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DUPLICATING INK COMPOSITIONS AND TRANSFER ELEMENTS PREPARED THEREFROM

Douglas A. Newman, Glen Cove, N.Y., assignor to Columbia Ribbon and Carbon Manufacturing Co., Inc., Glen Cove, N.Y., a corporation of New York
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This invention relates to duplicating, and to transfer elements therefor, and particularly to pressure-responsive transfer elements used in inscribe master sheets which may then be employed in one of the usual hectograph processes of duplication. The invention is also concerned with the transfer compositions employed in the manufacture of such elements, and is a continuation-in-part of my application Serial No. 588,630, filed June 1, 1956, now abandoned.

It has been the practice heretofore to provide a transfer element comprising a flexible fabric foundation sheet on which was placed a hot melt coating charged with coloring matter. In order to have the coating dry and relatively smudge-resistant and at the same time cause it to stencil properly under pencil pressure or a type blow, it has generally been considered necessary to formulate the same using binders primarily of wax or wax-like material compounded with non-volatile, non-drying softening oils and plasticizers. The coating is normally heated to molten condition, coated on the foundation sheet and solidified thereon by cooling.

One attempt to depart from this well-known coating procedure rests upon the production of a hectographic transfer layer by cold printing in which the base or binder for the coating was essentially a drying oil varnish, e.g. linseed oil, and includes antioxidizing materials to control drying of the same. While such a transfer layer may have certain limited application in situations where cleanliness is not too important, it fails altogether to comply with ordinary commercial requirements. Since the linseed oil coating must be coatable or printable to begin with, of necessity the transfer deposit is rather soft, and smeary, and possibly somewhat tacky, due to the presence of the antioxidant. On the other hand, if any attempt is made to modify the drying characteristics of the coating to permit a gradual hardening of the binder, a point will be reached at a certain time after coating or printing where the coating is not excessively dirty to handle, but since the exact time when the transfer sheet is to be used can rarely be predicted, and since storage beyond the intended period would cause hardening of the layer to a point where the transfer in response to pressure was altogether insufficient for practical purposes, such a coating would have little commercial usefulness.

It has also been known that various duplicating inks for producing hectograph image material directly by printing have been developed using a primarily resinous binder, but such materials have been found to produce only a limited number of copies and are useful only in printing applications where proper stenciling of a transfer layer is not a consideration, and where a small number of copies will serve the purpose.

In addition there have been examples of attempts to make by a volatile solvent coating process ordinary marking carbon papers in which a certain amount of resinous material was included in the solid base or binder. In the main these layers, however, are essentially waxy or oily layers modified by resins and including fillers rather than being primarily of resinous composition, and their makeups have been pertinent only to the production of a carbon marking layer of the ordinary reusable type so that they have no suggestive relation to a layer

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which (1) must transfer almost entirely in the impressed area at the first use, i.e. "stencil," so as to deposit a heavy image capable of providing long duplicating runs, and (2) will desirably be capable of dispersing and carrying an extremely high percentage of hectograph dye.

It is an object of the present invention to provide a duplicating transfer layer, carrying a large quantity of suitable hectograph coloring matter such as a soluble dye, in which the binder has a primarily resinous component, and to provide compositions, formulated on this basis, which will deposit transfer layers having the characteristic of stenciling properly under pencil pressure or under a type blow, and of releasing color repeatedly under solvent action to produce a large number of copies.

It has been known heretofore that conventional wax-base transfer compositions could be applied to a foundation surface by dispersing the ingredients in a volatile liquid solvent which dissolves a major portion of the wax. This process has not been widely practiced, however, for the low solubilities of the waxes normally used in the commercially and economically available solvents have made it necessary to employ large quantities of the solvent in proportion to the composition, and usually heat as well. Thus only a very thin layer of the composition could be placed at one time, and the complication of placing a plurality of superposed layers rendered the system uneconomical and impractical, while severe coating difficulties were encountered due to cooling or excessively rapid solvent exaporation.

