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2,743,191

METHOD FOR MANUFACTURING TRANSFER SHEETS FOR SPIRIT DUPLICATION

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No Drawing. Original application May 13, 1952, Serial No. 287,616. Divided and this application August 13, 1952, Serial No. 304,207

6 Claims. (Cl. 117—36)

This invention relates to a new spirit duplicating system for the production of multiple copies and it relates more particularly to a method for the manufacture of transfer sheets to be used in the production of duplicating masters from which multiple copies are secured. More specifically, this invention comprises a division of our copending application Ser. No. 287,616, filed on May 13, 1952.

In the aforementioned copending application, description is made of a new and improved spirit duplicating and hectographic process in which reaction to form a dyestuff in the production of copies takes place in the copy sheets upon passage through the duplicating machine so that the process is entirely free of the staining or soiling characteristic of present hectographic or spirit duplicating systems. In present systems, the transfer sheet or ink ribbon is compounded with a water and alcohol soluble basic dyestuff of the type crystal violet, Victoria green and the like. These dyestuffs are colloidal in character so that many difficulties are encountered in compounding the coating composition and application thereof to form the transfer sheet without contamination of the surrounding atmosphere and spread of dye onto the hands and clothing of the various operators. The transfer sheet in the master set and its use in the duplicating machine to produce copies raises still further problems of contamination with respect to the operator's hands and clothing with dyestuff which seemingly spreads and resists removal.

Many attempts have been made to obviate the color transfer value of the dyestuff in the transfer sheets and in the formed master. Various coatings have been applied to the surface of the transfer sheet in order to protect the operator but dyestuff is invariably removed upon contact with the master sheet to make corrections and the image formed on the master presents an unprotected surface identical to that of the conventional master. Other more recent modifications to obviate this problem of staining or soiling in the practice of present hectograph and spirit duplicating systems include attempts to insolubilize the surface portion of the transfer coating by reaction of the basic dyestuff with ammonia, as in the Holik Patent No. 2,554,909, but the image master again presents an unprotected surface and dye transfer from the imaged master occurs as readily as in present systems and dye transfers onto the hands and clothing of the operator merely by abrasion with the transfer sheet or contact with the cut edges during stacking or the like.

The problem of contamination is faced more directly by Neidich in Patent No. 2,146,976. Neidich attempts to overcome the ability of the dye to transfer to the hands of the operator by converting the dyestuff to a phase which is less soluble in water so that transfer will not as easily occur onto the moist hands or clothing which come in contact therewith. However, the dye base is capable of transfer by rubbing or by engagement of the hand with cut edges upon stacking and then a more difficult problem is presented because the less soluble dye

base presents the additional problem of removal. The system of Neidich corresponds with that of Holik previously described who reacts the water soluble dye with ammonia to form the base and thereby presents a less soluble surface. In both of these systems the transfer sheet is formed with a dye but in Neidich the dye is less soluble in water until reacted with acid and then the dye becomes a conventional water soluble dye capable of transfer in aqueous or in alcoholic medium. Before reaction with the acid the dye base is capable of transfer in alcoholic medium to form copies as in normal spirit duplicating systems.

Briefly described, in the process forming the subject matter of the present application, a dyestuff is not formed in the transfer sheet or in the master for transfer to the copy sheets but is formed substantially in its entirety by reaction in the copy sheets so that the dye is produced at a stage incapable of contamination of the operator and, when produced in the copy sheets, the dyestuff is in a substantially insoluble phase less likely to transfer or deteriorate even under humid conditions. In practice, the coating on the transfer sheet is formulated with less than all of the components from which an azo dyestuff is formed, such as the coupler, a diazo, or both, but when both are present in the transfer coating, the conditions are such as to forestall reaction therebetween to form the dyestuff until alkaline conditions are supplied in the fluid with which the copy sheets are wet prior to contact with the imaged master. Thus the coupling agent and diazo transferred from the imaged master to the copy sheets are able to react in the copy sheet to form the dyestuff. When the transfer coating contains only the coupler, the fluid is formulated not only to contain the alkali but also the diazo. When the transfer coating contains the diazo, then the fluid containing the alkali is formulated also to contain the coupler for reaction with the diazo to form the dyestuff in the copy sheets. Instead of supplying the missing components in the fluid for reaction with the component or components in the transfer coating or imaged master, the additional component for reaction to form the dyestuff may be supplied as a substance embodied in the copy sheets, as by impregnation or as an ingredient in the slurry from which the copy sheets are formed, or in a fluid applied to the surface of the copy sheets after contact with the imaged master. In any event, the transfer coating and the imaged master are completely free of color transfer and the dyestuff is formed principally in the copy sheets. Even then, the dyestuff is not formed immediately but reaction appears to take place slowly whereby the copy appears to develop on standing after the copy sheets have passed through the machine.

