

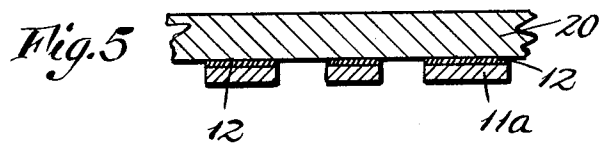
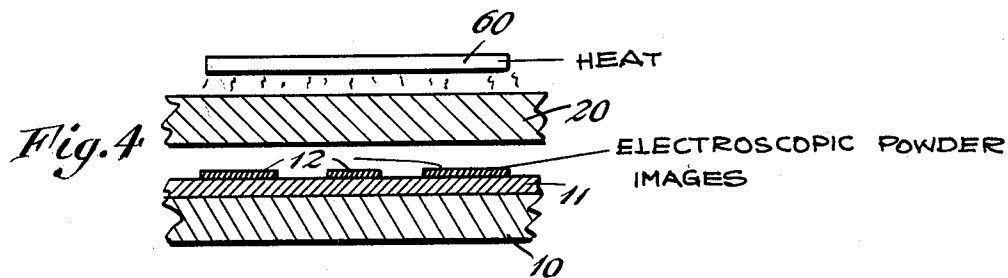
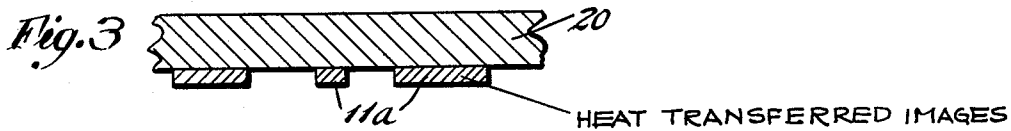
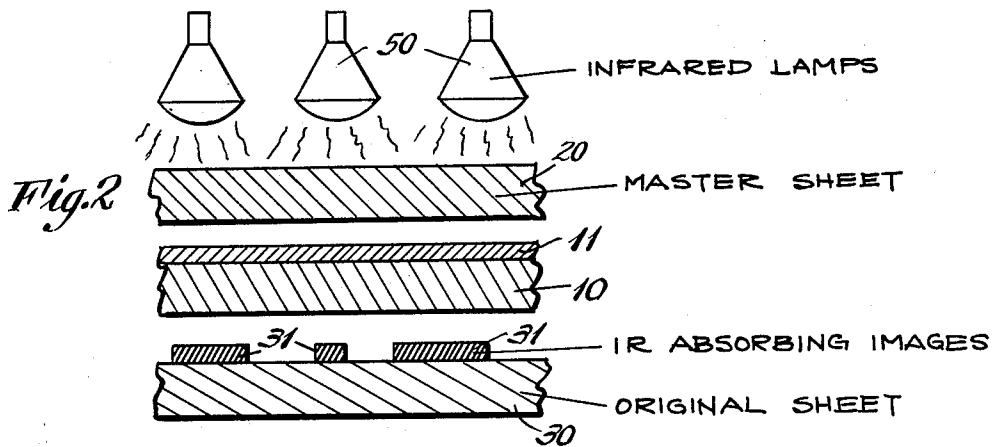
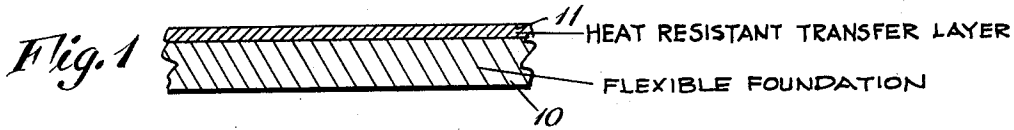
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D. A. NEWMAN ETAL

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PRESSURE-SENSITIVE HECTOGRAPH TRANSFER ELEMENT

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INVENTORS
Douglas A. Newman
Allan T. Schlottbauer
BY

ATTORNEYS

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3,177,086

PRESSURE-SENSITIVE HECTOGRAPH
TRANSFER ELEMENT

Douglas A. Newman, Glen Cove, and Allan T. Schlotz-
hauer, Locust Valley, N.Y., assignors 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 novel pressure-sensitive hectograph transfer elements.

Conventional hectograph transfer sheets carry a pressure-transferable hectograph layer of wax and dyestuff or other color-forming material. When a master sheet is superposed with a hectograph transfer sheet and pressure is applied, the said hectograph layer, corresponding to the pressured areas, transfers to the master sheet. In the spirit or gelatin duplication process, many copies can be made from the prepared master sheet.