It is an additional object of the present invention to provide a duplicating transfer layer in which the binder has a significant resinous component which is readily soluble in one or more solvents whereby a transfer layer of practical thickness can be deposited using a composition which partakes somewhat of the character of a lacquer or spirit varnish and which requires a minimum of solvent and no heat to maintain suitable coating consistency.

I have discovered that while waxy materials have certain drawbacks as binders for pressure-sensitive transfer layers, e.g. rather low solubility in solvents where cold deposition is desired, and resinous materials have other serious drawbacks, e.g. poor stenciling properties under pressure, mixtures of the two types of materials including primarily resins, rather than combining the drawbacks of each, in effect offset each other's drawbacks to a remarkable and unexpected degree. I have found that when waxes and resins having a common solvent and which in themselves immiscible or poorly miscible, are thus codissolved, the resins appear to assist in dispersion of the wax and help to maintain the same in solution or suspension in ordinary liquid vehicles at ordinary temperatures and with relatively low vehicle proportions. Moreover, I have discovered that the presence of a minor proportion of the waxy material which has limited miscibility in the resin, somehow interrupts the tendency to toughness which would normally be characteristic of resinous layers, and gives the coating a friability and stenciling quality which would normally be associated with hectograph coatings, the hardening ingredient of which was essentially wax. The provision of a hectograph transfer layer whose color-carrying base is essentially a combination of a major proportion of a resin and a minor proportion of codissolved but substantially resin immiscible wax is accordingly a primary feature of the invention.

While ready solvation of the color-carrying base is an important feature of the invention, it is likewise important that hectograph coloring material, when the same is a soluble dye, not have its physical structure impaired by the treatment with the solvent necessary for application to a

sheet. The dyes normally employed in hectograph work are reduced to usable condition by careful grinding which separates the dye material into extremely fine crystals or particles. So long as these maintain their individual identity they are quickly attacked and developed by the printing solvents and give a large number of bright copies. If, however, the crystals or particles become dissolved and are then precipitated by solvent evaporation, their discrete character so carefully achieved is largely destroyed, and the resulting deposit has rather poor susceptibility to the printing solvents, giving fewer copies. For this reason, I find that it is important to maintain a high percentage of the dye in its particulate crystalline form. In this connection, it is a feature of the invention that the resin which forms a significant portion of the binder is soluble in solvents which, at least in the quantities required, do not readily dissolve much of the dye material used, so that the dye material may be retained in the dispersed condition, achieved by grinding the ingredients of the composition.

It is another feature of the invention that the ingredients of the composition can be brought together and intermixed without the application of heat, not only materially reducing the cost of the operation, but also having important beneficial effects with respect to the dye materials sometimes used. In the latter regard, it is known that certain basic water- and spirit-soluble polyarylmethane dyes which would be otherwise suitable for hectograph work, particularly Victoria blue and certain methyl violets, are seriously impaired or entirely destroyed by the heat necessary for preparing molten wax compositions, and hence have never been successfully put to use in this field. This is particularly important where hectograph layers of various hues are being prepared. Since the water-soluble and spirit-soluble dyes available in certain color ranges are necessarily limited, the ability to assemble a fully operable, commercially acceptable transfer sheet without the use of heat makes a much wider range of colors possible for general use. Many of the hues which would be useful in compounding hectograph blacks suffer from this drawback, so that this invention makes the production of a good black hectograph coating much simpler than heretofore. Moreover, those dyes which are at present in use, and which are not rendered inoperative by heat, are unquestionably impaired to some extent by the heat required for preparing waxy compositions. The present invention consequently obviates this impairment of the dye materials, which are so costly as to represent by far the largest part of the material cost of hectograph transfer layers, and makes possible a reduction in the amount needed for the production of work of a given quality or brightness. On the other hand, where full amounts of dye material are used, a higher maximum brightness of work is achieved than was formerly possible, since the unheated dye is fully active.

Still another feature of the invention is the solubility, at least in part, of many of the suitable resins in one or more of the various spirit fluids used in the spirit process of hectograph duplication. This solubility is a property which distinguishes them from the usual wax color-carrying base, and has importance in that the repeated treatment of the image with the spirit fluid gradually removes minute quantities of the resinous binder fraction and exposes additional amounts of coloring material for use, thus prolonging the useful life of the image and augmenting the number of copies obtainable therefrom when the spirit process of duplication is used.

