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STABILIZED INK COMPOSITIONS, TRANSFER SHEETS COATED THEREWITH AND METHODS OF MAKING SAME

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This invention relates to transfer inks for duplication processes. More particularly, this invention deals with novel waxy compositions of matter adapted for use as coatings for transfer sheets which are employed in typing with so-called "carbon copies" or in preparing the master sheet for hectograph printing. This invention further embraces the novel transfer sheets thus obtained.

It is an object of this invention to provide transfer inks of the foregoing character which are essentially colorless in themselves or at least have no strong tendency to produce intensely colored stains upon the fingers of a person, while yet being adapted to produce, through the medium of a transfer sheet, an intensely colored type-written or handwritten message on a sheet of paper. A further object of this invention is to produce non-staining transfer sheets of the character and for the purposes aforementioned. Various other objects and achievements of this invention will become apparent as the description proceeds.

When we speak of essentially colorless transfer sheets in this specification, it will be understood that we are referring to the coating of the transfer sheet, not to the article as a whole. For clearly, it is possible to use for the background itself a colored sheet without stepping out of the teachings of this invention. In other words, our principal object in this invention is to produce articles of manufacture of the character and for the purposes mentioned, in which that component which normally rubs off onto a person's hands shall be essentially colorless or non-staining in the absence of acid. It follows further that absolute freedom from color is not essential to this invention, inasmuch as the purpose may be fully satisfied even if the film is weakly buff colored or dark, so long as it does not produce an objectionable and tenaciously adhering stain upon the fingers.

The current general practice in duplication processes, such as the spirit hectograph process, impact-printing and ordinary typing with carbon copies, is discussed at length in copending application of Walter Jean Balon and Otto Stallmann, Serial No. 400,776, filed December 28, 1953. The noxious problem of staining arising from the customary use in said practice of polyalkyl-triamino-triphenyl methane colors is also discussed there in detail. The term polyalkyl there is defined as indicating the presence of not less than 5 and not more than 6 lower alkyl radicals per molecule, wherein lower alkyl is typified by methyl to butyl. It will be used in the same sense throughout the instant specification and claims. As common commercially available illustrations of the colors in question are mentioned methyl violet, crystal violet and ethyl violet.

Balon and Stallmann then describe and claim novel, essentially colorless compositions of matter comprising the carbinol form of N-polyalkyl-tri(p-aminophenyl) methane colors in intimate association with a relatively smaller quantity of quaternary ammonium bases which contain alkyl, aralkyl, aryl, cycloalkyl, hydroxyalkyl and epihydrin groups in their structure, as typified by benzyl-

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trimethyl-ammonium hydroxide and several other compounds named in said specification. According to further teachings of said copending application, the only additional restriction upon the ammonium base is that it be soluble to a workable degree in the alcohol selected as solvent; and the preferred solvents are secondary and tertiary aliphatic, monohydric, saturated alcohols of 3 to 6 carbon atoms, for instance isopropyl, sec. butyl, tert. butyl, sec. amyl, tert. amyl and cyclohexyl.

The compositions are prepared by heating the normally highly colored commercial carbinol form of one of the aforementioned colors, in a secondary or tertiary alcohol which contains an excess of the mentioned quaternary base, until the intense blue color disappears, and then cooling and isolating the colorless crystals of the carbinol which presumably contain occluded quaternary base. The isolated solid is sufficiently retarded as to color development, to permit its handling in the various processes involved, such as filtration and drying, and to permit its storing for a few days or weeks.

As specific illustrations of their invention and mode of procedure said copending application of Balon and Stallmann brings numerous detailed examples, including Example 1 which reads as follows:

"To a stirred mixture of 50 g. of crude crystal violet carbinol in 3700 cc. of isopropyl alcohol at room temperature, 10 cc. of a commercial aqueous solution (36%) of benzyl trimethyl ammonium hydroxide were added. The mixture was stirred and heated during 45 min. to reflux temperature (82° C.), and held under reflux until completely discolored (about 1 hr.). The resulting pale yellow solution, after filtering at about 75° C. and cooling, gave the product in the form of long, white, orthorhombic prisms which melted at 194° C. to 196° C. These crystals analyzed 11.4% N (theoretical is 10.8%). They were characterized by unusual stability to color change, a sample having remained colorless for over 4 months when kept in a glass jar which was opened frequently.

