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AZO DYE DUPLICATING PROCESS

Robert J. Klimkowski, Chicago, and Robert T. Florence, Park Ridge, Ill., assignors to A. B. Dick Company, Niles, Ill., a corporation of Illinois

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This invention relates to a copy process, and more particularly to a new and improved spirit duplicating or hectograph process for the production of multiple copies from an imaged master.

This application is a continuation-in-part of our copending applications Serial No. 287,616, filed on May 13, 1952, now U. S. Patent No. 2,748,024, Serial No. 297,568, filed on July 7, 1952, now Patent No. 2,634,677, and Serial No. 316,948, filed on October 25, 1952, now U. S. Patent No. 2,795,504.

In the aforementioned copending applications, description is made of a new and improved copy process of the duplicating type which eliminates many of the objectionable features of the present spirit duplicating process. The improved process retains the simplicity and ease of operation characteristic of the spirit duplicating system but eliminates its objectionable soiling characteristics resulting from the use of a highly water-soluble dye in the composition of the imaging material. Instead of making use of a highly water and alcohol-soluble dye, the imaging composition of the inventions described in the copending applications embodies a dye-forming component which is substantially free of any dye color and which is soluble in the fluid applied to the surface of the impression paper and is thereby leached for transfer from the imaged master to the impression paper. In the impression paper, the dye-forming component combines with other materials necessary for reaction to form the dyestuff in the full development of the image.

In the diazo dye system described, the diazo compound may be provided in the imaging material with which the carbon sheet is formed and with which the master is imaged, while the coupler may be supplied in the fluid or in the copy sheet for reaction with the diazo to form the dyestuffs. In the alternative, the coupler may be provided as the essential component in the imaging material and the diazo supplied in the fluid or in the impression paper for reaction with the coupler upon transfer from the imaged areas of the master sheet to form the azo dyestuff. Instead, both the coupler and the diazo, stabilized against reaction with the coupler, may be provided in high concentration in the imaging material for reaction to form the azo dyestuff upon transfer to the impression paper in response to the adjustment of the pH with materials contained as an element in the fluid. By way of still further modification, the base or the coupler or the diazo adapted to be supplied in the fluid or in the copy sheet for reaction with the essential dye-forming component contained in the image of the master may be supplied in a second fluid for wetting the impression paper subsequent to contact with the imaged master.

The dirtiness and staining characteristics of the spirit duplicating process heretofore employed has been substantially completely eliminated by the processes described without loss of simplicity or ease of operation characteristic of the spirit duplicating system as it has been known up to the present date. It is believed, however, that still further improvements are possible in a system

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of the character described, as by modification to reduce the cost of the ingredients and to increase the stability of the ingredients to light and heat so as to provide for the production of uniform copies at less cost and without limitation as to the life of the imaging material or the conditions of storage of the various elements.

Improvements are also believed possible by way of modification to enable use of materials which are less corrosive to duplicator parts and which would enable a wider selection of compounds to increase the color range of the copy and with particular attention to the possible development of a more intense and complete black, which is not available now in duplicating systems of the type described.

It is an object of this invention to provide still further improvements in a copy process of the type described, and it is a related object to produce various compositions and elements for use in same.

Another object is to produce a new and improved composition for use in the production of copy by a spirit duplicating process wherein the imaging material is free of dye color but in which the dye color is developed fully in the impression paper in response to transfer of dye-forming components from the material forming the image in the master upon contact.

It is a related object to produce a new and improved imaging composition in the form of an ink, ribbon or transfer sheet and to produce a new and improved master, each of which are substantially free of dye color but which may be used in a conventional spirit duplicating machine for the production of copy of good quality, and it is a related object to produce a new and improved duplicating process which makes use of the same.

More specifically, it is an object of this invention to provide a new and improved duplicating process of the type described and materials for use in same in which no color of any consequence is present in the imaging material or in the master formed therewith, and in which compounds of a greater variety and lower cost may be used to produce copy in a greater range of colors, including black, in which the materials used in the practice of the process are more stable to heat and light and, therefore, capable of use in the production of a greater number of copies of a uniform quality with less effect from time, temperature or atmospheric conditions and which are less corrosive to duplicator parts and materials in contact therewith.

