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2,820,760

FLUID COMPOSITIONS FOR USE IN SPIRIT DUPLICATION

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This invention relates to the production of multiple copies by a spirit duplicating system and it relates more particularly to a new and improved fluid composition for use in wetting the surface of copy sheets to achieve the formation of a dye in the copy sheet by reaction between ingredients extracted from an imaged master in accordance with the concepts described and claimed in the copending application Ser. No. 287,616, filed on May 13, 1952, now Patent No. 2,748,024, of which this application is a continuation-in-part.

The improved process of the aforementioned copending application substantially eliminates what is considered to be the most objectionable characteristic in present spirit or hectographic duplicating systems—that is, the ease by which the dye color finds its way from the transfer sheet or from the imaged master onto the hands or the clothing of the operator whereby staining occurs and one's garments become soiled as an incidence to normal use of elements in the present processes. Numerous attempts have been made to eliminate or reduce the possibilities of staining and soiling such as by the surface coating of the transfer sheet with a wax composition or by modification of the surface portion of the dye by reaction with a base, such as ammonia, as in Holik, Patent No. 2,554,909, or by reaction with the entire dye component with an alkali to render the normally water soluble dye less soluble in water until reconverted by an acid, as in Neidich, Patent No. 2,146,976, but in each instance, staining by the transfer sheet continues to occur through the unprotected edges as an incidence to sheeting or stacking and the imaged master does not have the insolubilized or protected surface uppermost so that the objectionable features of staining or soiling occur as easily as in present hectograph or spirit duplicating systems.

The process described and claimed in the aforementioned copending application provides a duplicating process which differs basically from the processes heretofore developed in that no dye of any consequence is formed or contained in the transfer sheet or in the imaged master. It is formed substantially completely by reaction in the copy sheet where it is too late to cause any staining or soiling of the hands or clothing of the operator and the dye formed in the copy sheet may be of the insoluble type since no further transfer is necessary thereby to enable the production of copy more permanent in character and wholly free of color transfer value. This new and different process results from the system wherein the coating on the transfer sheet is formulated with less than all of the components necessary for reaction to form the dyestuff while the remainder to effect reaction is supplied as a component in the fluid with which the surface of the copy sheet is wet to cause dye formation to take place with components extracted from the imaged master to the copy sheet. While the dye formed in the copy sheets may be relatively water insoluble, the components in the transfer sheet and subsequently in the imaged master are adapted to be water or alcohol soluble for extraction in

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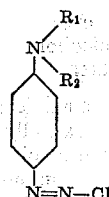
desired amounts from the master to the copy sheets for reaction.

In the practice of this invention a system is employed for the production of copy with an azo dyestuff. In such system, the transfer sheet may be formulated of a coating containing the diazo in which instance the fluid for wetting the copy sheets is formulated to contain an alkaline agent and a coupler for reaction with the diazo under alkaline conditions to form the azo dyestuff in the copy sheet, or the transfer sheet may be formulated to contain the coupler in the transfer coating whereby the fluid contains the alkali and the diazo for reaction with the coupler to form the particular dyestuff. In the preferred practice of this invention, the transfer coating is compounded to contain both the coupler and the diazo in desired proportions and the fluid with which the copy sheets are wet is adapted to contain only the solvent for extraction of the dye forming components from the imaged master and an alkaline agent which causes the coupler to combine with the diazo in formation of the dyestuff.

While some of the diazo compounds are incapable of reacting with the coupler until the alkali is present thereby to avoid dye formation in the transfer sheet or master, it is preferred to maintain acidic conditions in the transfer coating for adjustment of the pH below that at which coupling can take place to form the azo dyestuff. Dye formation in advance in the transfer sheet or in the imaged master not only would subject the operator to the possibility of soiling or staining as in the prior processes but the formed dye would be relatively insoluble and incapable of transfer to form copies except for insignificant amounts which might physically be transferred with the wax base from the imaged master to the copy sheets but in amounts insufficient to produce legible copy. With the azo system described, acidification to maintain the pH below 3.5 in the transfer coating is sufficient and the pH is usually held between 1.5 and 3.5.