"A product of the same quality was obtained when the hot filtration was omitted. Likewise, the use of 15 cc. and 25 cc. of the quaternary ammonium base gave the same results."

Other carbinols and dyestuffs specifically named in said copending application of Balon and Stallmann and treated by the general process therein set forth are:

Crystal violet itself (Col. Ind. 681);

Ethyl violet (Col. Ind. 682);

N-hexa(n-butyl) - tri(p - aminophenyl) - carbinol, obtained by condensing 2 moles of N-di-n-butyl-aniline with 1 mole of p-(di-n-butyl-amino)-benzaldehyde, followed by oxidation with chloranil.

N-tetra(n-butyl) - N - diethyl-tri(p-aminophenyl)-carbinol, obtained in similar manner except using p-diethyl-amino-benzaldehyde.

Other quaternary ammonium hydroxides named in said copending application are tetramethyl-ammonium hydroxide, phenyl-dimethyl-benzyl-ammonium hydroxide, N-methyl-pyridinium hydroxide and the reaction product of epichlorhydrin and ammonia produced according to U. S. P. 1,977,251.

Balon and Stallmann further found that the mentioned colorless carbinol composition may be further stabilized against discoloration in long storage or upon exposure to a humid atmosphere rich in CO₂ fumes, by coating the crystals with a fatty substance such as carnauba wax, provided the natural, residual acidity of the wax is first neutralized by treatment with a quaternary base of the type hereinabove discussed. Long-chain alkylamines may also be selected as fatty substance for the above purpose; but the quantity of coating agent in all cases has been

limited by said inventors to about 10 to 50% by weight of the crystalline carbinol composition being treated.

The invention of Balon and Stallmann is very useful in that it produces for the first time a composition of matter readily transformable into a triphenyl methane color, yet free of color itself and free of the inevitable nuisance normally attendant upon the handling and use of these colors in spreading intensely colored dusts and in producing difficultly removable stains upon the hands and clothes of persons. The said invention is also very effective insofar as its primary object of handling, storing and using the coloring agent per se is concerned. Samples of the coated, colorless carbinols, produced according to Balon and Stallmann, have been known to resist discoloration for many months, even when kept in the vicinity of a large chemical plant, wherein the atmosphere is apt to be laden with various acid fumes.

The color stability of the Balon and Stallmann product, however, appears to be dependent upon its crystalline form. When the product is dissolved in or ground into a molten wax and then coated as a thin film upon a transfer sheet, the color stability essentially disappears. In other words, colorless "carbon" paper prepared from the colorless carbinol composition of Balon et al. is not so stable to discoloration in storage or upon exposure to the atmosphere as is the crystalline coloring agent itself. Perhaps the thinness of the film and the high surface-to-volume ratio of the ground carbinol particle are contributing factors to this reduced discoloration stability.

It would appear off hand that increasing the proportion of residual quaternary base to color, which in the Balon-Stallmann product varies from 5 to 10% by weight, might have the power to increase the stability of the product in thin films. However, such a remedy is not applicable to the case of transfer sheets, because the liquid nature of the quaternary base tends to produce greasy and sticky coatings as its proportion is increased.

Now according to our invention, the above problem is solved, and stable thin films of essentially colorless N-polyalkyl-tri(p-aminophenyl) carbinols are produced by adding to the coating-ink compositions, in addition to its customary vehicle and the mentioned coloring agent, a relatively large proportion of an organic nitrogenous base whose physical state is selected to match the vehicle of the coating ink. Thus, for the purpose of producing a coated transfer sheet, the vehicle is customarily a wax such as carnauba or montan wax, softened usually by means of a cream-like hydrocarbon such as Vaseline or ester such as lanolin, all of which may be summarized by saying that the vehicle is a substance which is solid at room temperature but melts readily at the temperature generally selected for coating, that is in the range of 100° to 125° C. Accordingly, the base selected by us as third ingredient for coating inks of this nature is an amine or quaternary ammonium base having fatty or waxy qualities, that is one which is solid at room temperature but softens or liquifies in the range of 100 to 125° C. To avoid losing much of this base by evaporation during the coating process, we impose the further limitation that it shall boil at a temperature not less than 150° C.