A further feature of the invention resides in the adhesive characteristics of many resins which make it possible to apply the transfer coat to a smooth, non-absorbent foundation and have it properly attach itself thereto without the application of an intermediate adhesive coating. Such foundations, for example glassine paper or cellophane, are usually preferable because, whenever usable, they are capable of rendering a more accurate sharper

stencil and a more complete transfer of the color layer than are foundations of a more fibrous and porous character.

A still further feature of the invention is to be found in the fact that the resins which are otherwise suitable are, for the most part, of sufficiently high softening temperature that a direct molten waxy protective layer can be applied to the surface of the transfer coating without danger of seriously softening its surface, or of any substantial commingling therewith. The dye materials thus remain undiluted and in properly concentrated form throughout the transfer layer without necessitating any additional steps, e.g. the placing of an intermediate barrier coating, or the like in advance of the protective hot melt wax overcoat.

Additional features and advantages will hereinafter appear.

According to the invention, a composition or lacquer including hectograph coloring matter such as a spirit-soluble and water-soluble dyestuff is prepared by dissolving a color-carrying base material, a major proportion of which is a resinous component and a minor proportion of which is a waxy component in a suitable quantity of an appropriate solvent or vehicle of moderate volatility, and mixing the pigment or dyestuff therewith, preferably by grinding. The resultant composition has a fairly fluid consistency and may be handled in a manner similar to that employed with molten wax-base transfer compositions. In the usual case the composition will be coated in a stripe on a continuously moving paper web using equipment ordinarily employed for carbon paper coating. Thereafter the web may be traveled through a recovery zone where the volatile vehicle will be given up quite rapidly due to the large area and extreme thinness of the coating. If necessary, a moderate amount of heat may also be applied to the web at this point to assist in the volatilization of the vehicle, although volatilization without heat is preferred, as will hereinafter appear. When substantially all of the vehicle has been removed, the coating is a dry, pressure-transferable layer which will stencil clearly and sharply under normal writing pressure, and which is capable of producing an exceptionally large number of bright, clear hectograph copies.

As solvents in the present invention, it has been found that any volatile material which is a solvent for the color-carrying base and in which the dye material is substantially insoluble may be used. Many compounds are very suitable, among which are the hydrocarbons, halogenated hydrocarbons, ketones, esters such as ethyl acetate, etc.

In selecting a solvent for carrying out the invention, it is important to consider the solubilities of the dyestuffs employed since the dyestuff has been carefully reduced by grinding to discrete particle or crystal form which is the optimum condition for its subsequent contact with the printing or duplicating solvent. If the dye should dissolve to any great extent in the coating solvent and be precipitated when the solvent is evaporated, it will be found to assume a more massive particle form or layer form not well suited for color liberation. For this reason it is desirable to use as coating solvents, liquids which do not appreciably dissolve the dyestuff, or if they normally dissolve it to some extent, require use in such small amounts that they will affect the dyestuff only slightly. In the latter case there will be, accordingly, a large excess of dyestuff over what can be dissolved by the solvent present, and the suspended, undissolved particulate portion of the dye will fall within the operative hectograph range. Since most of the basic dyes employed in hectograph duplicating work are mainly soluble in water and alcohol, and relatively insoluble in hydrocarbons and halogenated hydrocarbons such as toluol, petroleum naphtha, benzol, carbon tetrachloride and trichloroethylene, the latter group will be particularly suitable for use as the coating solvents. Ketones such as methyl ethyl ketone and acetone will also prove to be suitable

with appropriate color-carrying base materials. It will be understood, however, that in some cases the quantity of vehicle required to dissolve the color-carrying base is small enough that an alcohol may still serve as the coating vehicle without putting an excessive portion of the dye into solution.

