $\frac{3}{4}$ -3 pounds per 3000 square feet of surface area.

5 7. The method as claimed in claim 5 in which the diazo dye forming components contained in the coating on the surface of the master are embodied in a carrier selected from the group consisting of wax, cellulose ethers, cellulose esters, and polyethylene glycol polymers which have limited solubility in the fluid with which the surfaces of the copy sheets are wet prior to contact with the imaged master.

10 8. The method as claimed in claim 5 in which the diazo component is present in amounts at least equal to that of the coupler.

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