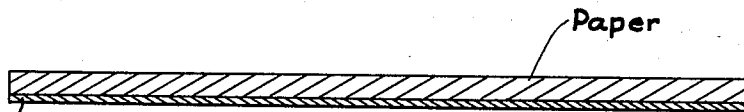


Aug. 16, 1960

2,949,381

D. W. STEINHARDT
DUPLICATING SHEET COATED WITH A COLORLESS
WAXY TRANSFER MATERIAL
Filed April 4, 1958

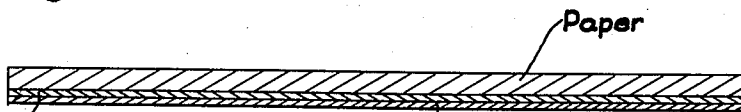
Fig. 1



Waxy coating including:-

- A color-former, e.g., carbinol base of malachite green
- A stabilizer, e.g., tris (hydroxymethyl) aminomethane
- A plasticizer, e.g., 3,3'-diaminodipropylamine

Fig. 2



Waxy coating as in Fig. 1

Protective layer of
excess stabilizer in
solvent, e.g., glycerin

1

2,949,381

DUPLICATING SHEET COATED WITH A COLORLESS WAXY TRANSFER MATERIAL

David W. Steinhardt, Rochester, N.Y.; Amos Steinhardt and Franklin A. Goldwater executors of said David W. Steinhardt, deceased

Filed Apr. 4, 1958, Ser. No. 726,502

2 Claims. (Cl. 117—36)

This invention relates to the art of duplicating written or printed matter, and is applicable to what may be called a dry process or solid-to-solid process, and also to what may be called a wet or spirit duplicating process.

An object of the invention is the provision of generally improved and more satisfactory duplicating materials and processes.

Another object is the provision of duplicating materials and processes having less likelihood of smudging and producing undesirable color, than those previously employed in the art.

Still another object is the provision of coating compounds of the type which are initially colorless or substantially colorless, and are capable of being readily and easily developed to the desired color by appropriate treatment, which compounds according to the present invention have an unusually high degree of resistance to accidental and unintentional color development such as by handling with the human hands or in the course of long continued storage.

A further object of the invention is the provision of such compounds or materials in a form suitable for use as a back coating on an impact duplicating sheet such as a so-called carbonless carbon sheet, and also suitable for use as the active coating of a so-called "master sheet" for a wet process or spirit duplicating process.

A still further object is the provision of such compounds or materials in a form suitable for incorporation or impregnation in a typewriter ribbon or similar printing ribbon, where it is desired to have the ribbon substantially colorless for ease of handling, or to have the initial impression invisible or substantially so, until it is later developed to a visible color.

These and other desirable objects may be attained in the manner disclosed as an illustrative embodiment of the invention in the following description and in the accompanying drawings forming a part hereof, in which:

Fig. 1 is a diagrammatic or schematic cross section through a sheet in accordance with a generic form of the present invention; and

Fig. 2 is a similar view illustrating other features of the invention.

The present invention is in some respects an improvement upon what is disclosed in my copending United States patent applications, Serial No. 584,397, filed May 11, 1956, now abandoned, and Serial No. 693,418, filed October 30, 1957, which may be hereafter referred to as the first application and the second application, respectively.

The present disclosure presupposes familiarity with the disclosures of said first application and said second application, and familiarity with the general problems present in this type of duplication, and with the generally understood techniques of providing a coating on the rear face of a "carbonless carbon" sheet or on a typewriter ribbon or on the front face of a sheet which is placed behind and used to produce the desired pattern on the rear face of a "master sheet" to be used later in a spirit

2

duplicating process. (See, for example, U.S. Patents 2,755,200 to 2,755,203, all issued July 17, 1956.) Also the present invention deals particularly with improved features of the coating composition, rather than with the developing agent or the step of developing to form a colored image. Except as otherwise mentioned below, the development techniques may be the same as those disclosed in the first and the second applications, and so need not be further discussed herein, the disclosure of the first and second applications being incorporated herein by reference.