Conventional wax-base hectograph transfer sheets have certain disadvantages which materially affect their performance. For instance, the transfer properties of these sheets vary depending upon the temperature at which they are being used due to the low hardening and softening temperatures of the wax binder material. When cold, the binder hardens and is less frangible, less tacky and has less affinity for the master sheet to which it is transferred. When warm, the binder softens and transfers readily but the transferred images are not sharp but rather are broad and somewhat fuzzy.

Also, wax-base hectograph compositions are applied to the transfer sheet foundation as a hot melt and the temperatures used must be high enough to melt the wax and reduce it to a smooth coatable consistency. Such temperatures have a detrimental effect on many dyestuffs and tend to "tar" them whereby the dye particles fuse together as non-uniform clusters. This results in transfer layers wherein the dyestuff is not uniformly dispersed.

Wax-base hectograph compositions also have the disadvantage that the wax binder material is insoluble in the spirit duplicating fluids so that much of the dyestuff carried in image form on the master sheet is insulated against contact with the spirit solvents by the wax binder. Only that amount of the dye which is at or near the surface of the images can be leached out in the duplicating process. Thus a relatively large percentage of the image on the master sheet constitutes wax binding material and trapped dyestuff which remains behind on the expired master sheet and is wasted for imaging purposes.

Another serious disadvantage of the conventional hot melt wax hectograph transfer layers is that they are melt-able at temperatures in the range of 140° F. and above and therefore give rise to many problems when used in heat transfer processes such as those involving the use of infrared radiation. Attempts to use these conventional hectograph transfer sheets in heat transfer processes have failed since the wax coatings melt at the prevailing temperatures which generally range between 150°–450° F. and flow or in some cases completely block off to the master sheet, giving rise to a blurred master sheet and inferior or unrecognizable copies.

Therefore it is an object of the present invention to prepare hectograph transfer sheets which are temperature-stable and which retain uniform frangibility characteristics over a wide range of temperatures.

It is another object to prepare hectograph transfer sheets in the cold by means of solvents thereby avoiding the problem of "tarring" the dyestuffs.

It is still another object to prepare hectograph transfer sheets on which the transfer layer does not melt or be-

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come flowable at the temperatures used in the heat-transfer processes.

It is another object of the present invention to prepare spirit hectograph transfer sheets in which substantially all of the dye is available for producing copies, thereby allowing for the preparation of more numerous copies through the spirit duplicating process than heretofore possible.

It is a further object of the present invention to prepare spirit hectograph transfer sheets in which the binding material does not interfere with the availability of the dye for the imaging of copy sheets, and which is not wasted on the expired master sheet.

These and other objects and advantages are accomplished as more fully set out in the following description and drawing in which:

FIGURE 1 represents a diagrammatic cross-section, to an enlarged scale, of a transfer sheet according to this invention.

FIG. 2 represents a diagrammatic cross-section, to an enlarged scale, of an imaged original sheet, master sheet and hectograph transfer sheet superposed and under the effects of infrared radiation, the sheets being separated for purposes of illustration.

FIG. 3 represents the imaged master sheet prepared according to the embodiment of FIG. 2.

FIG. 4 represents a diagrammatic cross-section, to an enlarged scale, of a master sheet and a transfer sheet bearing on the transfer layer surface xerographically-placed electroscopic powder images under the effects of heat, the sheets being spaced for purposes of illustration.

FIG. 5 represents the imaged master sheet prepared according to the embodiment of FIG. 4.

According to the present invention, hectograph transfer elements have been developed which have the aforementioned advantages and which provide for the sharper, cleaner, more reliable imaging of master sheets than heretofore possible.

The transfer elements of the present invention comprise a flexible foundation carrying a volatile-solvent-applied frangible transfer layer which is substantially completely transferable to a master sheet in areas impressed with imaging pressure, said transfer layer comprising from 3% to 25% by weight of a synthetic thermoplastic film-forming binder material, an amount of a miscible mixture of at least two oleaginous modifying agents in excess of the amount of said binder material, said miscible mixture including from 20% to 80% by weight of at least one oleaginous material which is substantially compatible with said binder material and from 80% to 20% by weight of at least one oleaginous material which is substantially non-compatible with said binder material, and from 35% to 65% by weight of a spirit-soluble hectograph dyestuff, said dyestuff being substantially insoluble in said oleaginous materials and insoluble in the volatile solvent used to apply said transfer layer.

