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COLOR REACTION TYPE DUPLICATION PROCESS

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The invention relates to a method of duplicating, and more particularly relates to a method of duplicating wherein an impression sheet and a master sheet having an image thereon are contacted and a reproduction of the image is formed on the impression sheet by the reaction of a component in the image material with a component on the impression sheet.

Various materials have been suggested for use in the image material and on the impression paper for bringing about a chemical reaction that will produce a color, the term "color" being used herein to include black. Many of the materials have been suitable for producing one or two copies of good color intensity, and some have produced by hand methods several copies of fair color intensity. However, so far as is known a large number of high intensity copies by a color reaction process has not been attained by duplicating machines, due at least in part to the short time of contact of the master sheet and impression sheet required by such machines, to the small amount of liquid used, and also in general to the pressure of contact being less in the machine process than in the hand process. In those instances in which oleaginous or other hydrophobic material is present with the color reactant, the attaining of a large number of high intensity copies is particularly difficult even by hand methods.

An object of this invention is to provide a new and commercially valuable duplicating process.

Another object of this invention is the provision of a method of producing a large number of high intensity copies on a duplicating machine by a color reaction type of duplicating process.

Another object is the provision of a method of obtaining a large number of high intensity copies by a color reaction duplicating process in which the image on the master copy is formed of a color reactant mixed with an oleaginous material.

A further object is to provide a method of producing black copies without discoloration of the copy paper.

Other objects and advantages of the invention will become apparent as the following description progresses.

In accordance with one embodiment of my invention a master sheet having an image formed of a composition containing a nickel salt is contacted with copy sheets moistened with a solution of rubeanic acid (dithio-oxamide) in a solvent for the nickel salt. Black reversed reproductions of the image are obtained on the copy sheets.

For machine duplication and the production of a large number of high intensity copies (improved black with rubeanic acid and nickel salts) there is incorporated in the color reactant solution an alkanol amine, or an ammonium or amine salt of a weak acid such as ammonium acetate or ammonium citrate, or an alkanol amine acetate or citrate. With solutions which are largely non-aqueous best results are obtained with alkanol amines such as diethanol amine, triethanol amine and dimethanol amine or the weak acid salts thereof. These materials initiate complex formation of the metal with the rubeanic acid and

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facilitate control of the shade of color. They are preferably used in solutions having pH of from 4 through 8.

Instead of using the nickel salt in the image material and the rubeanic acid on the copy sheet, the nickel salt may be used on the copy sheet and the rubeanic acid in the image material.

Also instead of moistening the copy sheet with a solution of the rubeanic acid or nickel salt, the reactant may be coated on the copy sheet either by surface coating or by impregnation of the sheet or the pulp from which it is made.

Similar results to those obtained with rubeanic acid and nickel salts, but not the preferred black copies, may be obtained with rubeanic acid and other heavy metal salts such as copper, cobalt, and also with alkyl dithiooxamides such as monomethyl and diethyl oxamides and heavy metal salts. Also glyoximes with heavy metal salts, particularly nickel, have given good results, and have been improved for machine duplication purposes by the use therewith of alkanol amines. Mixtures of these various color reactants may be used, one particularly advantageous mixture being the mixture of rubeanic acid and glyoxime reacted with a nickel salt to give reddish-black copies.

The alkanol amines and their weak acid salts are particularly useful in all processes wherein heavy metal salts, and particularly nickel salts, are reacted with color reactants such as dithio-oxamides and glyoximes in non-aqueous or largely non-aqueous solvents. The use of transfer liquids which contain only small proportions of water is an advantage in reducing curling of copy paper, and moreover, for rubeanic acid duplicating processes wherein one solution is used for both transfer and color reaction or development, it becomes necessary to keep the water content low in order to maintain the rubeanic acid in solution.

The alkanol amines, even in largely aqueous solution, have the advantage that they greatly increase transfer, especially of nickel salts, and apparently act as combined transfer fluids and buffering agents.

With solutions which are largely aqueous other buffering agents may be used, the most suitable being the ammonium salt buffers such as ammonium acetate and ammonium citrate. Also other materials which aid transfer may be used with them, as for example, surface active agents. However, since rubeanic acid is not soluble in water, it then becomes advisable to use a two-step process in which the surface active material is first applied to the impression paper, the impression paper applied to the master sheet to bring about transfer of the image material, and then rubeanic acid in its solvent applied to the impression paper to develop the color. However, when diethanolamine is used the diethanolamine is dissolved in an aqueous solution containing a major proportion of ethyl and/or methyl alcohol, this solution mixed with a solution of rubeanic acid in tetrahydrofurfuryl alcohol, and the resulting mixture applied to the impression paper, which is then contacted with the image on the master sheet. Due to the fact that there is a slow decomposition of rubeanic acid in the presence of diethanol amine, it is preferable to mix the two ingredients immediately before applying to the impression paper.

The preferred solvent for the rubeanic acid is tetrahydrofurfuryl alcohol. This was found to be the best non-toxic solvent. Acetone may also be used, but this is not as good a solvent as the tetrahydrofurfuryl alcohol, and is also somewhat of a fire hazard. Tetrahydrofuran is a good solvent for rubeanic acid but has the disadvantage of being more volatile than is generally desirable for office duplication.