Practical examples of suitable bases for transfer-sheet coatings are the saturated long-chain aliphatic amines such as primary alkyl amines having from 12 to 30 C-atoms in a straight chain and the corresponding dialkyl amines; unsaturated long-chain amines, for instance, octadecenyl amine and dioctadecenyl amine; commercial mixtures of such amines, e. g., stearyl amine (a mixture of octadecyl and hexadecyl amines), or the amines derived from coconut oil, soy bean oil, tallow and hydrogenated tallow; and quaternary ammonium hydroxides having at least one long-chain alkyl radical in their molecule, for instance, octadecyl-trimethyl-ammonium hydroxide and dioctadecyl-dimethyl-ammonium hydroxide.

The preferred quantity of the mentioned third ingredient is preferably based on the weight of the entire

ink rather than on its coloring constituent. It may vary from 5 to 50% by weight of the eventual coating film; that is, the organic nitrogenous base is added in quantity corresponding to from 5 to 50% of the combined weight of all ingredients except volatile liquids, which are in some cases employed as a transient vehicle to facilitate application of the coating film to the carrier sheet. (Compare Examples 13, 14 and 15 hereinbelow.) For practical purposes, however, we prefer to use a quantity of the nitrogenous base equal to from 20 to 40% by weight based on the combined weight of the non-volatile constituents of the ink composition, and we further prefer to make said quantity of nitrogenous base at least equal to 60% of the weight of said stabilized color agent employed.

It is noteworthy, that this is the first time in our experience that a coating ink for a transfer medium is finished on the alkaline side. Hitherto, the triphenyl methane colors themselves have been employed, for instance, methyl violet, crystal violet or ethyl violet. These being salts, more particularly chlorides, care has always been taken to produce a coating ink composition of acid reaction. Our novel compositions, however, when tested by dissolving a sample in aqueous alcohol, are alkaline to Brilliant Yellow. This test may indeed be taken as defining the lower limit of said third ingredient in our novel ink compositions.

The mode of incorporation of the several ingredients with each other is not critical. The colorless carbinol composition may be incorporated into the mixture of vehicle and base by grinding on an ink mill, or the carbinol composition may be dissolved in a solvent such as benzene, then added to a molten mixture of the waxy vehicle and nitrogenous base, and followed by heating to distil off the solvent. To our knowledge, the latter mode of incorporating the coloring agent is also novel.

The mode of preparing the coated transfer sheet may follow customary practice in this art.

Without limiting this invention, the following examples are given to illustrate our preferred mode of procedure. Parts mentioned are by weight.

PART I.—CARBON PAPER FOR ORDINARY TYPING

Example 1

Materials:	Parts
Montan wax (bleached)-----	16.7
Microcrystalline wax (white, melting range 90-95° C.) -----	12.5
Stearylamine wax (a commercial mixture of octadecyl and hexadecyl amines)-----	22.5
White mineral oil ("Nujol") -----	15.0
Petrolatum -----	12.5
Titanium dioxide -----	12.5
Colorless carbinol composition of the above reproduced Example 1 of copending application of Balon and Stallmann Serial No. 400,766 -----	8.3
Total -----	100.0

The first six ingredients are heated together at 96° C. until a uniform white liquid suspension is obtained. The colorless coloring agent is then stirred in at the same temperature. The resulting hot melt has a sufficient viscosity to run freely from a hot stirring rod. A spot of the molten ink dropped onto a cold glass surface solidifies to a pure white, opaque film having a medium hardness.

The melt is cooled, ground on a three-roll ink mill, returned to the melting vessel, heated to molten state and then used for coating paper, such as Yoshino tissue, on a conventional carbon coating machine, in the usual manner and at the customary temperature (about 96° C.).