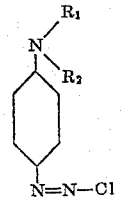
The invention described and claimed herein resides chiefly in the manufacture of transfer sheets used to produce the imaged master and it is an object of this invention to provide a new and improved method for manufacture of transfer sheets of the type described.

In order to produce a good image on the master for use in the manufacture of a large number of copies, it has been found desirable to prepare a transfer coating which is relatively poorly bonded to the base sheet so as to enable substantially complete release of as much material as possible to the master surface and with sufficient sharpness to produce copy of good quality. Further, it has been found that to produce a master capable of use in the manufacture of hundreds of copies of good quality, it is desirable also to load as much of the active ingredients for producing the image as is possible to incorporate in the transfer coating consistent with the ability of the carrier, such as the wax base, to maintain continuity in the coating for reproduction purposes. It has been found that to produce acceptable copy in the

amounts of one hundred or more from the imaged master, concentrations of the coupler and diazo alone or in combination in the transfer coating should correspond to not less than about 20 percent by weight of the coating up to about 50 percent by weight of the coating. When both elements are combined in the transfer coating, the amount of the active ingredients may be increased to about 75 percent by weight of the coating composition.

It has been found further that these characteristics are best embodied in a transfer coating applied to the base sheet in the form of a hot melt wherein an excess of the coating composition in molten form is applied to the surface of the base paper and then the excess is removed with a doctor knife or the like to smooth the coating and produce a continuous layer of uniform thickness.

When the transfer coating is formulated to contain only the coupler for reaction with the diazo in the fluid or in the copy sheet or after applied to the copy sheet, limitation as to temperature and conditions for coating are not so important. When the diazo is incorporated alone or in combination with the coupler in the transfer coating, then it is important to maintain the temperature of the melt below 90–95° C. unless certain stabilizers are present and to make use of diazos which are not destroyed by such temperatures. To the present diazo materials capable of use in compositions for application as a hot melt are found to have the general formula



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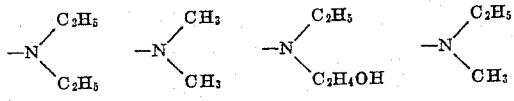

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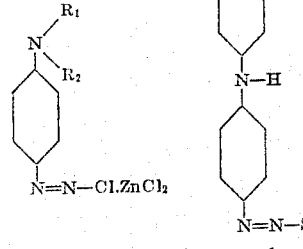
It has been found that the stability of the diazo dye forming components is vastly improved when embodied in the treating composition as their corresponding zinc chloride or sulfonic acid salts such as



For purposes of economy in reproduction and for purposes of simplicity in the process, it is desirable to incorporate the more expensive ingredients, such as the coupler and the diazo, in the transfer sheet for use in the preparation of the imaged master from which multiple copies are produced. While some of the diazo compounds remain unreactive in the presence of couplers until the alkali is applied with the fluid, it is better to maintain acidic conditions in the transfer coating as by the addition of acidic medium to maintain the pH of the composition below that at which coupling can take place to form the azo dyestuff. With the basic dyes of the azo type, coupling will generally not take place below a pH of about 3.5. In the coating composition it is preferred, for purposes of stabilization, to formulate the coating for a pH between 1.5 and 3.5.