The preferred heavy metal salts are the water soluble salts, particularly the chlorides and sulfates, although

the acetates and other salts may be used. With rubeanic acid and its homologues, particularly satisfactory results have been obtained with nickel chloride and nickel sulfate. Nickel sulfate has the advantage over the chloride of being less hygroscopic.

The image material may be made of various formulae, and may be applied to the master sheet in several ways. Preferably the image material comprises a mixture of the color reactant with hydrophobic material such as wax and oil. In order to obtain increased copy strength the composition may also comprise a hydrotropic material such as the alkali metal salts of xylene, benzene, toluene and p-cymene sulfonic acids. In order to obtain good dispersion of the color reactant, particularly the inorganic color reactant with the oleaginous materials, a dispersing or emulsifying agent may also be used. The non-ionic and cationic surface active agents give more uniform and stable dispersions than the anionic type and are therefore preferred. The buffering agent may be included in the image material. Pigments, fillers and the like also may be added, if desired.

The image material may be applied in the form of an image to the master sheet in several ways. For example, the image material may be coated on a ribbon to form a typewriter ribbon and the image produced on the master sheet by direct typing. In this case a duplicating machine would be used having an offset blanket which would receive a negative impression from the original image impression on the master. Color reactant would then be applied to a series of impression sheets and the impression sheets contacted with the image on the blanket so that each sheet picks up from its negative a corresponding positive impression. Instead of using an ordinary rubber or like offset blanket a hectograph blanket may be used.

In the preferred embodiment of the invention, the image composition is coated on a paper sheet to produce an impression transferable transfer sheet or carbon paper. Suitable carbon paper of this type is made by mixing a small proportion of the color reactant with any of the oleaginous compositions used to make ordinary carbon paper, preferably also using, as above pointed out, hydrotropic material and/or nonionic or cationic dispersing agents. Examples of suitable carbon paper and typewriter ribbon formulae are given below. This carbon paper may be used to produce positive image impressions on a master sheet which may be used for offset duplication but preferably to produce on a master sheet a negative or mirror reverse image of the matter to be duplicated. The method of doing this is well known in the hectograph and spirit process duplicating art, and involves simply the placing of a sheet of paper against the coated surface of the suitably prepared carbon paper, and then typing or writing on the side of the sheet of paper which is not in contact with the carbon paper. The typing may be carried out with an ordinary ribbon in the typewriter. The pressure of the type as the writing takes place causes a mirror reverse or negative impression image to be made on the surface of the sheet in contact with the carbon paper coating. This sheet, called the master sheet, is placed on the drum of a direct process duplicating machine and copies made in the usual manner by contacting copy paper moistened with a solution of the reagent which reacts with the reagent in the image material on the master. In the preferred embodiment of the invention, the color reactant in the image material is a water soluble nickel salt and the reagent which is applied to the paper is rubeanic acid.

There are described below a number of typical formulae for carbon paper, typewriter ribbons and writing inks. These formulae are merely illustrative of types of image material or inks which may be used in carrying out this invention, it being understood that these formulae illustrate several embodiments which have given

satisfactory results and are not intended to restrict the invention thereto.

I. FORMULA FOR COATING TYPEWRITER RIBBON OR CARBON PAPER

Item No.	Ingredients	Batch Charge, grams	Pounds per 1,000 pounds ink
1	Nickel sulfate hexahydrate	180	600
2	Alkaterge C (substituted oxazoline)	3	10
3	Gum Arabic	3	10
4	Red Z Oil	51	170
5	Carnauba Wax	33	110
6	Beeswax	6.1	20
7	Lanolin	9	30
8	Sugar	15	50
9	Castor Oil	14	
10	Sodium-p-cymene sulfonate	15	
11	Red Z Oil	3	

¹ Charge for each 100 grams of base ink from items 1 to 8.

Red Z oil in the above table is a mineral oil of A.P.I. gravity 29.3, viscosity 195 seconds Saybolt at 100° F.

The procedure for making carbon paper using the above formula is as follows:

(a) The two grinding rolls of a three roll paint mill are heated to approximately 200° F. by passing water at 200° F. through the rolls. The hot water is supplied by mixing steam and cold city water. The temperature is controlled by a mixing valve.

(b) The materials including items one to eight only are added to the mill and grinding started. Shortly after starting the mass becomes fluid. The rolls are set so that a heavy film of liquid is carried on the rolls. After about fifteen minutes all the batch is taken off the cold roll, which is kept cool by circulating cold city water. The dope is put back on the mill, allowed to melt down, then taken off again. When this operation is repeated about three times, the batch is well mixed. If not, the operation is continued until the ink is thoroughly mixed.

(c) The dope is weighed and put back on the hot mill. Items 9 to 11 then are added. The charge is based on each 100 grams of base ink obtained from the above operation. Milling is continued until the particle size has been reduced to seven gauge or less.

(d) The ink taken off the cold roll is flaky in appearance and is ready for coating.