The resulting coating on the carbon sheet is a pure white and is remarkably stable against color development

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in subsequent handling and storage over extended periods of time. An impact transfer from this carbon sheet onto an ordinary colorless copy sheet by the use of a pencil, stylus or typewriter produces an impression which is colorless initially, but develops slowly a strong violet color upon exposure to the atmosphere, or more rapidly upon exposure to heat.

Example 2

The same materials as in Example 1, except exclude the Montan wax and increase the microcrystalline wax to 29.2 parts.

The ink thus obtained possesses all the merits of that obtained in Example 1, and in addition forms a somewhat softer coating on the carbon sheet; it is therefore particularly adapted for use in a pencil-copy carbon paper.

Example 3

The same materials as in Example 1, except substitute refined carnauba wax for the montan wax.

The white carbon paper thus obtained is more resistant to marring during general handling operations, gives greater copy clarity on the typewriter and develops to the highly colored violet impression much more swiftly than the product of Example 1.

Example 4

The same materials as in Example 1 except exclude the montan wax, decrease the quantity of stearylamine to 5 parts, and increase the quantity of microcrystalline wax to 46.7 parts.

The colorless ink thus obtained has a somewhat lower order of resistance against color development in the carbon sheet, but shows an advantage in giving a greater number of copies of a lower color intensity and which develop to the violet shade much more rapidly than the product of Example 1.

Example 5

The same materials as in Example 1 except exclude the titanium dioxide and increase the quantity of microcrystalline wax to 17.5 parts.

A translucent white ink is thus obtained which is practically invisible after coating on the normal tissue carrier sheet, but at the same time exhibits the same general advantages described under Example 1.

Example 6

The same materials as in Example 1, except substitute 6.5 parts of calcium carbonate for the equivalent amount of the titanium dioxide.

The resultant pure white ink has slightly greater transparency and increased resistance to color development on the carbon sheet, presumably through the further alkaline influence of the carbonate. Copy impressions made by transfer sheets containing this ink are developed to a satisfactorily strong violet intensity on standard hectograph copy sheets having a pH of about 5 to 6.

Example 7

The same materials as in Example 1, except substitute zinc oxide for the titanium dioxide.

The pure white ink thus obtained possesses an appreciably greater but workable viscosity, which permits a heavier deposit of the ink on the carrier sheet. This is an advantage, because it increases the durability of the carbon sheet and also increases the intensity of impressions obtained therewith.

Example 8

The same materials as in Example 1, except exclude the titanium dioxide, reduce the colorless crystalline color-forming agent to 1 part and increase the microcrystalline wax content to 32.3 parts.

In this lower ratio of the color-giving ingredient, complete solubility is obtained at the elevated temperature,

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which eliminates the necessity for any grinding operation to disperse the colorless particles in the wax oil system.

A colorless ink is obtained which shows the same advantages as that of Example 1 but is invisible when coated on a tissue carrier sheet and produces a legible, but weaker, violet copy impression.

Example 9

The same materials as in Example 1, except substitute 10 parts of lard oil and 5 parts diethanolamine for the mineral oil.

Practically the same results are obtained as in Example 1.

Example 10

The same materials as in Example 1 except substitute 10 parts of castor oil and 5 parts of mono-ethanolamine for the mineral oil.

The resultant pure white ink when coated on the carbon sheet possesses a higher gloss after cooling than a sheet similarly coated wherein the mineral oil has been used. A slight advantage of this ink is also shown in the finer outline of the violet copy impression.

PART II.—TRANSFER SHEETS FOR HECTOGRAPH PRINTING

Example 11.—Melting and grinding procedure

Materials:	Parts
Montan wax (bleached).....	16.9
Microcrystalline wax (white, melting range 90-95° C.).....	12.6
Stearylamine wax.....	22.7
White mineral oil.....	15.2
Petrolatum.....	12.6
Colorless crystalline product of the above reproduced Example 1 of copending application of Balon and Stallmann, Serial No. 400,776.....	20.0
Total.....	100.0

The above materials are made into a uniform coating ink by the same melting and grinding procedure as in Example 1. The so obtained white ink is coated at 96° C. on a regular hectograph carrier sheet by the customary apparatus and procedure.