The thermoplastic binder preferably comprises a material which is soluble in the spirit duplicating fluids. Thus, alcohol- and preferably ethanol-soluble materials such as ethyl cellulose and polyvinyl acetate are preferred. However, in many instances the spirit duplicating fluid may consist of or have added thereto any organic solvent which dissolves the particular resin or film-former used.

The oily mixture forms a critical part of the present composition since it is the oily materials which render the thermoplastic binder frangible. It has been found that at least two different oily materials must be used. These materials must be miscible with each other and at least one of them must be compatible with the binder material while at least one other is substantially incompatible with the resinous binder.

The incompatible oily material, if used alone with the thermoplastic binder, tends to be exuded or sweated from the resinous layer. This is detrimental in that the exuded oil tends to stain master sheets stored in contact therewith. More important, however, is the eventual loss of frangibility of the transfer layer as the amount of incompatible oil therein gradually decreases.

The compatible oily material, if used alone with the thermoplastic binder, may render it frangible in some cases, depending upon the degree of compatibility. However, the compatible oil acts as a plasticizer for the binder and gradually the frangibility is lost as a solid plastic film is formed.

Where non-miscible incompatible and compatible oils such as mineral oil and castor oil are used, each oil acts independently and the transfer layer "sweats" the mineral oil while the castor oil plasticizes the layer and frangibility is lost. However, these two oils may be used together provided that a third oil is added which is miscible with both of them. For instance, when rapeseed oil is added, a miscible solution of the three oils is formed, the mineral and rapeseed oils being incompatible with the resinous binder material, in the case of ethyl cellulose, while the castor oil is compatible therewith.

It is not completely clear why the incompatible oily material of the present invention is not exuded or sweated from the present transfer layers or why the compatible oily material does not gradually plasticize the binder therein and change the frangibility of the layer. It appears that the incompatible oil, while it has no attraction for the binder material per se, gains an attraction or bonding to the binder by means of the compatible oil, with which it is miscible. Likewise the compatible oil is prevented from plasticizing the binder and forming a continuous solid non-frangible film by the presence of the incompatible oil which gives the layer a discontinuous or porous structure and prevents the formation of a continuous layer. The compatible oil seems to lose its plasticizing properties due to its mixture with the incompatible oil while the incompatible oil seems to lose its tendency to be sweated from the layer due to its mixture with the compatible oil.

It has been found that the miscible oily mixture must contain from at least 20% by weight up to about 80% by weight of the compatible oil. Oil mixtures containing over 80% compatible oil and less than 20% incompatible oil exhibit a tendency to plasticize the binder and cause loss of frangibility upon extended periods of storage whereas mixtures containing over 80% incompatible oil and less than 20% compatible oil exhibit a tendency to sweat or exude oil from the binder and also cause loss of frangibility.

The preferred oily mixtures generally contain approximately an equal amount by weight of one or more compatible oils and one or more incompatible oils.

The total amount of oily material present in the transfer layers of the present invention always exceeds the amount by weight of the resinous or film-forming binder material. The upper limit is determined only by the degree of softness desired, amounts up to about ten times the weight of the binder material being suitable in some cases.

The transfer sheets of the present invention are prepared by coating a suitable flexible foundation such as paper, cellulose acetate or Mylar, etc. with a coating of a synthetic thermoplastic resinous or film-forming binder material which is preferably at least partially soluble in the conventional spirit duplicating fluids, a miscible mixture of at least one non-volatile oily material which is incompatible with the binder and at least one non-volatile oily material which is compatible with the binder, and a quantity of spirit-soluble hectograph dyestuff. The coating may take place by dissolving the components in a volatile solvent, or by applying such coating in the form of an organosol or plastisol in a manner well known to

the art. The preferred method, however, is the solvent application in which one or more volatile organic solvents are used which dissolve the binder material and are at least substantial non-solvents for the hectograph dyestuff.

After application of the coating to the foundation, the solvent is evaporated and there results the formation of a frangible and stable hectograph layer which does not melt at elevated temperatures but becomes soft but not liquid or flowable at temperatures equal to or exceeding 450° F., which is the maximum temperature generally used in thermographic or heat-transfer processes.

While the advantages of the present invention are important from the standpoint of straight spirit or gelatin hectograph duplication, there is also the other consideration involving the use of heat in preparing masters.

There are at present two principal methods for accomplishing this which are applicable to forming hecto masters. One is xerography and the other, thermographic means involving infrared radiation.