To be commercially acceptable, the coating composition should be one which (1) is relatively clean both to manufacture and to handle under normal conditions of use, and which (2) is capable of being developed by an inexpensive developer presenting no particular hazards as to fire, toxicity, or corrosion, to make a print of (3) high tinctorial value and (4) high degree of sharpness. All of these conditions are met to a reasonable extent and some of them are met to a very high extent in certain compositions disclosed in the above-mentioned first and second applications. Still better results are attained, however, by the improved compositions disclosed in the present or third application.

Like the previous applications, the present application deals with a coating composition the active color-forming ingredient of which is colorless or substantially so until it comes into contact with a developing substance. This colorless color-forming ingredient may be, for example, the carbinol base of malachite green (c.b.m.g., for brevity) or certain alternatives for c.b.m.g. as mentioned below and in the second application.

It has already been shown in the second application that improved results as to cleanliness are obtained if the coating composition includes tris(hydroxymethyl)aminomethane (Examples 4-6 of the second application) or triethanolamine (Example 7 of the second application). But certain compositions giving still better results have now been discovered, as well as a generic principle which appears to explain the improved results.

The generic principle of the present invention is that the composition should contain, in addition to the wax and the color-forming or dye-forming ingredient, at least two other ingredients: (1) a strongly basic ingredient having a primary stabilizing action, and (2) a "plasticizer" ingredient which has a high degree of solubility for the color-forming or dye-forming ingredient and preferably also for the primary stabilizer. Of course this "plasticizer" or solvent ingredient may also be a secondary stabilizer, that is, it may itself have some stabilizing action; and if so, so much the better. Likewise the ingredient which acts as the primary stabilizer may itself have some solvent or "plasticizer" action, which would be an advantage. Thus the pair of ingredients just mentioned may be (but are not necessarily) closely allied to each other chemically, and each may exhibit some of the characteristics of the other. But according to the present invention it is best to use two separate ingredients, for the materials which perform best as primary stabilizers are not the same ones which best perform the plasticizer function of the present invention, and vice versa.

The primary stabilizer, according to this invention, is an amino compound which has a high degree of solubility in water and which is strongly basic in aqueous solution, yet may have little or no solubility for the color-forming or dye-forming ingredient. Such a material is tris(hydroxymethyl)aminomethane; others will be mentioned in the following examples. When the coating composition on the paper sheet or typewriter ribbon, etc., comes into contact with the human hand, the acidic perspiration on the hand dissolves off some of the stabi-

lizer from the coating composition, and the stabilizer solution neutralizes the acidic perspiration before the latter can act as an unwanted developer of color in the c.b.m.g. or other color-forming ingredient.

The plasticizer, according to the present invention, is preferably also an amino compound, the requirements being that it is a good solvent for the c.b.m.g. or other color-forming ingredient; that it has a low vapor pressure, not more than about 0.1 mm. of mercury at room temperature, so that it will not evaporate from the coating composition during storage; that it is a strong base, preferably stronger than the c.b.m.g. or other color-forming ingredient, so as to assist the primary stabilizer in the stabilizing action above discussed, but it need not be as strong a base as the primary stabilizer itself; that it preferably has high solubility for the primary stabilizer; and that it is either very soluble in or completely miscible in water. Of course both the stabilizer ingredient and the plasticizer or solvent ingredient are subject to the further requirement that they must be compatible with each other and with all other ingredients in the composition, and must be able to maintain their desired characteristics over a long period of time.

It is the combination, then, of the stabilizer and the plasticizer which accounts for the greatly improved results attained by the present invention, especially with respect to the above mentioned requirements of cleanliness and high degree of sharpness. The highly basic nature of the primary stabilizer, aided by the basicity of the plasticizer acting as a secondary stabilizer, produces the result of cleanliness in the manner already explained. The fact that the plasticizer is a solvent for the c.b.m.g. or other color-forming ingredient enables the desired reproduction to be made by a true solution of the color-former rather than by a dispersion, with the result that the reproduction or print is sharper and also that the coloring material is used more efficiently, thereby enabling the satisfactory use of a lesser quantity of the color-forming ingredient per unit of area of the coated sheet or typewriter ribbon, etc. The fact that the primary stabilizer is soluble in the plasticizer results in more efficient use of the primary stabilizer and better performance of its function.

Examples of compositions in accordance with this invention will now be given.