The resulting hectograph transfer sheet is essentially colorless and non-staining. Master sheets produced on the typewriter or by the aid of a stylus from the above coated sheet may be used in customary manner on a rotary spirit duplicating machine, except that the moistening fluid is made acid. For instance, it may consist of ethyl alcohol containing 5% by weight of acetic acid. In tests made by us with coated transfer sheets, master sheets and a moistening fluid as above described, we have obtained as many as 100 to 150 legible copies of medium violet intensity. The imprint on the master sheet was essentially colorless and non-staining, until moistened by the mentioned fluid in the duplicating machine.

Similar results were obtained by us in further experiments wherein the colorless carbinol composition indicated in the above formulation was replaced by similar decolorized crystals, prepared according to said Balon and Stallmann application, but prepared from the following crude (hence, intensely colored) carbinols: Tri-(p-diethylaminophenyl) carbinol; Tri-(p-n-propylaminophenyl) carbinol; Di-(p-dimethylaminophenyl) - p-diethylaminophenyl-carbinol.

The first of these will be recognized as the carbinol of ethyl violet. The other two are not commercial products but were prepared specially for these tests by the mentioned inventors.

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Example 12.—Eliminating need for grinding

Materials:	Parts
Montan wax (bleached).....	10.6
Microcrystalline wax (white, melting range 90–95° C.).....	7.9
Stearylamine wax.....	14.2
White mineral oil.....	9.5
Petrolatum.....	7.8
Colorless crystalline product as in Example 11 above.....	50.0
Total.....	100.0

The first five ingredients are heated together at 198–204° C. until fluid. The coloring agent is then stirred in until dissolved. Coating is done in the usual manner except at the rather abnormal temperature of 198–204° C.

The clean, non-staining, essentially white, coated transfer sheets thus obtained, when used through a master sheet and an acid moistening fluid as described in Example 1, give copies which compare favorably in number and quality with those made in customary manner from prior art transfer sheets employing the corresponding dye chloride (i. e., crystal violet).

Example 13.—Color ingredient added in solution

Materials:	Parts
Microcrystalline wax (as in prior examples).....	13.0
Montan wax (bleached).....	17.4
Stearylamine wax.....	13.0
White mineral oil.....	8.7
Colorless crystalline product as in Example 11 above.....	4.3
Benzene.....	43.6
Total.....	100.0

The first four ingredients are melted together at 96° C. until a homogeneous liquid mass is obtained. The crystalline coloring agent is dissolved in the benzene at 78° C., and the molten mass is stirred into it. The mixture is then maintained at 78° C. for 10 minutes.

The hot solution is applied to the carrier sheet in normal manner. The benzene rapidly evaporates from the hot film, and the color ingredient recrystallizes in a very fine state of suspension in the film, closely simulating the fineness of particle size obtained on the ink mill.

This solvent transfer technique results in a normally hard, white coating closely approximating the general properties of a conventional carbon sheet. The elimination of grinding simplifies the entire process and constitutes a great economic advantage.

Example 14.—Coating at room temperature

Materials:	Parts
Montan wax (bleached).....	12.1
Microcrystalline wax.....	9.1
Stearylamine wax.....	9.1
White mineral oil.....	6.1
Colorless coloring agent as in Example 11.....	3.0
Benzene.....	60.6
Total.....	100.0

The waxes, oil and benzene are added together and heated to 85° C. Heating and agitation are continued until a uniform solution is obtained having a slight yellow coloration. Add the color ingredient and stir until completely dissolved. Cool to room temperature.

The resultant ink has a rather thick consistency and a faint amber coloration. It may be applied to paper by the draw-down method using a straight edged blade, or it may be applied by the aid of a Bird applicator, which regulates the thickness of the film deposited. The resultant sheet is allowed to dry under normal conditions during which time the benzene completely evaporates from the film.

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A pure white carbon sheet is obtained which exhibits the same advantages as those of the preceding examples, when compared against products currently in use.