It has been found that the aforementioned improvements in the processes previously described are achieved in a system which makes use of a diazotizable amine in the form of an aromatic amine in a sufficiently acidified environment for reaction to cause an alkali nitrite to decompose into nitrous acid which reacts with the amine to form a diazo compound. The diazo formed is capable of reaction with a coupler, as before, to form the azo dyestuff. The coupler may be provided in the form of the amine when present in excess of that required to react with the nitrite, or it may be provided as an auxiliary compound of the type described in the copending applications. The acidifying medium may constitute an acid introduced as a separate component, or it may be present in the form of an acid group, such as a sulfonic acid group, or as a part of the amine salt.

As in the process of the co-pending applications which make use only of a diazo and coupler, with or without a base for pH adjustment, numerous permutations are possible in the practice of this invention, a number of which will hereinafter be described. Since the diazotizable amine constitutes the more expensive of the elements, and since the amine sometimes causes the development of background color, it is preferred to embody the amine as one of the essential components in the imaging ma-

terial. It will be understood, however, that the diazotizable amine, or an amine salt, may, in the alternative, be incorporated as a component in the impression paper or may be applied as a component in the fluid applied to the impression paper in advance of contact with the image master or even in a second fluid applied to the surface of the impression paper after contact with the image master. In either event, the amine is provided in the impression paper to react with the latent image formed on the surface of the impression paper to form the dyestuff.

When, as is preferred, the diazotizable amine is embodied as an element in the imaging composition, the following combinations are possible:

A. With the amine salt in the imaging material, the nitrite, such as sodium nitrite, may be incorporated (1) in the fluid with which the surface of the impression paper is wet in advance of contact with the imaged master; (2) the sodium nitrite may be embodied in the impression paper as by a prior coating process or by providing the nitrite in the slurry from which the impression paper is prepared; or (3) the sodium nitrite may be applied from a second solution with which the surface of the impression paper is wet after contact with the imaged master.

B. With the amine salt and acid in the imaging material, the disposition of the nitrite may be in either of the elements (1), (2), or (3) of A above.

C. Both the amine salt and the nitrite may be compounded as components of the imaging material and the acid for reaction with the nitrite incorporated in (1) the fluid, (2) the impression paper, or (3) in a second fluid applied to the impression paper after contact with the imaged master.

When a separate coupler is used, it may be incorporated either in the imaging material or in the fluid, or in a second fluid in each of the combinations (A), (B) and (C) previously described.

It will be apparent that a number of permutations are also possible with the nitrite in the imaging material and the amine, coupler and acids arranged together or separately in the other elements, including the fluid with which the impression paper is wet in advance of contact with the imaged master, or a second fluid applied to the surface of the impression paper after contact with the imaged master. It is only necessary that a separation between the respective elements be maintained as between the acid and the nitrite so as to avoid the premature formation of nitrous acid used to form the diazo of the amine, and it is also essential in governing the arrangement of elements in accordance with the practice of this invention to make use of only those components in the imaging material which are soluble in the fluid applied to the surface of the impression paper so as to effect the desired leaching of the dye-forming components from the image of the master to the impression paper for reaction to form the dyestuff.

The following will illustrate the practice of this invention in a combination wherein the imaging material is formulated to contain the amine salt and the fluid used therewith in the production of brown copy contains the nitrite:

EXAMPLE 1

Imaging material for use in the production of a transfer carbon

12.0% by weight carnauba wax
17.0% by weight oxidized microcrystalline wax (Cardis 262)
14.5% by weight heavy mineral oil
13.0% by weight light mineral oil
1.5% by weight sodium oleate
42.0% by weight m-phenylene diamine dihydrochloride

In the preparation of the transfer carbon, the materials are combined together to form a hot melt at a temperature of between 80° to 100° C. as by a milling machine

using heated rolls, and then coated onto a web of paper to form coating weights of about 15 to 25 lbs. per 3,000 sq. ft. of surface area. The coating formed constitutes a surface coating which is weakly bonded to the backing sheet so as to enable easy displacement onto the surface of the master in response to applied force.

EXAMPLE 2

Fluid composition for use with the imaging composition of Example 1

86.0% by weight methanol
10.0% by weight water
4.0% by weight sodium nitrite

In use, the coated surface of the transfer carbon produced with the composition of Example 1 is placed in contacting relation with the surface of a master sheet. The image is formed on the master sheet by transfer of coating from the carbon in response to applied force as by a die impression, typewriter key, or by a stylus.