Resinous binder ingredients which are suitable are those which are dissolved by the appropriate solvents indicated above. In the form of the invention at present preferred, the resinous binder fraction consists of a chlorinated polyphenyl resin, sold under the name Arochlor. These materials are prepared by the chlorination of crude biphenyl and are resinous materials possessing high melting points and containing from 18 to 66 percent chlorine. Useful chlorinated polyphenyl resins include Arochlor 1260, Arochlor 1262, Arochlor 1268, Arochlor 1270, Arochlor 4465, Arochlor 5442, Arochlor 2565 and Arochlor 5460, the most preferred being the latter, which has a softening point of about 100°-105° C.

Other suitable resinous materials which may replace the chlorinated polyphenyls are, for example, rosin modified alkyd resins such as Amberol 750 (unesterified rosin-maleic resin); styrene copolymers such as Isopol P-114-RM (styrene isoprene) having a softening point of 85°-95° C.; vinyl polymers such as polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride (Saran), vinyl chloride-vinyl acetate copolymers of medium molecular weight such as Vinylite VYLF and VYHH; and cellulose resins such as ethyl cellulose and cellulose acetate.

It will be understood that the term "resin" is here being used in its usual sense including natural, semi-synthetic, and synthetic resins and includes solid amorphous organic film-forming substances chiefly of vegetable or synthetic origin, soluble in organic solvents such as ether, alcohol, etc., but not in water and having no distinct melting point or tendency to crystallize. They are also characterized by being made by polymerization or appearing in initial form as natural polymers (as in the case of cellulose derivatives). The resins used are those generally applied in the coating arts and those of moderate molecular weight which do not demonstrate excessive inherent toughness. While a few materials answering to the term "resin," e.g. polyethylene, will be found to have an excessive natural toughness and will not lend themselves readily to modification for the present purposes, these are the exception and their inapplicability will be readily recognized by chemists skilled in the art of hectograph transfer deposit formulation.

Combined with the resin to make up the remainder of the color-carrying base is a minor proportion of a waxy ingredient which markedly reduces the undesirable characteristics normally present in the resin, e.g. cohesiveness, brittleness, and lack of ability to stencil cleanly under pressure. At the same time the waxy ingredient by some interaction not at present entirely understood, is itself modified by the presence of the resin so that its solubility or dispersibility in the volatile organic liquid is significantly improved. The essential properties of the wax selected are that it shall be soluble to some extent in the solvent to be employed with the resin, and that it shall be immiscible in the resin, so that when the solvent is driven off the combined deposit appears as separate phases, i.e. the wax is uniformly dispersed in the resin matrix but does not form an actual homogeneous mixture in the nature of solid solution. At the present time, the waxy ingredient which is preferred for the purpose is pure beeswax. Other materials which may be used in place of the beeswax include solid polyethylene glycols of the harder varieties, particularly ones having a melting point of about 50°-55° C. and especially a product of this nature sold as Carbowax 4000. There are also many other waxes which will perform as intended providing they are selected on the basis of the properties stated above in relation to the resin chosen.

While not normally preferred, it may occur in some instances that small amounts of non-volatile oils or liquid plasticizers will be found to improve the composition, and these may be employed in restricted amounts if desired. The composition is, however, for all practical purposes substantially oil-free.

The amounts of resin and wax needed will vary to some extent with the particular resin and wax used, but the wax will not be present in amounts equal to the weight of the resin. In fact the resin is the predominant ingredient of the color-carrying base and will normally exceed in weight all the other ingredients present in the dried layer, excepting the coloring matter. Wax in amounts equal to as little as 2% of the weight of the resin is sometimes found sufficient. In many cases about 50% of the weight of the resin is satisfactory.

One important feature of the invention resides in the fact that, when desired, significantly more coloring matter or dye may be employed than in the usual waxy hectograph transfer layer. For example, 70% and upwards of the weight of the final transfer layer can be made to consist of soluble dye in particulate form using the resin-wax binder of this invention, as opposed to the usual 55% to 59% which is considered a good working average, or the 63% which is considered the maximum obtainable under any circumstances for conventional waxy hectograph layers. Exact studies into the maximum color retainable have not yet been made, but tests indicate that amounts of dye well in excess of 70% and up to 80% of the weight of the transfer layer can be supported when required.