Example 1.—A composition is made of the following ingredients thoroughly mixed together and heated until all organics are melted:

	Grams
Carnauba wax	24.0
Carbinol base of malachite green (c.b.m.g.)	36.0
Diocetyl phthalate (known as di-2-ethylhexyl-phthalate and as "DOP")	13.4
Primary aliphatic amine having a melting point of about 41 degrees C. and a mean molecular weight of about 262 (available on the market under the name "Armeen TD," made by Armour & Co.)	16.8
Precipitated calcium carbonate	10.0
Tris(hydroxymethyl)aminomethane (hereinafter referred to as "THAM" for brevity)	0.5

These six ingredients are the same as those in Example 4 of my second application, although the proportions are slightly different. But the exact proportions are not critical, and any proportions of approximately the same magnitude may be used. This example, essentially repeated from the second application, is given here for the sake of comparison with other examples to follow.

This composition of the present example gives good results when coated on paper and used as a coloring agent for a transfer duplicating process, either dry process or wet process. It readily develops to a brilliant green color of high tinctorial value, when subjected to a developing agent in the form of a dilute solution of a suitable acid, such as a dilute solution of 2-hydroxy-3-

naphthoic acid, as explained in the prior applications. The developing agent may be previously incorporated in the sheet of paper to which the composition is transferred by the writing strokes, or it may be applied later as in a spirit duplicating process. But the sharpness of the print is not entirely satisfactory.

See the second application for a discussion of the importance of using precipitated calcium carbonate, which gives better results than other forms of finely divided calcium carbonate. Also, as explained in the second application, the precipitated calcium carbonate may be replaced by precipitated barium sulfate, or by kieselguhr, or by mixtures of two or all three of these substances, and in all the examples here given it will be understood, without further mention, that such substitution may be made.

Example 2.—Same as Example 1 except for the addition of 3 grams of polyoxyethylene ether alcohol, of the kind known as "Renex 30" available on the market from Atlas Powder Co. This composition gave equally clean results as those obtained by using the composition of Example 1, but the quality (sharpness) of the print was greatly improved.

The improved sharpness as compared with Example 1 is apparently due to the use of the "Renex 30" as a surface active agent to augment the action of the DOP ingredient. Thus the DOP, in the presence of the surface active agent, performs fairly well the above-discussed functions of the plasticizer or solvent, and the THAM performs the above-discussed functions of the primary stabilizer. But this, like the next following example, may be regarded as a special case falling within the present invention, since the plasticizer (DOP plus surface active agent) does not fall within the preferred plasticizer class of amines, but it does perform well.

The Armeen TD performs the neutralizing function described in the first application. That is, it neutralizes the acidity of the unpurified wax, and enables a lower and more acid grade of wax to be used as the spreading vehicle for the color-forming ingredient without premature development of color.

Example 3.—Same as Example 2, but substituting 3.0 grams of glycerol mannitan laurate (available from Atlas Powder Co. under the name "NNO") in place of the Renex 30. The results were approximately the same as those in Example 2. The NNO surface active agent augments the action of the DOP to a sufficient extent so that the DOP performs the plasticizing function sufficiently well.

Various other surface active agents have been tried in addition to those mentioned in Examples 2 and 3, but the results were not so good as those obtained by using the surface active agents specifically mentioned in Examples 2 and 3.

Example 4.—Same as Example 2, except that the 10 grams of precipitated calcium carbonate is replaced by 5 grams of finely ground urea. The print quality is somewhat improved as compared with Example 2, apparently due to the fact that the finely ground urea is soluble in the developing solution which is used to develop out the color on the print.

Example 5.—A composition is made up and used as a coating in the same manner described in connection with Example 1, except that the following ingredients are used in place of those mentioned in Example 1.

	Grams
Carnauba wax	12
C.b.m.g.	15
Armeen TD	7
Precipitated calcium carbonate	5 to 10
THAM	3
Renex 30	2 to 5
3,3'-diaminodipropylamine	10

This coating gives excellent print quality, and cleanliness is improved in addition to the improvement in the sharpness of the print. It is apparent that the 3,3'-diaminodipropylamine is more effective as a plasticizer or solvent, than the DOP which was used as the plasticizer in Example 2. The c.b.m.g. is more soluble in the coating composition after solidification of the composition, which results in the sharper print, and also enables a reduction in the percentage of the color-forming ingredient (the c.b.m.g.) in the composition, since with the greater solubility the c.b.m.g. is used more efficiently. The fact that the plasticizer or solvent (3,3'-diaminodipropylamine) and the primary stabilizer (THAM) are both water soluble enables them to be extracted readily from the coating by the perspiration on the hands of the user, thus keeping the coating cleaner for the reasons already explained above.