Suitable couplers for use in the azo system described include the aromatic amines such as aniline, substituted aniline such as dimethyl aniline; phenolic compounds such as phenol, resorcinol, phloroglucinol, 2,3-dihydroxy naphthalene, 6-sulfonic acid and water soluble salts thereof; thio compounds such as thio-barbituric acid and cyano compounds such as cyanoacetamide.

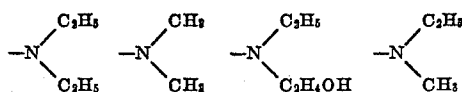
When the transfer coating is formed on the transfer base sheet at relatively low temperatures, such as from solvent solution or aqueous dispersion, any diazo capable of coupling to form an azo dye in alkaline medium may be used. It is preferred, however, to prepare the transfer sheet by application of the transfer coating composition as a hot melt onto the base sheet whereby the desirable concentration of materials and coating weights can be achieved in a single application with better control of the freedom with which the coating material is released from the base sheet to form the image on the master. When applied as a hot melt, it is preferred to make use of a diazo having the general formula



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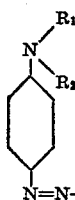
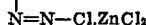
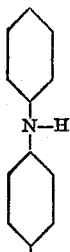
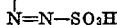
group comprises



and



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



Obviously it is necessary to make use of a new and different fluid composition for use in combination with masters imaged with materials of the type described in order to produce copy by reaction to form a relatively water insoluble azo dyestuff in the copy sheets and it is an object of this invention to provide fluid compositions of the type described for use in the production of copy with a master imaged with a composition containing both a coupler and a diazo, preferably in acidic medium.

In accordance with the practice of this invention, a new fluid composition is provided consisting essentially of an amine base soluble in alcohol and water and present in concentrations ranging from 4 to 10 percent by weight in the composition. The amine is dissolved in methanol or ethanol or mixtures thereof or other suitable alcohol which may contain up to 10 percent by weight of water. When less than 4 percent by weight of the amine base is dissolved in the alcoholic medium, the reaction to form the dyestuff is materially hindered and very often the reaction ceases before readable copy has been produced. With certain couplers, such as 2,4-diamino toluene dihydrochloride, the amount of amine base necessary to produce copy may be reduced to about 1 percent by weight.

As indicated in the foregoing description, the alcoholic medium may be replaced with a small amount of water which has been found to increase the intensity of the copy but the amount of water should not exceed 10 percent by weight.

The following broadly represents a fluid composition which may be used in the practice of this invention:

Example 1

4-10 percent by weight of an amine base
80-90 percent by weight alcohol
0-10 percent by weight water

It has also been found possible and desirable under a number of circumstances partially to substitute a small amount of the alcohol with a solvent of the type methyl Cellosolve (ethylene glycol monomethyl ether), ethyl Cellosolve (ethylene glycol monoethyl ether) or the like ethylene glycol ethers. When such substitution is made, the amount of Cellosolve should not exceed 5 percent by weight of the fluid composition. Thus a further modification of a fluid composition which may be used in the practice of this invention is represented by the following:

Example 2

4-10 percent by weight amine base
75-90 percent by weight alcohol
0-10 percent by weight water
1-5 percent by weight Cellosolve

Suitable amines as the alkaline component in the fluid composition include the alkyl amines of the type propylamine, benzylamine and the like; naphthyl amines such as cyclohexylamine; diamines and polyamines, such as ethylene diamine, hexamethylene diamine, triethylene tetramine and the like; ether amines such as morpholine; amino alcohols such as diethanolamine, diethyl amino ethanol, dimethyl amino ethanol, 2-amino 1-butanol, amino ethyl etherolamine, 2-amino 2-ethyl 1,3 propanediol, methyl diethanolamine, and i-propanolamine, or quaternary ammonium compounds such as tetra ethanol ammonium hydroxide, dimethyl ammonium dimethyl carbamate, dicoco dimethyl ammonium chloride, and morpholine.