The master having the image in reverse is then mounted in a standard spirit duplicating machine and the impression paper is fed into contacting relation with the imaged surface of the master after the surface of the impression paper has been wet, as by means of a wick or a wiper blade, with the fluid of Example 2. Upon contact, the solvent portion of the fluid leaches some of the amine salt from the imaged areas of the master for transfer to the impression paper. The acidic salt causes the nitrite in the fluid on the impression paper to revert to nitrous acid, which reacts with the amine portion to form a diazo compound. The diazo couples with the remainder of the amine to form an azo dye to produce copy in the impression paper. These reactions occur substantially simultaneously so that the formation of a dyestuff becomes apparent by the time the impression paper passes from between the printing couple of the duplicating machine, but the intensity of the dyestuff increases upon standing, especially if the papers are stacked in a manner to hold in some of the fluid which functions as an ionizing medium to continue the reaction.

The following example illustrates the combination when the imaging material contains both the amine and acid as separate ingredients for reaction with a nitrite contained in a fluid as in Example 2, or in a second fluid:

EXAMPLE 3

12.0% by weight carnauba wax
17.0% by weight microcrystalline wax
14.5% by weight heavy mineral oil
13.0% by weight light mineral oil
1.5% by weight sodium oleate
21.0% by weight chromotropic acid
21.0% by weight 2,5 diaminotoluene sulphate

A transfer carbon is formed as previously described from a hot melt of the above composition. When used in combination with the fluid of Example 2 to produce copy on the impression paper, a blue dyestuff is formed.

In this system, the acid and the amine salt, soluble in alcohol and water, are leached from the imaged master for transfer to the impression paper upon contact with the surface of the impression paper wetted with the fluid of Example 2. There the acid reduces the nitrite to nitrous acid. The nitrous acid reacts with the amine salt to form a diazo and then the diazo couples with the remainder of the amine to form the blue azo dyestuff.

The following will illustrate the combination wherein a separate coupler is incorporated with the amine in the form of an acid salt in the imaging material and the nitrite is provided either in the fluid, in the impression paper, or in a second fluid:

EXAMPLE 4

12.0% by weight carnauba wax
17.0% by weight microcrystalline wax

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14.5% by weight lactic acid
 13.0% by weight heavy mineral oil
 1.5% by weight sodium oleate
 21.0% by weight 2,4 diaminotoluene
 21.0% by weight paranitroaniline hydrochloride

A transfer carbon is formed as previously described, using a hot melt of the composition of Example 4. When impression paper having its surface wet with the fluid of composition 2 is brought into surface contact with a master imaged with the composition of Example 4, the 2,4 diamino toluene and paranitroaniline hydrochloride are leached from the image to the impression paper for reaction to transpose the nitrite into nitrous acid which reacts with the amine to produce a diazo. The diazo reacts with the coupler to produce the azo dyestuff.

The following are further modifications of the system described in which various combinations of amine salts and acid salts are formulated into the imaging material:

EXAMPLE 5

12.0% by weight carnauba wax
 17.0% by weight Cardis 262 wax
 14.5% by weight heavy mineral oil
 13.0% by weight light mineral oil
 1.5% by weight sodium oleate
 42.0% by weight triaminotoluene trihydrochloride

EXAMPLE 6

12.0% by weight carnauba wax
 17.0% by weight Cardis 262 wax
 14.5% by weight heavy mineral oil
 13.0% by weight light mineral oil
 1.5% by weight sodium oleate
 15.0% by weight m-phenylenediamine dihydrochloride
 27.0% by weight p-amino-N,N-diethylaniline hydrochloride

EXAMPLE 7

12.0% by weight carnauba wax
 17.0% by weight Cardis 262 wax
 14.5% by weight heavy mineral oil
 13.0% by weight light mineral oil
 1.5% by weight sodium oleate
 42.0% by weight p-amino-N,N-diethylaniline hydrochloride

EXAMPLE 8

12.0% by weight carnauba wax
 17.0% by weight Cardis 262 wax
 14.5% by weight heavy mineral oil
 13.0% by weight light mineral oil
 1.5% by weight sodium oleate
 15.0% by weight m-phenylenediamine dihydrochloride
 27.0% by weight benzidine dihydrochloride