Many other amino compounds have been found, which can be used as plasticizers or solvents, in place of the 3,3'-diaminodipropylamine mentioned in Example 5. In each of the following Examples 6 through 18, the material mentioned is used as a substitute for the 3,3'-diaminodipropylamine of Example 5, and in the same amount unless otherwise specified. In each case, satisfactory results are achieved, substantially the same as those achieved in Example 5, unless otherwise specified.

Example 6.—Aminoethyl ethanolamine.

Example 7.—Triethanolamine.

Example 8.—Diethanolamine.

Example 9.—Monoisopropanolamine.

Example 10.—Diisopropanolamine.

Example 11.—N-(3-aminopropyl)morpholine.

Example 12.—Methyldiethanolamine.

Example 13.—N-hydroxyethylmorpholine.

Example 14.—Triethylenetetramine.

Example 15.—Tetraethylene pentamine.

Example 16.—N^L-(2-hydroxyethyl)-2-methyl-1,2-propanediamine.

Example 17.—N^L-(2-hydroxypropyl)-2-methyl-1,2-propanediamine.

Example 18.—Any two or more of the solvents or plasticizer substances mentioned in Examples 5 through 17 may be employed, the total quantity of the mixture of plasticizer substances being approximately the same as the quantity of plasticizer (3,3'-diaminodipropylamine) mentioned in Example 5.

Various other amino materials may be used as the primary stabilizer, in accordance with the following Examples 19 through 21, in place of the THAM mentioned in Example 5. In each case it will be understood that the substitute is used in approximately the same quantity as the THAM in Example 5, unless otherwise mentioned, and that the results are satisfactory and approximately the same as those resulting from Example 5, except as otherwise mentioned. Also, each of the substitute stabilizers mentioned in the following Examples 19 through 21 may be used with any of the various plasticizers mentioned in Examples 5 through 18, so each of the following Examples 19 through 21 constitutes, in effect, a series of examples, depending upon which of the various plasticizers mentioned in Examples 5 through 18 is used with the stabilizer mentioned in Examples 19 through 21. All are approximately equally satisfactory.

Example 19.—2-amino-2-methyl-1,3-propanediol.

Example 20.—2-amino-2-ethyl-1,3-propanediol.

Example 21.—Any two or all three of the stabilizers mentioned in Examples 5, 19, and 20 may be used, in a total quantity approximately the same as that specified for the stabilizer (THAM) in Example 5.

Example 22.—In each of Examples 4 through 21, the surface active agent NNO (see Example 3) may be substituted for the surface active agent Renex 30, in approximately the same quantity.

Example 23.—In each of Examples 4 through 21, mix-

tures of the two surface active agents NNO and Renex 30 may be employed, in place of the agent Renex 30 alone, the total quantity of this mixture being approximately the same as that specified in Example 4 for the Renex 30 alone.

In the previous Examples 5 through 23, the primary stabilizer and the plasticizer have been used in such quantities that for practical purposes they are sufficiently compatible with each other and with the other ingredients in the whole coating composition or "dope." However, according to another aspect of the invention, it is desired at times to use excess quantities of the stabilizer in order purposely to produce what may be referred to as incompatibility, so that the coating composition, when coated on the sheet, will tend to separate into layers, for the purpose mentioned below. An example of this excess and somewhat incompatible quantity of stabilizer is as follows:

Example 24.—A composition is made of the following ingredients. The composition is then coated on paper as a hot melt by the usual coating techniques.

	Grams
Carnauba wax	15
Carbinol base of malachite green (c.b.m.g.)	15
Armeen TD	7
Precipitated calcium carbonate	5 to 10
THAM	9
Renex 30	2 to 6
3,3'-diaminodipropylamine	12
Glycerin	2 to 5

When this is compared with Example 5, it is seen that about three times as much THAM is used as was the case in Example 5, for the same amount of wax and c.b.m.g. as before. The amount of the plasticizer has been slightly increased, but the other ingredients remain substantially the same as in Example 5, save for the great increase in the quantity of THAM and in the addition of the glycerin.