The following will illustrate specific fluid compositions embodying features of this invention capable of use in the wetting of copy sheets to produce copy by reaction between the coupler and the diazo extracted from the image of a master:

Example 3

79 percent by weight methanol
10 percent by weight water
8 percent by weight diethanolamine
3 percent by weight Cellosolve

Example 4

83 percent by weight methanol
6 percent by weight ethylene diamine
10 percent by weight water

Example 5

70 percent by weight methanol
10 percent by weight ethanol
5 percent by weight diethanolamine
5 percent by weight morpholine
10 percent by weight water

Example 6

8 percent by weight tetraethanol ammonium hydroxide
5 percent by weight water
80 percent by weight methanol
7 percent by weight ethanol

Example 7

4 percent by weight diethanolamine
91 percent by weight methanol
5 percent by weight Cellosolve

Example 8

6 percent by weight cyclohexylamine
10 percent by weight water
3 percent by weight propylamine
81 percent by weight methanol

In practice, an imaged master is formed by transfer from a manifold sheet coated with a composition represented by the following examples:

Example 9

11.0 percent by weight Carbowax
15.0 percent by weight oxidized microcrystalline wax
27.5 percent by weight mineral oil
27.0 percent by weight p-diazo dimethyl aniline zinc chloride
18.0 percent by weight 2-amino, 5-naphthol, 7-sulfonic acid
1.5 percent by weight sodium oleate

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Example 10

11.0 percent by weight Carbowax
 15.0 percent by weight oxidized microcrystalline wax
 28.0 percent by weight mineral oil
 20.0 percent by weight p-diazo diethyl toluidine zinc salt
 24.5 percent by weight 1-amino, 8-naphthol, 3,6-disulfonic acid
 1.5 percent by weight sodium oleate

Example 11

5 percent by weight Carbowax
 20 percent by weight microcrystalline wax
 15 percent by weight paraffin wax
 20 percent by weight petrolatum
 20 percent by weight p-diazo dimethyl aniline zinc chloride
 20 percent by weight 1-amino, 8-naphthol, 4-sulfonic acid

Example 12

15 percent by weight microcrystalline wax
 15 percent by weight paraffin wax
 30 percent by weight petrolatum
 30 percent by weight p-diazo dimethyl aniline zinc chloride
 10 percent by weight 2,4-diamino toluene dihydrochloride

For description of manufacture of the transfer sheet and the preparation of an imaged master therefrom, reference may be had to the aforementioned copending application.

The imaged master which is free of any color transfer value or any dye color is mounted in a standard spirit duplicating machine and any one of the fluid compositions of Examples 1-8 may be used in the machine to wet the surface of the copy sheets immediately prior to engagement with the imaged surface of the master. The alcoholic solvent medium functions to dissolve a portion of the coupler and diazo from the master and upon transfer to the copy sheet is caused to react in the basic medium to form the azo dye-stuff in the imaged areas of the copy sheet. This reaction to form the dyestuff may take place relatively quickly but the intensity of the dye color is substantially increased upon standing, especially when allowed to remain in the stack whereby the evaporation of solvent is substantially retarded.

It will be understood that when the transfer coating

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contains only one of the components for reaction to form the dyestuff, the other component may be supplied as a further ingredient in a fluid composition of the type described.

It will be further understood that the materials described and claimed herein to form the fluid composition combine in a true solution so that the technique and order of combining the ingredients to form the composition is unimportant and that various systems may be used to apply the fluid composition onto the surface of the copy sheet without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. A composition for application to copy sheets in a spirit duplicating process to produce copy with diazo and coupler extracted from the imaged portion of a duplicating master, the fluid composition consisting essentially of 4-10 percent by weight of an amine base soluble in alcohol and water, 80-90 percent by weight alcohol selected from the group consisting of ethanol and methanol and up to 10 percent by weight water.

2. A composition for application to copy sheets in a spirit duplicating process to produce copy with diazo and coupler extracted from the imaged portion of a duplicating master, the fluid composition consisting essentially of 4-10 percent by weight of an amine base soluble in alcohol and water, 75-90 percent by weight alcohol selected from the group consisting of ethanol and methanol up to 10 percent by weight water and 1-5 percent by weight ethylene glycol monoethyl ether.

3. A composition for application to copy sheets in a spirit duplicating process to produce copy with diazo and coupler extracted from the imaged portion of a duplicating master, the fluid composition consisting essentially of 4-10 percent by weight of an amine base soluble in alcohol and water, 75-90 percent by weight alcohol selected from the group consisting of methanol and ethanol and mixtures thereof, up to 10 percent by weight water, and from 5-10 percent by weight of an ethylene glycol monoethyl ether.

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