In the first case, a xerographic image comprising conventional resinous electroscopic powders may be formed electrostatically on a Xerox plate and transferred to the transfer layer of the solvent type of hectograph sheet or to the working surface of a master sheet. The imaged sheet, together with a master or a solvent type of hectograph sheet under sufficient pressure to hold the two firmly together, are subjected to heat or infrared radiation in which action the xerographic resin powder comprising the xerographic image is tackified and fused in the imaged area so that the master and hectograph layer are "welded" together at said imaged areas. On separation after cooling, the frangible dye layer is picked off in said imaged areas and adhered to the master sheet.

In the second case, the solvent type hectograph sheet is placed together with a master sheet and infrared radiation-absorbing original images which are generally carried by a separate original sheet as shown by FIG. 2 of the drawing, but may also be present on the surface of the master sheet. The superposed sheets are fed through a thermographic machine having infrared radiation, in which act heat is developed in the original infrared radiation-absorbing images, thereby causing a heating and softening of the hectograph layer and a "welding" thereof to the master in said areas. On cooling and separation, hectograph images are formed on the master sheet corresponding either directly or in reverse to the original images.

To further improve upon the "welding" of the master to the hectograph layer, it may be advisable to either film over the hectograph layer or apply a film to the master, said film having particular affinity for the master on the one hand or the hectograph layer on the other, as the case may be, when hot, thereby effecting a better, more complete transfer after cooling and separation. The whole point is that these solvent resin bonded type coatings, while they might soften with heat, do not liquefy or flow out as does a wax coated sheet. Naturally it should be understood that a coating that becomes liquid under these temperatures is inoperable in the case of xerography to form a master as described because the whole hectograph mass would block off and adhere to the said master. Similarly, in the case of the thermographic method, the criticality would be much greater when flowable ink is used because of ambient temperature developed in the machine and the tendency of the foundation and master sheets to absorb some radiation, whereas with a hectograph coating that does not become molten or fluid but merely softens, the criticality of the temperature factor is greatly reduced. Naturally, various modifications can be made in the composition of the resin bonded layer and/or undercoatings or supercoatings to fit an intended use, all of which will be well known in the art. The fact is that besides having a better copying hectographic composition for regular work, an added advantage can

be found in the application of the element to thermographic or xerographic duplicating methods.

As the non-volatile, non-compatible oily component, it has been found that any normally liquid or semi-solid oleaginous material may be used so long as it is not essentially compatible with the binder employed at room temperature. Such materials vary of course with the binder but include, in the case of ethyl cellulose binder, oleaginous compositions such as most of the animal and mineral oils, petrolatum, lanolin and the like.

Illustrative of the non-volatile compatible oleaginous materials useful in conjunction with ethyl cellulose binder material are the vegetable oils such as castor oil, linseed oil and soybean oil, esters such as dioctyl phthalate and tricresyl phosphate, and the like.

The preferred oily material mixture is one which has a high viscosity and contains one or more oleaginous materials having this characteristic. For instance, mixtures containing high viscosity oils such as heavy bodied mineral oil and the like, or pasty semi-solid oily materials such as fats, lanolin, petrolatum and the like, provide excellent results. The high viscosity of the mixture tends to render it even less migratory than more fluid mixtures and thus improves upon the aging characteristics of the hectograph transfer sheets containing the same.

It should be emphasized that the compatibility and incompatibility of the various oily materials differ depending upon the particular binder material used and that the selection of an oil phase containing the aforesaid ratio of compatible and incompatible oils is within the skill of the art in view of the present teachings.

The following table is set forth as an illustration of several miscible oil mixtures which may be used according to the present invention together with an ethyl cellulose binder material. The numbers listed designate the relative parts by weight of each oil.

A	B	C
Oil Compatible with Binder	Oil Incompatible with Binder	Oil Necessary to Render A and B Oils Miscible, if any
2 Castor.....	8 Refined Rapeseed.....	
5 Castor.....	5 Refined Rapeseed.....	
2 Castor.....	4 Mineral.....	4 Refined Rapeseed.
6 Castor.....	2 Mineral.....	2 Refined Rapeseed.
3 Castor.....	3 Light Mineral.....	4 Butyl Stearate.
4 Castor.....	2 Heavy Mineral.....	4 Refined Rapeseed.
2 Castor.....	4 Mineral.....	4 Lard Oil.
6 Castor.....	2 Mineral.....	2 Lard Oil.
2 Castor.....	4 Mineral.....	4 Butyl Stearate.
6 Castor.....	2 Mineral.....	2 Butyl Stearate.
5 Castor.....	5 Lard Oil.....	
5 Castor.....	5 Butyl Stearate.....	
3 Tricresyl Phosphate.....	4 Mineral.....	3 Refined Rapeseed.
3 Tricresyl Phosphate.....	4 Mineral.....	3 Butyl Stearate.
3 Dioctyl Phthalate.....	7 Mineral.....	