When this relatively high quantity of the stabilizer (THAM) is used, the quantity thereof is more than can go into solution in the composition, and so the THAM tends to form two phases, some of the THAM going into solution in the main body of the composition, the rest of the THAM apparently going into solution in the glycerin. The two phases reach an equilibrium with each other. When the thoroughly mixed composition is coated on paper by ordinary coating techniques, the coating tends upon solidification to form layers, an underneath layer (next to the surface of the paper on which it is coated) which solidifies first and which is essentially the same as the layer which results from coating paper with the composition of Example 5, except that this layer also contains some glycerin. On top of this layer is another layer which solidifies more slowly and does not dry for a day or two. The exact composition of this upper layer is unknown, but it appears to be largely a dried film of the stabilizer (THAM) dissolved in glycerin, containing little or none of the color-forming material.

This top layer therefore acts as a protective layer for the layer which contains most or all of the color-forming material. Hence if the coated sheet of paper is touched by the hands, the hands touch only the upper or protective layer and do not come into contact with the lower layer, with the result of added cleanliness.

This coating composition forming layers is particularly advantageous for transfer sheets used in making "master sheets" for spirit duplicating processes. It will be recalled that when the master sheet and the transfer sheet for making the master sheet are placed in the typewriter, the transfer sheet is behind the master sheet and has its coated face toward the master sheet, so that the impact of the typewriter keys will transfer minute quantities of the coating from the coated transfer sheet to the back face of the master sheet, in a reverse image pattern, the transferred material remaining on the back of the master

sheet and being subsequently transferred little by little to the face of the copy sheet which is brought against the back of the master sheet when the latter is used, in effect, as a printing plate. Therefore it is seen that when the coating is transferred by impact from the face of the coated sheet to the back of the master sheet, the protecting layer which was originally outermost on the coated sheet will now be next to the paper of the master sheet, and the active or color-ingredient-containing layer from the original coated sheet will now be the outermost layer of the composition transferred to the back of the master sheet. This is, of course, as it should be, since the active dye-forming part of the transferred coating will now be in position to make contact with the copy sheet when the latter is pressed against the master sheet. Hence the above mentioned protective coating serves admirably to protect the composition on the original coated sheet until it is time to use it in making a master sheet, but does not interfere in any way with the full activity of that part of the coating which is transferred to the master sheet.

While this aspect of the invention in which a protective coating layer is formed over the active coating layer serves especially well for the making of master sheets for spirit duplication, its usefulness is not confined to this. It is found in practice that this coating composition is also quite satisfactory for the normal carbonless carbon paper use. At first glance, the protective layer form of the invention would seem to be unsuitable for use for carbonless carbon paper, because it would seem that the protective layer from the coated sheet would come into contact with the sheet to which the coating composition is transferred, and withhold the layer containing the active ingredient away from the face of such sheet, thereby preventing the proper development of color. However, actual tests show that this is not the case. The explanation is apparently that the impact or pressure of the writing stroke serves to shatter the outer layers of the composition to such extent that the material of the active layer reaches the face of the second sheet to enable good color development of the desired image or print.

Example 25.—Same composition as Example 24, except that the quantity of THAM is increased to 12 grams instead of 9 grams. Substantially the same results are obtained as with Example 24.

Example 26.—Same as Example 25 except that in addition to the 12 grams of THAM, the composition also contains 12 grams of 2-amino-2-methyl-1,3-propanediol.

Example 27.—Same as Example 25 plus the addition of 12 grams of 2-amino-2-ethyl-1,3-propanediol.

Example 28.—Same as Example 25 plus the addition of 12 grams of 2-amino-2-methyl-1-propanol.

Example 29.—Same as Example 25 plus the addition of 12 grams of 2-amino-1-butanol.

Example 30.—Same as Example 24 except that the THAM is omitted and is replaced by 9 grams of 2-amino-2-methyl-1,3-propanediol.

Example 31.—Same as Example 30 except that the substitute material therein mentioned is increased to 12 grams.