Example 15.—Spray gun application

Materials:	Parts
Microcrystalline wax.....	13.5
Stearylamine wax.....	5.8
Petrolatum.....	3.8
Coloring agent as in Example 11.....	1.9
Benzene.....	75.0
Total.....	100.0

Dissolve the non-dyeing ingredients in the benzene by warming slightly until a complete solution is obtained. Add the coloring agent and stir until dissolved. Cool to room temperature. Spray onto a resin-backed tissue sheet by using a paint spray-gun in the conventional manner.

A pure white coating is obtained which has a slightly pitted appearance from the rapid evaporation of the solvent under these conditions. The sheet may be subjected to buffing under normal conditions to obtain a semi-gloss coated sheet closely corresponding to that normally obtained from a hot application of the ink, but much more opaque. The sprayed sheet may also be passed rapidly over a heated roll to melt and resolidify the sprayed coating whereby to obtain a very smooth coating.

The copy impression resulting from this technique is of the same order of superiority as listed in the preceding examples when compared against the prior art products.

Example 16

A carbon sheet tissue was coated with the following mixture:

	Parts
Coloring agent as in Example 11.....	1.0
Stearylamine wax.....	49.5
Paraffin wax.....	49.5
Total.....	100.0

The carbon sheet thus obtained had good storage stability against color development in the carrier sheet. After transfer to a copy sheet sensitized with an organic acid, a legible impression of medium intensity was obtained.

It will be understood that the details of the above examples may be varied within wide limits.

Thus, in lieu of stearylamine in the above examples, any other of the long-chain nitrogenous bases above indicated may be employed. In lieu of the several non-nitrogenous waxes named in the above examples, any other wax or combination of waxes customarily employed in the art as vehicles for transfer films may be employed in this invention. Typical classes of such, commonly used, vehicles are high molecular weight petroleum oils and waxes; higher fatty alcohols such as cetyl and stearyl alcohols; polyhydric alcohol fatty acid esters such as the glyceryl stearates, glycol stearates, sorbitol stearates and pentaerythritol stearates; ketone waxes such as hexatri-acontanone; amines such as hexadecyl or octadecylamine; amides such as octadecanamide; and nitriles such as octadecane nitrile. If an amine is used, it can be present to the extent of up to 50 wt. per cent serving both as the wax and as the basic stabilizer. These components are mixed in varying proportions to give the desired consistency. The mixtures can be modified by incorporating plasticizers and hygroscopicity control substances if desired. Nitrogenous bases not having any long-chain alkyl radicals may also be added, where desired, to adjust the consistency of the ink composition.

The quantity of colorless carbinol incorporated into the coating ink formulation, will naturally vary according to the purpose of the ink, but may otherwise follow the corresponding practice in the art when using the colored dyes. In other words, for ordinary carbon paper, the

quantity of coloring agent is generally from 5 to 20% by weight of the entire coating ink. For hectograph carbon on the other hand, 20 to 50% by weight of the ink is the quantity of coloring agent commonly used.

PART III.—SPECIALLY TREATED COPY SHEETS

Because of the remarkable stability of the colorless coatings in the transfer sheets hereinabove discussed, it is necessary that the colorless imprint be put in contact with an agent of acid reaction, to achieve full development of the color. In the case of hectograph duplication in a rotary machine using an alcoholic moistening agent, the acidic agent can be readily added to the moistening fluid. In the case of impact printing from a colorless carbon, however, it is desirable that the paper itself have an acid reaction.

Many commercial papers have a natural acid reaction by virtue of clays, aluminum silicates or acid-reacting salts incorporated into the paper fiber during manufacture. On the other hand, the paper intended as copy paper may be treated with certain acids, whereby to adapt it better for use with the novel transfer media of this invention. The treatment consists of impregnating the paper with an aqueous, alcoholic, or aqueous-alcoholic solution of an organic acid, and allowing the vehicle to evaporate. As organic acid is preferably chosen one which is solid at room temperature, is soluble in water, alcohol or mixtures of the two, has no color of its own and is free from bad odors or toxicity. As examples of suitable acids may be mentioned acetic, oxalic, citric, tartaric, benzoic, salicylic, pyrogalllic, naphthalene sulfonic, p-toluene sulfonic, and various others.