It should be understood that the foregoing miscible oil mixtures may be used with other binder materials provided that the compatibility and incompatibility requirements are met. For instance, many vinyl resins such as polyvinyl acetate are compatible with oils such as tricresyl phosphate and dioctyl phthalate and incompatible with oil such as mineral oil, rapeseed oil and the like.

The following examples are illustrative only and should not be considered as limitative.

Example 1

The following ingredients were thoroughly intermixed to a coatable consistency:

	Parts by weight
Refined rapeseed oil (incompatible)	12
Castor oil (compatible)	4
Filler (if desired—may be graphite or carbon black)-	4
Hectograph dye (Du Pont Spirit Black #3)	20
Ethyl cellulose	5
Solvent (toluol or the like)	55

The mixture was then spread evenly on a suitable flexible foundation 10, such as paper, by suitable coating apparatus and allowed to cool and to set by evaporation of the solvent to form a smooth, pressure-transferable and heat-transferable hectograph coating 11 having the properties described.

The prepared transfer sheet is compared with a conventional hot melt wax hectograph sheet in the following manner: Two original sheets 30 which are desired to be copied are placed face-up; then the novel hectograph sheet of the present invention is placed face-up over the first original and the conventional hectograph sheet is placed face-up over the second original; next a suitable master sheet 20 is placed over each of the transfer sheets, in contact with the hectograph layer, to form a pack. Each pack is then passed through a Thermo-Fax machine. The infrared radiation of the machine is focussed on the master sheet and penetrates through to the original sheet where it is absorbed by the images 31 on the original sheet and converted to heat in these areas. The heat generated by the images causes the overlying transfer sheet to heat up over the imaged areas thereby bonding the master to said imaged areas.

Upon emergence from the machine, the pack carrying the conventional hectograph sheet is found quite inferior for many reasons. It appears that the imaging layer of the conventional hectograph sheet melts and becomes fluid at the existing temperatures and spreads onto the master sheet due to the overall ambient temperature of the thermographic machine, the radiation-absorbing tendency of the foundation and master sheets, and the lack of heat resistance of the transfer layer.

None of these defects are present in the pack containing the novel hectograph sheet of the present invention. The imaging layer of this sheet does not become fluid at the temperatures of the thermographic machine but merely becomes softened and adhesive or tacky over the image areas of the original sheet. The hectograph layer over these areas fuses itself to the master sheet and transfers thereto as images 11a in a substantially stenciling manner to give a sharp, clear master sheet having minimal background stains. Likewise the present transfer sheets permit for varying the density of the copies produced due to their heat resistance over a relatively wide temperature range. For instance, where denser copies and a longer running master sheet are desired, the speed at which the pack is run through the thermographic machine may be decreased, thus allowing for increased heat formation in the imaged areas and a denser imaged master sheet.

Each of the prepared master sheets are tested in a spirit duplicating machine and the novel sheets of the present invention result in cleaner, sharper and over 50% more numerous copies than the master sheet prepared from the conventional hectograph sheet.

Example 2

	Parts by weight
Castor oil (compatible)	4.8
Mineral oil (incompatible)	8.0
Butyl stearate (compatible)	8.0
Hectograph dye material (Du Pont Spirit Black #3)	19.2
Ethyl cellulose	5.0
Solvent (toluol or the like)	55.0
	100.0

The above ingredients are mixed to a coatable consistency and coated on a suitable foundation as in Example 1 to form a hectograph transfer sheet.

This transfer sheet is then placed in face-to-face contact with a selenium plate carrying electrostatic images comprising electroscopic resinous thermoplastic powder under sufficient pressure to keep the two elements in close contact. A corona discharge is applied, thereby reversing the polarity, and upon removal of the hectograph sheet the powdered images 12 are adhered to the hecto-

graph layer 11. The hectograph sheet bearing the powdered images is then placed in face-to-face contact with a master sheet 20 to form a pack which is heated to a temperature of between 400°-450° F. The powdered images tackify and fuse to the master sheet and the hectograph layer in the areas overlying the powdered images. Thus, upon separation of the sheets there is formed a master sheet 20, carrying a substantial amount of hectograph material 11a in the electrostatic image areas 12, which may be used to prepare many sharp copies in the spirit process.