Compounds capable of use as couplers with the diazo in accordance with the practice of this invention are somewhat limited in character. Generally such couplers should be capable of removal of a hydrogen atom for combination with the chloride ion of the diazo compound to form the dyestuff. Such reactions are secured by the use of aromatics having amine groups such as aniline and substituted aniline like dimethyl anilin, or phenolic compounds such as phenol, resorcinol, phloroglucinol, 2,3-dihydroxy naphthalene, 6,sulfonic acid and water soluble salts thereof and the like, or thio compounds such as thio-barbituric acid or cyano compounds such as cyanoacetamide.

The following will illustrate the practice of this invention in the manufacture of a transfer sheet embodying the coupler and diazo which are reacted to form the azo dyestuff in the copy sheets:

Example 1

5.0 percent by weight carnauba wax
20.0 percent by weight of microcrystalline wax
15.0 percent by weight paraffin wax
20.0 percent by weight of petrolatum
20.0 percent by weight p-diazo diethyl aniline zinc chloride
20.0 percent by weight 1,amino-8,naphtol-4,sulfonic acid

Example 2

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

The following examples will illustrate the practice of this invention in the manufacture of a transfer sheet embodying the coupler only or the diazo only for reaction with the other in the presence of the base and supplied with the fluid to form the dyestuff in the copy sheets:

Example 3

8.0 percent by weight carnauba wax
11.0 percent by weight oxidized microcrystalline wax
3.0 percent by weight polybutene
6.0 percent by weight petrolatum
17.0 percent by weight mineral oil
55.0 percent by weight p-diazo diethyl aniline zinc chloride

Example 4

8.5 percent by weight carnauba wax
14.0 percent by weight oxidized microcrystalline wax
12.0 percent by weight dark petrolatum
15.5 percent by weight mineral oil
50.0 percent by weight p-diazo ethyl hydroxyethyl aniline zinc chloride

Example 5

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

Example 6

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

Example 7

8.5 percent by weight carnauba wax
14.0 percent by weight oxidized microcrystalline wax
12.0 percent by weight petrolatum
15.5 percent by weight mineral oil
50.0 percent by weight phloroglucinol

The following example will illustrate the practice of this invention in the manufacture of a transfer sheet embodying the coupler and the alkali for use in the manufacture of the azo dyestuff in the copy sheets upon reaction with the diazo contained in the fluid:

Example 8

5.0 percent by weight carnauba wax
20.0 percent by weight microcrystalline wax
15.0 percent by weight paraffin wax
15.0 percent by weight petrolatum
35.0 percent by weight phloroglucinal
10.0 percent by weight triethanol amine

In each of the above examples, the coating composition is ground to achieve uniform distribution with the wax base carrier in a roller mill and, at the same time, it is possible to heat the composition to a temperature of about 80–90° C. for the purposes of reducing the composition to molten condition. Application is made of the hot melt to a base sheet in the form of a web of paper to achieve a relatively nonadherent coating in weights of about 15–20 pounds per 3,000 square feet of surface area. The hot melt is applied over the surface of the web in excess of the coating weight required and then the excess is removed by a doctor blade or the like. The coating composition becomes soft and flexible upon cooling to room conditions but is substantially incapable of offset unless forces are applied to cause displacement of the coating onto a receptive surface in contact therewith.

The coated web is sheeted and positioned with the coated side adjacent the master sheet in a formed master set. When the opposite side of the master is inscribed or impacted as by die impression or by a typewriter key, the coating in the impression areas transfers from the base sheet to the adjacent surface of the master sheet in reverse image. Instead of impression forces to effect transfer, thermal forces may be employed such as are made available by the process described and claimed in the copending application of Allan I. Roshkind, Ser. No. 273,530, filed on February 26, 1952, to produce the imaged master directly from an original. Thereafter, the master may be mounted in the duplicating machine for subsequent engagement with copy sheets, wetted with a suitable fluid to cause transfer of fractional portions of the dye forming components from the imaged master to the copy sheet where such components are caused to react and form the dyestuff.