The coloring matters which may be used include the water-soluble and alcohol-soluble dyes normally employed in hectograph work such as the basic polyarylmethanes, ketonimines, exanthenes, acridines and thiazoles. Likewise, where a spirit process only is aimed at, water-insoluble dyes such as the dye bases of the basic dyes enumerated above may be employed. In fact, coloring matter of any sort which has been found useful in manufacture of hectographic carbons may be employed in carrying out the invention.

The ingredients of the initial composition include the above-mentioned resin, wax, and coloring matter, and a suitable, moderately volatile liquid vehicle having the aforementioned solvent properties such as petroleum naphtha, benzol, carbon tetrachloride or trichloroethylene. In some cases, a very small proportion of oil or liquid plasticizer may also be found desirable as mentioned above. The proportion of vehicle will be adjusted to provide a composition whose viscosity is suited to the use to be made of the composition, i.e. so that it can be readily coated on a foundation strip or, in certain cases, may be printed from type on a printing press. For most ingredients, a vehicle proportion of from 40% to 80% by weight of the initial composition will prove satisfactory, and in many instances a proportion of about 65% of the weight of the composition proves suitable.

The aforementioned ingredients are mixed by grinding the same together, in a ball mill for example, at temperatures which are not substantially above ordinary room temperature. The fact that the ingredients can be thus mixed without heating is an important feature of the invention, since many of the dyes which would be otherwise acceptable for hectograph purposes, when they must be mixed with molten wax in the usual manner, are seriously affected by the sustained high temperatures to such a degree that they become useless. Even the dyes which survive the heating and which can hence be employed, are impaired somewhat in their color producing power. As a result of the present invention, therefore, it becomes possible to utilize dyes in such a way that their coloring power is not unduly impaired, and many dyes of varying hues which were heretofore unavailable for making pressure-transferable hectograph layers due to the heat susceptibility, may now be used. This is particularly

important in preparing black hectograph layers which require a delicate mixture of a number of different dyes, no suitable single black water-soluble or alcohol-soluble dye of high coloring power being known at present. By making available a wider range of hues to choose from, hectograph blacks of better color and of superior resistance to fading can now be devised.

When the ingredients are thoroughly mixed, the resulting composition is striped onto the surface of a moving web by conventional coating machinery. As the web leaves the coating point it is passed through suitable hoods designed for solvent recovery if the cost of the solvent warrants, and the solvent is evaporated. At this point a slight heating treatment of about 60° C. for a very short period of time may be employed to help speed up the driving off of the solvent, if required, but the heat is preferably omitted if possible. As the web emerges from the hood, the coating will be dry and firm and will have the characteristics of the usual waxy, pressure-transferable layer with the added advantages previously noted. The web may be slit and chopped into sheets for use, or slit into narrow strips for use as a typewriter ribbon, and packaged for storage and shipment.

While the composition has been described above as suitable for the formation of a transfer coating, it will be realized that by slight adjustment in the vehicle content a composition which is printable, but otherwise the duplicate of the transfer layer, can be achieved. In this fashion it is possible to provide masters for hectograph duplication in which the preprinted headings and form matter have similar characteristics to the matter later filled in by transfer, and thus all portions of the copies will be uniform in brightness during all parts of the run, the printed portion of the master image having just as long a duplicating life as the transferred portion.

At this point it should be emphasized that, in carrying out the present invention, the foundation web, which would normally be of paper, can be less porous than normally required. Glassine paper and cellophane webs are suitable without preliminary treatment due to the adhesive character of the resinous fraction of the coating composition. This is frequently of advantage inasmuch as homogeneous foundation webs of this character are conducive to the production of sharp, clear images, and also give a better defined cleavage plane, thus releasing the color more fully to the image under pressure, and by this invention, a transfer composition is produced which can be coated directly on the surface of such webs, to remain reliably in position until the desired pressure-induced release is effected.

Examples of compositions according to the invention are given below by way of explanation, but are not intended as limitations on the invention hereinafter claimed.