EXAMPLE 9

12.0% by weight carnauba wax
 17.0% by weight Cardis 262 wax
 14.5% by weight heavy mineral oil
 13.0% by weight light mineral oil
 1.5% by weight sodium oleate
 20.0% by weight p-aminodiphenylamine hydrochloride
 22.0% by weight 1-phenyl-3-methyl-5-pyrazolone

With the fluid of Example 2, brown copy is produced on the impression paper with the imaging material of Example 5; green-black copy is produced with the imaging material of Example 6; red-brown copy is produced with the imaging material of Example 7; orange-red copy is produced with the imaging material of Example 8; and red copy is produced with the imaging material of Example 9.

In the examples given for the preparation of an imaging material embodying features of this invention, illus-

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tration was made of formulations for use in the preparation of a transfer carbon which is the means most often used for imaging a master. Use may also be made of other waxes such as paraffin wax, ozokerite wax, and other natural, petroleum, coal tar or vegetable waxes, or synthetic waxes, alone or in combination with softening or fluidizing agents such as mineral oils, vegetable oils, fatty acids, fatty acid esters, hydrogenated rosin, plasticizers, and the like, in various amounts and proportions, depending on whether use is to be made to produce a transfer carbon or whether a more fluid composition is desired for use in a typing ribbon, or an ink for application by a writing pen, stylus, or the like, to image the master.

As will be evident from the examples, the amines, amine salts, or amine acid salts, may be selected of a large number of commercially available diazotizable aromatic amine compounds. When incorporated as a component of the imaging material, it is important that the diazotizable amine components and the other components entering into the reaction to form the dyestuff be soluble in the fluid composition with which the impression paper is wet and the amines should be reactive with nitrous acid to form a dye compound capable of reaction with the coupler to form the dyestuff.

When the coupler is applied as a component of the imaging material, separate and apart from the amine, it is preferred to make use of a coupler in the form of an organic compound such as an aromatic amine of the type aniline or a substituted aniline such as dimethylaniline or phenolic compounds such as phenol, resorcinol, phloroglucinol, 2,3 dihydroxy naphthol sulfonic acids, or thio compounds such as thiobarbituric acid, or cyano compounds such as cyanoacetamide, or pyrazolone, or derivatives thereof.

While dilute solutions of inorganic acids may be used as the acidic medium when incorporated in a fluid or when incorporated as a component in the imaging material separate and apart from the nitrite, it is preferred to make use of organic acids of the type stearic acid, lactic acid, formic acid, propionic acid, benzoic acid, and the like. The amount of acid is unimportant, since it is only necessary to have sufficient acid present to cause the formation of nitrous acid upon reaction with alkali metal nitrite.

For the proper production of a maximum number of copies, it is desirable to incorporate as high concentration of the diazotizable amine or other components of the dye as is possible into the imaging composition consistent with the ability of the composition to embody the characteristics necessary for imaging purposes or for the manufacture of a suitable transfer carbon. Generally, it is desirable to have a concentration of the dye-forming component present in amounts greater than 20% by weight of the imaging composition and concentrations up to 75% by weight can be tolerated without interfering with the characteristics of the material for the purpose for which it was intended. Where the dye-forming components contained in the imaging material or the composition for forming the coating on the transfer carbon comprise two components such as a diazotizable amine, a diazotizable amine and coupler, or a diazotizable amine and nitrite, the concentrations are preferably reduced to an amount greater than 20% by weight but less than an amount capable of forming a total of 75% by weight of the imaging composition. In a diazotizable amine-coupler system it is preferable to have more amine than coupler such as in a ratio of 1-3 to 1. Lesser concentrations of the nitrites are required, it being sufficient when the amount in the imaging material is within the range of from 1-15% by weight.

The following examples are illustrative of other permutations which may be made with respect to the distribution of the various components in the compositions used in the practice of the duplicating process.

For example, the following will illustrate the system

wherein an amine salt or an amine salt and a nitrite are formulated to be contained in the imaging material while the fluid contains the solvent or the acidic medium necessary under certain circumstances for conversion of the nitrite to nitrous acid.