When the master is prepared of a transfer sheet in which the coating corresponds to the compositions of Examples 1 and 2, the fluid with which the copy sheets are wet may be formulated as follows:

Example 9

0.5 percent by weight phloroglucinol
5.0 percent by weight b-naphthol
2.0 percent by weight diethanol amine
92.5 percent by weight methanol

Example 10

5.0 percent by weight phenyl methyl pyrazolone
2.0 percent by weight diethanol amine
93.0 percent by weight methanol

Example 11

2.0 percent by weight potassium hydroxide
98.0 percent by weight methanol

When the transfer coating is prepared with the compositions of Examples 3–7, the fluid with which the copy sheets are wet may be formulated of the following:

Example 12

5.0 percent by weight 2,3-dihydroxy naphthalene, 6-sulfonic acid
8.0 percent by weight diethanol amine
10.0 percent by weight water
77.0 percent by weight methanol

Example 13

3.0 percent by weight phloroglucinol
2.0 percent by weight resorcinol
1.0 percent by weight sodium hydroxide
94.0 percent by weight ethyl alcohol

When the transfer sheet is formulated to contain the coupler, as in Example 8, the fluid used to wet the copy sheets may be formulated of the following:

Example 14

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

The specific composition of the base in which the azo dye forming component is embodied in the manufacture of a transfer sheet may be formulated of waxy materials in various combinations including carnauba wax, microcrystalline wax, paraffin wax, and the like, preferably in combination with softening or plasticizing agents such as mineral oils, fatty acids and the like. Modification to improve the strength and the film forming characteristics may be made by the addition of small amounts of polyethylene, polybutene and other polymeric compounds formed by addition polymerization and other materials capable of miscibility with the waxy substances to form a stable composition. The composition for preparation of the transfer coating should be capable of providing a continuous layer having the characteristics of transferability to adjacent surfaces responsive to impression forces or previously described thermal forces and it is preferred to form the composition with materials having slight solubility in spirit solvents so as continuously to cleanse the surface of the imaged master during the production of copy.

While it is preferred to apply the composition of the transfer coating as a hot melt, it may be possible to achieve the desired formation of the transfer layer by application of the materials in corresponding proportions from solvent solutions or aqueous emulsions. However, the cost and dangers involved for the elimination of such solvents and the necessity for the application of multiple coatings to achieve the desired coating weights makes it highly undesirable to employ such systems but, when such solvent or emulsion systems are employed, limitation as to the type of diazo stable at elevated temperatures is not so critical so that use of other diazo systems for the production of various colors in the copy sheets may be employed.

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

Example 15

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

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

Example 16

4.0 percent by weight potassium dichromate
1.0 percent by weight nitric acid
45.0 percent by weight ethanol
50.0 percent by weight methanol

Example 17

Carbon coating composition:

33.0 percent by weight polyethylene glycol having an average molecular weight of 6000–7500 (Carbowax 6000)
33.0 percent by weight polyethylene glycol having an average molecular weight of 1500 (Carbowax 1500)
34.0 percent by weight phenolphthalein

A fluid for use in combination with the composition of Example 17 and with which the copy sheet may be wetted to form the dye color therein is formulated of the following:

Example 18

1.0 percent by weight sodium hydroxide
99.0 percent by weight ethyl alcohol

Example 19

Carbon coating composition:

33.0 percent by weight polyethylene glycol having an average molecular weight of 6000–7500 (Carbowax 6000)
33.0 percent by weight polyethylene glycol having an average molecular weight of 1500 (Carbowax 1500)
17.0 percent by weight sodium persulphate ($Na_4S_2O_8$)
17.0 percent by weight p-phenylenediamine

A fluid composition for use in wetting a copy sheet to develop a dye therein by reaction with the active ingredient in the imaging composition of Example 19 may contain the following:

Example 20

20.0 percent by weight aniline
80.0 percent by weight glacial acetic acid

It will be understood that the transfer sheets formed by the method described and claimed herein constitute a new and improved article of manufacture and that changes may be made in the specific formulations and methods of application within the limitations defined to produce the transfer sheet without departing from the spirit of the invention, especially as defined in the following claims.