An alternative xerographic method is to transfer the Xerox images from the plate to master sheet and then superpose the master with the hectograph transfer sheet and place them in the Xerox oven.

An attempt to employ conventional hot melt wax hectograph transfer sheets in either of these processes fails due to the fact that the dye layer melts to a fluid state at the required temperatures and the fluid transfers to the master sheet throughout.

It has been found that amounts of binder as low as 2% or as high as 25% based upon the total dry weight of the transfer composition may be used, and that the amount of hectograph dye may be as high as 10 times the weight of binder used. It is preferred that the dye-stuff be present in an amount ranging from about 35% to about 65% of the dry weight of the transfer composition.

As the resinous or film-forming binder material in the present hectograph compositions, it is preferred to employ those which are at least partly soluble in the conventional spirit duplicating fluids which comprise alcohol, such as ethyl alcohol, and water. In this regard, the preferred film-forming materials include cellulosic resins such as ethyl cellulose; vinyl resins such as polyvinyl acetate; alcohol-soluble nylon polyamides; chlorinated polyphenyl resins such as the Aroclors; unesterified rosin-maleic resins such as the Amberols and the like. Other suitable binders include vinyl chloride-vinyl acetate copolymers such as Vinylite VYHH, cellulose acetate, methyl cellulose, carboxymethyl cellulose, styrene homopolymers and copolymers such as Isopol P-114-RM (styrene-isoprene), and others. It is useful in some instances to overcoat the hectograph layer with a wax supercoating containing frangible, tacky material such as beeswax, Indopol and Vistanex to improve the attraction of the transfer layer for the master sheet.

In the formulations set forth hereinbefore it should be emphasized that the named "substantially compatible" oils are not usually completely compatible with the binder materials, nor are the "substantially incompatible" oils completely so. In determining the relative compatibilities the binder material and oil are mixed in the cold, using a mutual volatile organic solvent, if necessary, and in the proportions given in the examples. If more than seventy-five percent of the oil mixes with the resin without separating therefrom, it is said to be substantially compatible therewith. If less than twenty-five percent of the oil mixes therewith without separation, it is said to be substantially incompatible with the binder material. It is within these definitions that these terms are used herein and in the appended claims.

It has been found that when the novel transfer sheets of the present invention are to be used in the reflex

thermographic processes as illustrated by FIG. 2, then it is preferred that the master and transfer sheets be of such a nature as to allow the radiation to easily pass through. In this regard, transparent, translucent and transpicious sheets are very satisfactory, such as clear plastic, frosted or crazed plastic, glassine paper, etc. Likewise the hectograph dye layer should be permeable to infrared radiation and should not contain any materials which absorb infrared radiation to any substantial degree. Suitable infrared-permeable dyes include rhodamine dyes, malachite green, safranin dyes and the like.

As defined by the appendant claims, the particular dye-stuff used is one which is insoluble to the volatile solvent used to apply the transfer layer and insoluble in the miscible mixture of oleaginous modifying agents present in the transfer layer. Preferred volatile coating solvents include the halogenated hydrocarbons such as carbon tetrachloride, dichloroethane and the like, as well as hydrocarbon solvents such as toluol, xylene and the like.

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

We claim:

1. A pressure-sensitive hectograph transfer element comprising a flexible foundation carrying a volatile-solvent-applied frangible transfer layer which is substantially completely transferable to a master sheet in areas impressed with imaging pressure, said transfer layer comprising from 3% to 25% by weight of a synthetic thermoplastic film-forming binder material, an amount of a miscible mixture of at least two oleaginous modifying agents in excess of the amount of said binder material, said miscible mixture including from 20% to 80% by weight of at least one oleaginous material which is substantially compatible with said binder material and from 80% to 20% by weight of at least one oleaginous material which is substantially non-compatible with said binder material, and from 35% to 65% by weight of a spirit-soluble hectograph dyestuff, said dyestuff being substantially insoluble in said oleaginous materials and insoluble in the volatile solvent used to apply said transfer layer.

2. A pressure-sensitive hectograph transfer element according to claim 1 in which the binder material is a cellulose plastic.

3. A pressure-sensitive hectograph transfer element according to claim 1 in which the oleaginous materials are liquid oils.

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RICHARD D. NEVIUS, *Primary Examiner*.

MURRAY KATZ, DAVID KLEIN, *Examiners*.