EXAMPLE 10

Carbon-coating composition

- 12.0% by weight carnauba wax
- 17.0% by weight microcrystalline wax
- 14.5% by weight heavy mineral oil
- 13.5% by weight light mineral oil
- 1.5% by weight sodium oleate
- 5.0% by weight sodium nitrite
- 37.0% by weight m-phenylenediamine dihydrochloride

EXAMPLE 11

Fluid

- 90% by weight methanol
- 10% by weight water

With the system set forth in Examples 10 and 11, copy is formed of an azo dyestuff of an orange-brown color.

In practice, the master imaged with the composition of Example 10 is contacted with an impression paper having its surface wet with the fluid of Example 11. The sodium nitrite and m-phenylenediamine dihydrochloride is leached for transfer from the imaged master to the impression paper where it reacts in the solvent medium with the sodium nitrite to form the diazo compound which further reacts to form the azo dyestuff.

EXAMPLE 12

- 45.0% by weight 1-amino-2-naphthol-4-sulfonic acid
- 15.0% by weight sodium nitrite
- 5.0% by weight carnauba wax
- 10.0% by weight oxidized microcrystalline wax
- 25.0% by weight light mineral oil

EXAMPLE 13

Fluid composition for use with the imaging composition of Example 12

- 4.0% by weight 1-phenyl-3-methyl-5-pyrazolone
- 2.0% by weight lactic acid
- 94.0% by weight methanol

With the system of Examples 12 and 13 used in a copy process of the type previously described, a red dyestuff forming the copy in the impression paper will result.

Another system similar to that of Examples 12 and 13 wherein the amine salt and nitrite are contained in the imaging material and the acid contained in the fluid, is illustrated by the following further examples:

EXAMPLE 14

Imaging composition

- 25.0% by weight 1 amino, 2-naphthol, 4-sulfonic acid
- 20.0% by weight phloroglucinol
- 15.0% by weight sodium nitrite
- 5.0% by weight carnauba wax
- 10.0% by weight oxidized microcrystalline wax
- 25.0% by weight light mineral oil

EXAMPLE 15

Fluid composition for use with Example 14

- 3.0% by weight lactic acid
- 7.0% by weight water
- 90.0% by weight methanol

When the impression paper having its surface wet with the fluid composition of Example 15 is brought into surface contact with the master imaged with the com-

position of Example 14, the dye-forming components transfer from the imaged areas of the master to the impression paper, where the lactic acid causes the sodium nitrite to form into nitrous acid. This forms the diazo compound of the 1-amino, 2-naphthol, 4-sulfonic acid, which then reacts with the phloroglucinol coupler to form the azo dyestuff.

The following example illustrates the practice of this invention when the amine salts and coupler are contained in the imaging material and the sodium nitrite is contained, as is often desirable, in the impression paper while the fluid merely constitutes a solvent for the amine salt and coupler to effect transfer from the imaged master to the impression paper for reaction in the manner previously described.

EXAMPLE 16

Imaging composition

- 12.0% by weight carnauba wax
- 17.0% by weight microcrystalline wax
- 14.5% by weight heavy mineral oil
- 13.0% by weight light mineral oil
- 1.5% by weight sodium oleate
- 27.0% by weight p-amino-N,N-dimethylaniline monohydrochloride
- 15.0% by weight m-phenylenediamine dihydrochloride

EXAMPLE 17

Composition for coating the impression paper to introduce sodium nitrite

- 86.0% by weight methanol
- 10.0% by weight water
- 4.0% by weight sodium nitrite

In the use of the compositions of Examples 16 and 17, the impression paper is first coated with the fluid system of Example 18 and then allowed to dry to set the sodium nitrite in the surface portion of the paper. In the production of copy, paper which has been treated with the composition of Example 17 is wet with methanol before being brought in contact with the master imaged with the composition of Example 16. The methanol causes the amine salts and coupler to be leached for transfer from the imaged master to the impression paper, where reaction takes place to form nitrous acid from sodium nitrite, followed by diazotization of the amine and coupler to form the azo dyestuff.

The following will illustrate the practice of this invention wherein the nitrite is contained as the dye-forming component in the imaging material and the amine salt is contained as a component in the fluid.

EXAMPLE 18

- 12.0% by weight carnauba wax
- 17.0% by weight microcrystalline wax
- 14.5% by weight heavy mineral oil
- 13.0% by weight light mineral oil
- 1.5% by weight sodium oleate
- 42.0% by weight sodium nitrite

EXAMPLE 19

Fluid for use with composition of Example 18

- 5.0% by weight methyl-p-phenylenediamine dihydrochloride
- 10.0% by weight water
- 85.0% by weight methyl alcohol

With the system of Examples 18 and 19, intense black copy will be produced.