Example 1

Ingredients:	Parts by weight
Amberol resin -----	20
Carbowax -----	1
Ethyl alcohol -----	50
Crystal violet -----	50

Example 2

Ingredients:	Parts by weight
Isopol resin P114 RM -----	10
Beeswax -----	5
Carbon tetrachloride -----	85
Crystal violet -----	30

Example 3

Ingredients:	Parts by weight
Isopol resin P114 RM -----	10
Beeswax -----	5
Petroleum naphtha -----	85
Crystal violet -----	30

Example 4

Ingredients:	Parts by weight
Archlor resin 5460 -----	10
Beeswax -----	5
Carbon tetrachloride -----	85
Crystal violet -----	30

Example 5

Ingredients:	Parts by weight
Archlor resin 5460 -----	10
Beeswax -----	6.8
Ethyl cellulose -----	.7
Carbon tetrachloride -----	85
Crystal violet -----	30

Example 6

Ingredients:	Parts by weight
Archlor resin 5460 -----	10
Beeswax -----	6.8
Ethyl cellulose -----	.7
Acetone -----	85
Crystal violet -----	30

A further advantage of this invention when employed in connection with the spirit process of duplication is that certain of the suitable resins are readily alcohol soluble, or if primarily soluble in the hydrocarbons, halogenated hydrocarbons, or ketones as indicated above, are also moderately soluble in the alcohols and solvents of similar nature used in the spirit process of hectograph duplication. This means that the master image will have the resin fraction of its binder very gradually eroded to continually expose fresh dye surfaces to the solvent-moistened copy sheets, whereby bright copies will be produced over a longer proportion of the total run in comparison to the usual hectographic layer whose base is primarily of waxes having a low degree of alcohol solubility. The resins which prove particularly advantageous in this respect are chlorinated polyphenyl, unesterified rosin-maleic resins, ethyl cellulose and polyvinyl acetate.

It will be realized that the principles of this invention can also be taken advantage of by using mixtures of various resins, waxes and vehicles as well as the customary mixtures of coloring matter, merely having regard for the above-indicated miscibility and solubility relationships of the various ingredients, and that so long as these classes of materials are employed in suitable proportions indicated generally above, the purposes of the invention will be achieved.

Variations and modifications may be made within the scope of the claims and portions of the improvements may be used without others.

I claim:

1. A cold-coating ink composition for use in forming a stencilable pressure-sensitive hectograph transfer layer on a flexible foundation consisting essentially of a color-carrying base material, from 10 to 20 parts by weight of which is a resinous component selected from the group consisting of chlorinated polyphenyls, vinyl polymers, rosin modified alkyd resins and water-insoluble cellulose plastics and from 1 to 6.8 parts by weight of which is a wax having low miscibility with the resinous component alone but which is dispersible in a volatile liquid vehicle which is a solvent for said resin; spirit soluble hectograph coloring matter in undissolved discrete minute particulate form; and a volatile liquid vehicle which is a solvent for the resinous and waxy components but will not additionally dissolve a substantial amount of the particulate coloring matter, said vehicle being present in an amount sufficient to render the composition workable for coating purposes.

2. The composition as defined in claim 1 in which the resinous component is primarily a chlorinated polyphenyl.

3. The composition as defined in claim 1 in which the resinous component is primarily an unesterified rosin-maleic resin.

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4. The composition as defined in claim 1 in which the resinous component is a styrene copolymer having a softening point of about 85° to 90° C.

5. The composition as defined in claim 1 in which the resinous component is primarily a chlorinated polyphenyl, the wax is essentially beeswax, and the volatile liquid vehicle is essentially acetone.

6. The composition as defined in claim 1 in which the resinous component is essentially ten parts of a friable chlorinated polyphenyl component and five parts of a wax, namely beeswax, the coloring matter is thirty parts of crystal violet in discrete particulate form and the volatile liquid vehicle is eighty-five parts of carbon tetrachloride which is a solvent for the resinous component; and in which the wax remains dispersed in the presence of the resinous component and the coloring matter substantially retains its particulate form.