Moreover, it has been observed that the shade of the color developed upon the copy paper can be varied to some extent by the choice of the acid. Thus, using the carbinol of crystal violet as coloring agent, stearic, citric and tartaric acids develop purple impressions; oxalic acid gives a blue; and pyrogalllic acid gives a jet black.

The speed of color development also can be varied to some extent by the choice of acid. Of the acids that have been tested thus far, citric, tartaric and salicylic developed the color most rapidly and gave intensely colored imprints.

The following additional examples will illustrate the improved results obtained with the transfer sheets of our instant invention when used in conjunction with acidic copy paper of the above type.

Example 17

A sheet of white copy paper is impregnated with a 5% solution of oxalic acid in alcohol and allowed to dry thoroughly at room temperature.

A record made on this paper using the "carbon" sheet of Example 1 above, develops a strong violet shade immediately after typing. This intensity increases somewhat during the next 24-hour period. Thereafter a progressive shade-change takes place to an ultimate black impression.

Example 18

The procedure is the same as in Example 17, except that citric acid is used in place of oxalic acid.

The treated paper thus obtained gives a violet copy which is many times stronger within 15 minutes than the untreated sheet gives after several days.

It is distinguished over the product of Example 17 by a more rapid development of an intensity print, which does not change its violet shade in storage.

Essentially similar results are obtained with copy paper which had been impregnated with any of the other acids named above, except for the individual differences in rate of color development and ultimate shade, as already noted above. In the case of tannic acid, a special further improvement obtained is that the copy impression is non-bleeding in water. That is, water flowed over the copy

sheet shows no evidence of bleed from the letters into the adjacent uncolored areas.

Numerous other changes and variations in the details of our invention will be readily apparent to those skilled in the art.

We claim as our invention:

1. An ink composition for duplication processes comprising a vehicle and a color producing agent, said vehicle comprising a waxy solid adapted for use as a film forming agent for coating a transfer sheet, and said color producing agent comprising the carbinol of an N-polyalkyl-tri(p-aminophenyl methane dye having from 5 to 6 alkyl radicals of not more than 4 C-atoms each attached to its N-atoms; said N-polyalkyl dye being in a state of purity essentially free of the corresponding color and being stabilized in said state by having occluded in its crystals not more than 10% of its own weight of a quaternary ammonium hydroxide which has in its quaternary N-atom at least one radical of the group consisting of alkyl, aralkyl, aryl, cycloalkyl, hydroxyalkyl and epihydrin but is soluble in secondary and tertiary aliphatic, monohydric, saturated alcohols of 3 to 6 carbon atoms; said ink composition comprising further a nitrogenous organic base selected from the group consisting of aliphatic primary, secondary and tertiary amines and quaternary ammonium hydroxides and having in its molecule at least one alkyl radical of more than 11 C-atoms in a straight chain; said nitrogenous base being a fusible solid which becomes liquid at a temperature between 100° and 125° C. but does not boil below 150° C. and being present in quantity not less than 5% and not greater than 50% by weight based on the combined weight of the non-volatile constituents of the ink composition and not less than 60% by weight with reference to the weight of said stabilized N-polyalkyl dye.
2. An ink composition as in claim 1, said base being a monoalkyl amine of 12 to 30 C-atoms.
3. An ink composition as in claim 1, said base being a dialkyl amine of 12 to 30 C-atoms in each alkyl group.
4. A composition of matter as in claim 1 the quantity of said color producing agent being from 5 to 20% by weight of the entire composition, whereby the composition is adapted for use in coating transfer sheets for impact-printing duplication processes.
5. A composition of matter as in claim 1, the quantity of said color producing agent being from 20 to 50% by weight of the entire composition, whereby the composition is adapted for use in coating transfer sheets for hectograph printing.
6. The process of preparing a non-staining inking composition for transfer media employed in duplication processes, which comprises incorporating into an ink-vehicle a coloring agent and an organic nitrogenous base, said coloring agent being the carbinol of an N-polyalkyl-tri(p-amino-phenyl) methane dye which has from 5 to 6 alkyl radicals of not more than 4 C-atoms each attached to its N-atoms; said N-polyalkyl dye being in a state of purity essentially free of the corresponding color and being stabilized in said state by having occluded in its crystals not more than 10% of its own weight of a quaternary ammonium hydroxide which is soluble in secondary and tertiary aliphatic, monohydric, saturated alcohols of 3 to 6 carbon atoms; said organic nitrogenous base being an aliphatic compound selected from the group consisting of primary, secondary and tertiary amines and quaternary ammonium hydroxides, and containing in its molecule at least one alkyl radical of more than 11 C-atoms; said nitrogenous base being a fusible solid which becomes liquid at a temperature between 100° and 125° C. but does not boil below 150° C. and being added in quantity not less than 5% and not greater than 50% by weight based on the combined weight of the non-volatile constituents of the ink composition and not less than 60% by weight with reference to the weight of said stabilized N-polyalkyl dye.
7. The process of preparing a non-staining transfer