Example 32.—Same as Example 30 except that the substitute material therein mentioned is increased to 24 grams.

Example 33.—Same as Example 24 except that the THAM is omitted and is replaced by 9 grams of 2-amino-2-ethyl-1,3-propanediol.

Example 34.—Same as Example 33 except that the substitute material therein mentioned is increased to 12 grams.

Example 35.—Same as Example 33 except that the substitute material therein mentioned is increased to 24 grams.

Example 36.—Same as Examples 24 and 25 except that the amount of THAM is increased to 24 grams.

Example 37.—Same as Example 24 except that in

place of using merely THAM, mixtures of any two or more of the substitutes or additives specified in Examples 26-29 are used, with or without THAM also in such mixture, in the total quantity for this mixture of 9 to 24 grams.

The results attained by each of Examples 25-37 are substantially the same as the results from Example 24, except that there is some slight improvement both in cleanliness when the amount of stabilizer is increased to about 24 grams. There is little noticeable difference in increasing the stabilizer from 9 grams to 12 grams (e.g., Example 25 as compared with Example 24, or Example 31 as compared with Example 30, or Example 34 as compared with Example 33) but there is some noticeable improvement when the stabilizer increases to 24 grams (e.g., Examples 26, 27, 28, 29, 32, 35, and 36).

Example 38.—In each of Examples 24-37, the plasticizer therein mentioned (3,3'-diaminodipropylamine) may be replaced by an equal quantity of any of the other plasticizers or mixtures of plasticizers mentioned in Examples 6-18. This substitution causes substantially no change in result.

Example 39.—In each of Examples 24-38, ethylene glycol may be substituted for glycerin, with no substantial change in result.

Example 40.—In each of Examples 24-38, 1,3-propanediol may be substituted for the glycerin, with no substantial change in result.

Example 41.—In each of Examples 24-38, 1,2-propanediol may be substituted for the glycerin, with no substantial change in result.

Example 42.—In each of Examples 24-41, NNO may be substituted for the Renex 30, with no substantial change in result.

Example 43.—In each of Examples 24-41, a mixture of Renex 30 and NNO may be employed, in place of the Renex 30 alone, with no substantial change in result.

Example 44.—In each of the foregoing Examples 24-43, any color-forming or dye-forming triphenylmethylcarbinol or mixture of two or more such triphenylmethylcarbinols may be employed in place of the c.b.m.g., provided the following limitations are observed:

(1) The amount of the color-forming material which can be used is limited to the amount which is soluble in the remainder of the composition at a temperature of about 100 degrees C. A smaller quantity than the maximum which is soluble in the composition may, of course, be used.

(2) The acid derivatives and the salts of the acid derivatives of the triphenylmethylcarbinol must not be used.

(3) The carbinol derivative employed must contain no functional group that will react with the other materials present in the coating composition or both. For example, the derivative employed must contain (a) no aldehyde group; (b) no active ketone group; and (c) no group that forms acids with active hydrogens such as acid chlorides.

It is seen from the foregoing disclosure that the above mentioned objects of the invention are well fulfilled. It is to be understood that the foregoing disclosure is given by way of illustrative example only, rather than by way of limitation, and that without departing from the invention, the details may be varied within the scope of the appended claims.

What is claimed is:

1. A duplicating sheet comprising a layer of sheet material having on one face thereof a coating, the portion of said coating next to said sheet material being a waxy substance containing as its active color-forming ingredient a substantially colorless carbinol base of a color-forming material capable of being developed by acid to a visible color, mixed with 3,3'-diaminodipropylamine as a plasticizer and with a minor quantity of glycerin as a solvent and with tris(hydroxymethyl)aminomethane as a

stabilizer, said stabilizer being in such excess quantity with respect to the other ingredients in said coating that it tends to separate into two phases to form a first layer next to said sheet material and an overlying protective layer containing a greater concentration of stabilizer and glycerin than that in said first layer.

2. A sheet as defined in claim 1, in which said carbinol base is the carbinol base of malachite green.

References Cited in the file of this patent

UNITED STATES PATENTS

5	2,755,200	Balon -----	July 17, 1956
	2,755,201	Webber -----	July 17, 1956
	2,755,202	Balon -----	July 17, 1956