(e) An aliquot (3 to 4 grams) of the ink is melted down on a hot plate held at 190–200° F. The molten ink is poured directly onto the paper of the coating machine heated to 180° F. (The platform and knife are both held at this temperature by electrical heating elements built into the machine.)

(f) The paper is slowly pulled through the coater and allowed to cool to room temperature and stand overnight before testing.

The duplicating may be carried out using any of the well known spirit process duplicating machines modified by having the fluid tank and pump replaced by two smaller tanks and pumps. Metal parts of the machine contacted by the fluid are preferably made of aluminum or stainless steel. The outlet of each pump is attached to a T-tube.

In the preferred process of this invention involving the use of rubeanic acid as the color reactant or developer to be applied to the impression sheet and the use of diethanolamine as the buffer and transfer fluid, the rubeanic acid and the diethanolamine are mixed together immediately before applying to the impression paper.

A suitable diethanolamine composition is as follows:

Parts by volume	
Water	60
Methanol	20
Diethanolamine	20

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A suitable rubeanic acid composition is as follows:

Tetrahydrofurfuryl alcohol -- 40 parts by volume.
Diethylene glycol ----- 40 parts by volume.
Methanol ----- 20 parts by volume.
Rubeanic acid ----- 2 grams per 100 cc. fluid.

Instead of mixing the two solutions together and applying the mixed solution to the copy sheets, the process may be carried out in two steps, consisting of first applying to the copy paper a transfer fluid which will dissolve and transfer a portion of the color reactant of the image material to the paper, and then applying to the treated paper a developing fluid containing an ingredient which reacts with the transferred color reactant to produce a color. A suitable transfer fluid consists of water 30 parts, diethanolamine 10 parts, diethylene glycol 20 parts, tetrahydrofurfuryl alcohol 20 parts, and methanol 20 parts, all by volume. A suitable developing solution consists of a 2% solution of rubeanic acid and a mixture of tetrahydrofurfuryl alcohol 40 parts, diethylene glycol 20 parts, and methanol 20 parts, all by volume.

In the above compositions water, diethanolamine and rubeanic acid are the most important components of the combined fluids. Elimination of any one results in greatly decreased intensity of the copies. Diethylene glycol and tetrahydrofurfuryl alcohol adds slightly to copy intensity. Substitution of acetone for tetrahydrofurfuryl alcohol has little or no effect on copy intensity and greatly increases drying speed of the copy.

The proportions of the above ingredients may be varied widely. The rubeanic acid may be used in a 1% or less solution in a solvent, and the amount of rubeanic acid solution required for satisfactory copy intensity is of the order of 5 cc. per 20 copies.

The following example illustrates another ink formulation and another transfer fluid and development fluid which has also been found to be satisfactory.

II. INK FORMULATION

1. Bill of materials

Item No.	Ingredients	Batch Charge, grams	Pounds per 1,000 pounds ink
1-----	Nickel sulfate hexahydrate....	165	550
2-----	Alkaterge O (substituted oxazoline).	3	10
3-----	Triethylene glycol.....	3	10
4-----	Red Z Oil.....	72	240
5-----	Carnauba Wax.....	33	110
6-----	Beeswax.....	6	20
7-----	Gum Arabic.....	3	10
8-----	Sodium bicarbonate.....	15	50

2. Procedure

The procedure is essentially the same as that described in part I. The ingredients are weighed and added at once onto a hot mill and milled to a seven gauge or less by allowing the material to melt down, grinding for a short while and taking off the cold roll. This is repeated until mixing and grinding is complete.

The preparation of carbon papers is the same as in part I.

The major differences in this process compared to that described in part I are the type of fluids employed and the procedure for making copies.

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(a) Fluid composition:

Transfer fluid—

1:1 water-ethanol mixture by volume
Diethanolamine 2 parts¹
Igepal C.A. ethylene oxide condensation product with an alkylated phenol 1 part¹

¹Unit weight per 100 cc. mixed solvent.

(b) Development fluid:

2:3 tetrahydrofurfuryl alcohol ethanol mixture (by volume)
Rubeanic acid 2 parts¹

¹Unit weight per 100 cc. mixed solvent.

The proportions of ingredients in the transfer and developing fluid may vary widely, the essential ingredients being simply a solution of rubeanic acid in a solvent which will dissolve or transfer the nickel salt. The solution will in general contain water, as well as an organic solvent for the rubeanic acid. It is desirable, however, to keep the water content low in order to eliminate curling of the paper, and this is done by using ethyl or methyl alcohol and other volatile solvents which alone or in the presence of hydrotropes will transfer nickel salts and yet allow the rubeanic acid or its alkyl derivatives to remain in solution.

Although the present invention has been described with particular reference to the specific details of certain embodiments thereof, it is not intended that such details shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

We claim:

1. The method of duplicating which comprises applying to a copy sheet an alkanol amine and rubeanic acid, and contacting said copy sheet with a master sheet having thereon an image of a composition comprising an oleaginous material and a water soluble nickel salt.

2. The method of duplicating which comprises moistening a copy sheet having thereon rubeanic acid with a solution of an alkanol amine, and contacting the copy sheet with a master sheet having thereon an image of a composition comprising an oleaginous material and a nickel salt.

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