sheet for typing with carbon copies, which comprises coating a web with a liquified ink composition comprising a waxy vehicle, a coloring agent and an organic nitrogenous base, the coloring agent being the carbinol of an N-polyalkyl-tri(p-aminophenyl) methane dye having from 5 to 6 alkyl radicals of not more than 4 C-atoms each attached to its N-atoms; said N-polyalkyl dye being in a state of purity essentially free of the corresponding color and being stabilized in said state by having occluded in its crystals not more than 10% of its own weight of a quaternary ammonium hydroxide which has in its quaternary N-atom at least one radical of the group consisting of alkyl, aralkyl, aryl, cycloalkyl, hydroxyalkyl and epihydrin but is soluble in secondary and tertiary aliphatic, monohydric, saturated alcohols of 3 to 6 carbon atoms; said ink composition comprising further a nitrogenous organic base selected from the group consisting of aliphatic primary, secondary and tertiary amines and quaternary ammonium hydroxides and having in its molecule at least one alkyl radical of more than 11 C-atoms in a straight chain; said nitrogenous base being a fusible solid which becomes liquid at a temperature between 100° and 125° C. but does not boil below 150° C. and being present in quantity not less than 5% and not greater than 50% by weight based on the combined weight of the non-volatile constituents of the ink composition and not less than 60% by weight with reference to the weight of said stabilized N-polyalkyl dye, and the quantity of coloring agent being from 5 to 20% by weight based on said combined weight of non-volatile constituents.

8. The process of preparing a non-staining transfer sheet for hectograph duplication which comprises coating a web with a liquified ink composition comprising a waxy vehicle, a coloring agent and an organic nitrogenous base, the coloring agent being a colorless carbinol of an N-polyalkyl-tri(p-aminophenyl) methane dye having from 5 to 6 alkyl radicals of not more than 4 C-atoms each

attached to its N-atoms; said N-polyalkyl dye being in a state of purity essentially free of the corresponding color and being stabilized in said state by having occluded in its crystals not more than 10% of its own weight of a quaternary ammonium hydroxide which has in its quaternary N-atom at least one radical of the group consisting of alkyl, aralkyl, aryl, cycloalkyl, hydroxyalkyl and epihydrin but is soluble in secondary and tertiary aliphatic, monohydric, saturated alcohols of 3 to 6 carbon atoms; said ink composition comprising further a nitrogenous organic base selected from the group consisting of aliphatic primary, secondary and tertiary amines and quaternary ammonium hydroxides and having in its molecule at least one alkyl radical of more than 11 C-atoms in a straight chain; said nitrogenous base being a fusible solid which becomes liquid at a temperature between 100° and 125° C. but does not boil below 150° C. and being present in quantity not less than 5% and not greater than 50% by weight based on the combined weight of the non-volatile constituents of the ink composition and not less than 60% by weight with reference to the weight of said stabilized N-polyalkyl dye, and the quantity of coloring agent being from 20 to 50% by weight based on said combined weight of non-volatile constituents.

9. A transfer sheet for typing with carbon copies, comprising a web coated with an essentially colorless waxy film of a composition as defined in claim 7.

10. A transfer sheet for hectograph duplication comprising a web coated with an essentially colorless waxy film of a composition as defined in claim 8.

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