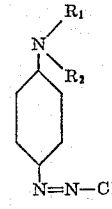
We claim:

1. The method of preparing a transfer sheet of the type described comprising the steps of formulating a coating composition having a wax base and from 20 to 75 percent by weight of a water and alcohol soluble diazo dye intermediate stable at temperatures up to and including the temperature of the wax melt, heating the composition to a molten stage, and applying the hot melt onto a base sheet to form a continuous layer which is poorly bonded to the base sheet.

2. The method of preparing a transfer sheet of the type described comprising the steps of formulating a

coating composition comprising a wax base and containing a high proportion of a diazo dye intermediate stable at temperatures up to 95° C. and lacking in color transfer value and a coupler capable of reaction with the diazo at pH's above 3.5 to form a diazo dyestuff, the composition being acidified to maintain the pH below 3.5, heating the composition to a temperature below 95° C. to reduce the composition to a molten state and applying the hot melt onto a base sheet to form a continuous coating which is poorly bonded to the base sheet.

3. The method of preparing a transfer sheet of the type described comprising the steps of formulating a coating composition having a wax base and from 20 to 75 percent by weight of a water and alcohol soluble diazo having the general formula



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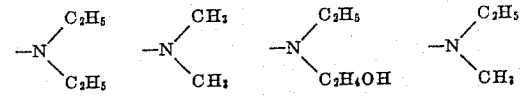
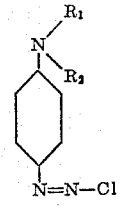


and

and the stabilized salts thereof heating the composition to a molten state, and applying the hot melt onto a base sheet to form a continuous layer.

4. The method of preparing a transfer sheet of the type described comprising the steps of formulating a coating composition comprising a wax base and containing a high proportion of a diazo having the general formula



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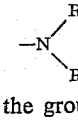

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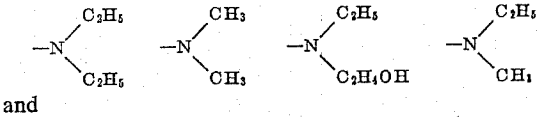


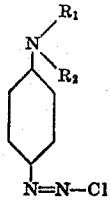
and

and the stabilized salts thereof, and a coupler capable of

reaction with the diazo at pH's above 3.5 to form a diazo dyestuff, the composition being acidified to maintain the pH below 3.5, heating the composition to a temperature below 95° C. to reduce the composition to a molten state and applying the hot melt onto a base sheet to form a continuous coating which is poorly bonded to the base sheet.

5. The method of preparing a transfer sheet of the type described comprising the steps of formulating a coating composition comprising a wax base and containing a high proportion of a diazo dye intermediate stable at temperatures up to 95° C. and lacking in color transfer value and a coupler capable of reaction with the diazo at pH's above 3.5 to form a diazo dyestuff and selected from the group of aromatic compounds consisting of aromatic amines, phenols, aromatic thio compounds and aromatic cyano compounds, the composition being acidified to maintain the pH below 3.5, heating the composition to a temperature below 95° C. to reduce the composition to a molten state and applying the hot melt onto a base sheet to form a continuous coating which is poorly bonded to the base sheet.

6. The method of preparing a transfer sheet of the type described comprising the steps of formulating a coating composition comprising a wax base and containing a high proportion of a diazo having the general formula



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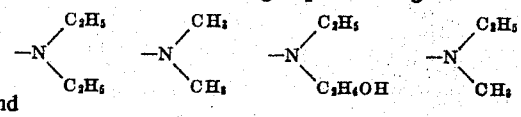

and

and the stabilized salts thereof, and a coupler capable of reaction with the diazo at pH's above 3.5 to form a diazo dyestuff and selected from the group of aromatic compounds consisting of aromatic amines, phenols, aromatic thio compounds and aromatic cyano compounds, the composition being acidified to maintain the pH below 3.5, heating the composition to a temperature below 95° C. to reduce the composition to a molten state and applying the hot melt onto a base sheet to form a continuous coating which is poorly bonded to the base sheet.

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