7. A cold-coating ink composition for use in forming a stencilable pressure-sensitive hectograph transfer layer on a flexible foundation consisting essentially of a color-carrying base material, from 10 to 20 parts by weight of which is a resinous component selected from the group consisting of chlorinated polyphenyls, vinyl polymers, rosin modified alkyd resins and water-insoluble cellulose plastics and from 1 to 6.8 parts by weight of which is a wax having low miscibility in the resinous component alone but which is dispersible in a volatile liquid vehicle which is a solvent for said resin; spirit soluble hectograph coloring matter in undissolved discrete minute particulate form; and from 50 to 85 parts by weight of a volatile liquid vehicle which is a solvent for the resinous and waxy components but will not additionally dissolve a substantial amount of the particulate coloring matter.

8. A cold-coating ink composition for use in forming a stencilable pressure-sensitive hectograph transfer layer on a flexible foundation consisting essentially of a color-carrying base material, from 10 to 20 parts by weight of which is a resinous component selected from the group consisting of chlorinated polyphenyls, vinyl polymers, rosin modified alkyd resins and water-insoluble cellulose plastics and from 1 to 6.8 parts by weight of which is a wax having low miscibility in the resinous component alone but which is dispersible in a volatile liquid vehicle which is a solvent for said resin; spirit soluble hectograph coloring matter in undissolved discrete minute particulate form; and a volatile liquid vehicle which is a solvent for the resinous and wax components but will not additionally dissolve a substantial amount of the particulate coloring matter, said coloring matter being present in an amount equal to at least 70% of the weight of the dried layer after said vehicle is volatilized.

9. As a new article of manufacture a pressure-responsive hectograph transfer sheet comprising a flexible foundation; and a stencilable layer of pressure-transferable imaging material thereon which is the dried residue of an ink composition consisting essentially of a color-carrying base material, from 10 to 20 parts by weight of which is a resinous component selected from the group

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consisting of chlorinated polyphenyls, vinyl polymers, rosin modified alkyd resins and water-insoluble cellulose plastics and from 1 to 6.8 parts by weight of which is a wax having low miscibility in the resinous component alone, but which is dispersible in a volatile liquid vehicle which is a solvent for said resin; spirit soluble hectograph coloring matter in undissolved discrete minute particulate form; and a volatile liquid vehicle which is a solvent for the resinous and waxy components but will not additionally dissolve a substantial amount of the particulate coloring matter.

10. A cold-coating ink composition for use in forming hectograph images consisting essentially of a color-carrying base material, from 10 to 20 parts by weight of which is a vinyl resin and from 1 to 6.8 parts by weight of which is a wax having low miscibility in the resin alone, but which is dispersible in a volatile liquid vehicle which is a solvent for said resin; spirit soluble hectograph coloring matter in undissolved discrete minute particulate form; and a volatile liquid vehicle which is a solvent for the resin and waxy components but will not additionally dissolve a substantial amount of the particulate coloring matter.

11. As a new article of manufacture a pressure-responsive hectograph transfer sheet comprising a flexible foundation; and a stencilable layer of pressure-transferable imaging material thereon, said layer being frangible under normal writing pressure and pressure-adherent to a receiving sheet and consisting essentially of a flexible color-carrying base material made up of from 10 to 20 parts by weight of a resinous component selected from the group consisting of chlorinated polyphenyls, vinyl polymers, rosin modified alkyd resins and water-insoluble cellulose plastics and from 1 to 6.8 parts by weight of a codissolvable wax having low miscibility in said resinous component, and a spirit soluble hectograph coloring matter in discrete minute particulate form.

12. As a new article of manufacture a pressure-responsive hectograph transfer sheet comprising a flexible foundation; and a stencilable layer of pressure-transferable imaging material thereon, said layer being frangible under normal writing pressure and pressure-adherent to a receiving sheet and consisting essentially of a flexible color-carrying base material made up of from 10 to 20 parts by weight of a resinous component selected from the group consisting of chlorinated polyphenyls, vinyl polymers, rosin modified alkyd resins and water-insoluble cellulose plastics and from 1 to 6.8 parts by weight of a codissolvable wax having low miscibility in said resinous component, and a spirit soluble hectograph coloring matter in discrete minute particulate form in an amount equal to at least 70% of the weight of said layer.

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