When a two-fluid system is used to produce copy, the essential component for completion of the reaction may be incorporated in a second fluid applied to the surface of the impression paper after the latter has been in contact with the imaged master and contains a latent image

formed therein. For example, the sodium nitrite of Example 2 may be deleted from the solution and incorporated in a corresponding concentration in a separate aqueous system. In use, the master imaged with the compositions of either Examples 1 and 3 to 9 is first contacted with the impression paper having its surface wet with a solvent such as methanol and water. The amine salts, and acid when present, and coupler when present, will be extracted by the solvent for transfer from the imaged master to the impression medium to form a latent image therein. When the surface of the impression paper is subsequently wet with a solution containing the nitrite, the acid will function to convert the nitrite to nitrous acid which will react then with the amine to form the diazo, which then couples to form the respective azo dyestuff in the development of copy.

The acid may be separated from the fluid of compositions 13 and 14 for incorporation in a second fluid as described for use in a two-fluid system with a master imaged with the composition of either Example 12 or Example 14, respectively.

It will be apparent from the description that the process described herein provides for further improvements in a duplicating system which has the simplicity of the present spirit duplicating process without the handicap of dye transfer and stain during the manufacture of imaging material or in the handling thereof to produce a transfer ribbon or a transfer carbon or in the use thereof in the preparation of an imaged master and the use thereof to produce copies. A system of the type described enables the production of a greater range of colors in the formation of copy and it permits the formation of copy from a dyestuff which is relatively insoluble and, therefore, incapable of being destroyed in response to moisture or high humidity. The elimination of a diazo as a component of the described system also permits the utilization of lower cost of materials in the copy process and the production of elements for use in the multiple copy process which are substantially free of color and substantially devoid of the development of any background color when incorporated into the impression paper.

It will be understood that a system of the type described may be employed when the essential dye-forming components in the imaging material are substantially soluble in water in the copy process heretofore referred to as the process of "hctographic" duplication.

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

We claim:

1. The method of producing copy with a master imaged with a composition containing an acidic medium and an amine compound capable of diazotization, comprising the steps of wetting the surface of an impression paper with a fluid containing a solvent for the diazotizable amine and acid and also containing a nitrite and a coupler, and contacting the imaged surface of the master with the wetted surface of the impression paper, whereby some of the diazotizable amine compound transfers from the imaged portion of the master to the impression paper for reaction to form the azo dyestuff.

2. The method of producing copy with a master imaged with a composition containing an alkali metal nitrite and a diazotizable amine compound present in a concentration ranging from 20-75% by weight of the composition and capable of coupling reaction to form an azo dyestuff, comprising the steps of wetting the surface of an impression paper with a fluid containing a solvent for the amine compound and the nitrite and also containing an acid and coupler for reaction to form nitrous acid of the nitrite, and contacting the imaged surface of the master with the wetted surface of the impression paper, whereby some of the diazotizable amine compound and nitrite transfers

from the imaged portion of the master to the impression paper for reaction to form the azo dyestuff.

3. The method of producing copy with a master imaged with a composition containing a diazotizable amine compound present in an amount within the range of 20-75% by weight of the composition and an acidic medium for reaction to form nitrous acid of a metal nitrite, comprising the steps of wetting the surface of an impression paper with a fluid containing a solvent for the diazotizable amine compound and the acidic medium and which also contains a soluble nitrite and a coupler, and contacting the imaged surface of the master with the wetted surface of the impression paper, whereby some of the diazotizable amine and acidic medium is leached from the imaged portion of the master to the impression paper and reacts with the nitrite to form the azo dyestuff.

4. The method of producing copy with a master imaged with a composition containing a diazotizable amine and a coupler capable of reaction to form an azo dyestuff with the diazotized amine, comprising the steps of wetting the surface of an impression paper with a fluid containing a solvent for the diazotizable amine and coupler and which also contains a nitrite and an acidic medium for reaction with the diazotizable amine compound in the presence of nitrous acid, and contacting the imaged surface of the master with the wetted surface of the impression paper, whereby some of the diazotizable amine and coupler is leached for transfer from the imaged portion of the master to the impression paper and reacts with the nitrite to form an azo dyestuff.

5. The method of producing copy with a master imaged with a composition containing a diazotizable amine compound capable of reaction with a coupler to form an azo dyestuff, a coupler and an acidic medium, comprising the steps of wetting the surface of an impression paper with a fluid containing a solvent for the diazotizable amine, coupler and acidic medium and which also contains a nitrite, and contacting the imaged surface of the master with the wetted surface of the impression paper, whereby some of each of the dye-forming components in the imaged portion of the master are leached for transfer to the impression paper for reaction to form the dyestuff.

6. The method of producing copy with a master imaged with a composition containing an alkali metal nitrite present in a connection within the range of 1-15% by weight of the composition, comprising the steps of wetting the surface of an impression paper with a fluid containing a solvent for the nitrite and which also contains an acidic medium and a diazotizable amine salt capable also of acting as a coupler to form an azo dyestuff, contacting the image surface of the master with the wetted surface of the impression paper, whereby some of the nitrite is leached for transfer from the imaged portion of the master to the impression paper for reaction to form an azo dyestuff.

7. The method of producing copy with a master imaged with a composition containing an alkali metal nitrite present in a concentration within the range of 1-15% by weight, comprising the steps of wetting the surface of an impression paper with a fluid containing a solvent for the nitrite and also containing a diazotizable amine compound, a coupler, and an acid, and contacting the imaged surface of the master with the wetted surface of the impression paper, whereby some of the nitrite is leached for transfer from the imaged portion of the master to the impression paper for reaction to form the dyestuff.

8. The method of producing copy with a master imaged with a composition containing an alkali metal nitrite and a coupler capable of reaction with a diazo compound to form an azo dyestuff, comprising the steps of wetting the surface of an impression paper with a fluid containing a solvent for the nitrite and coupler and which also contains a diazotizable amine compound and an acid, and contacting the imaged surface of the master with the wetted surface of the copy sheet, whereby some of the

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nitrite and coupler is leached for transfer from the imaged portion of the master to the impression paper for reaction to form an azo dyestuff.

9. The method of producing copy with a master imaged with a composition containing an acidic medium and an amine compound capable of diazotization, comprising the steps of contacting the imaged surface of the master with an impression paper, wetting the surface of the impression paper, prior to contact with the imaged master and again subsequent to contact with the imaged master, with fluids, the first of which contains a solvent for the diazotizable amine compound and the acidic medium and the second of which contains a nitrite and a coupler for reaction with the diazotizable amine compound, to form an azo dyestuff.

10. The method of producing copy with a master imaged with a composition containing an alkali metal nitrite and a diazotizable amine compound present in an amount within the range of 20-75% by weight of the composition and capable of coupling reaction to form an azo dyestuff, comprising the steps of contacting the imaged surface of the master with an impression paper, and wetting the surface of the impression paper before and after contact with the imaged master with fluids, the first of which contains a solvent for the diazotizable amine compound and nitrite, and the second of which contains an acid and a coupler.

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References Cited in the file of this patent

UNITED STATES PATENTS

	831,582	Thorpe	Sept. 25, 1906
5	1,514,222	Murray	Nov. 4, 1924
	1,571,320	Clavel	Feb. 2, 1926
	1,646,296	Kirchseisen	Oct. 18, 1927
	1,825,342	Dreyfus et al.	Sept. 29, 1931
	2,146,976	Neidich	Feb. 14, 1939
10	2,217,349	Neidich	Oct. 8, 1940
	2,364,359	Kienle et al.	Dec. 5, 1944
	2,526,995	Clark	Oct. 24, 1950
	2,554,909	Holik	May 29, 1951
	2,596,756	Yutzy et al.	May 13, 1952
15	2,634,677	Klimkowski et al.	Apr. 14, 1953

FOREIGN PATENTS

193,646	Great Britain	Mar. 1, 1923
---------	---------------	--------------

OTHER REFERENCES

- Diserens: The Chemical Technology of Printing and Dyeing, 1948, Reinhold Pub. Co., N. Y. Only pp. 266 to 269.
- 25 Saunders: The Armatic Diazo Compounds, 2nd edition, 1949, Arnold & Co., London. Only pp. 95, 96 and 97.