Sept. 21, 1965 D. A. NEWMAN ETAL 3,207,621

NOVEL HECTOGRAPH TRANSFER SHEET AND PROCESS

Filed Aug. 16, 1960

Fig. 1

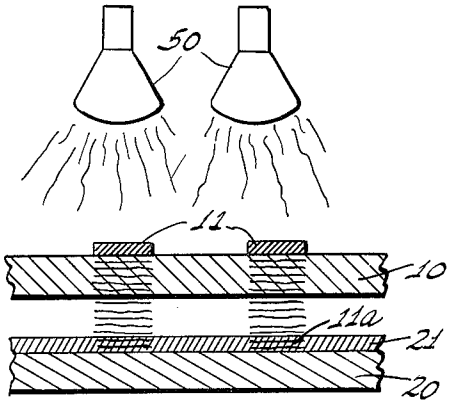


Fig. 2

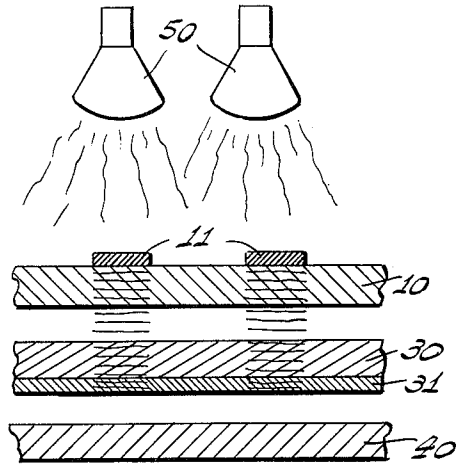
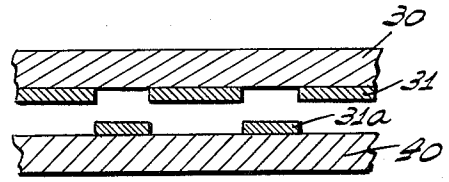


Fig. 3



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NOVEL HECTOGRAPH TRANSFER SHEET AND PROCESS

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6 Claims. (Cl. 117—36.1)

This invention relates to the preparation of thermographically-reproducible hectograph copy sheets, and to the novel hectograph transfer sheets for preparing the same.

In the spirit duplicating process, a master sheet is reverse-imaged with a wax composition containing water- and/or alcohol-soluble dye stuffs. Then the desired number of copies is produced in a spirit duplicating machine by contacting the master sheet with copy sheets which have been moistened with water and/or alcohol. The water and/or alcohol of each copy sheet dissolves a small amount of the dyestuff from the reverse images on the master sheet, thereby forming duplicate copies of the master sheet in direct-reading form.

It is known to prepare duplicate copies of an original sheet through the use of thermographic machines and heat-sensitive copy sheets. However, it is necessary that the images on the original sheet have the property of absorbing infrared radiation and converting it to heat. In this way, only the imaged areas of the original sheet absorb the radiation and generate heat to the superposed heat-sensitive copy sheet which responds in the heated areas to form a facsimile copy of the original sheet.

Heretofore is was impossible to prepare hectograph copies which, in turn, could be reliably reproduced thermographically due to the fact that the water- and/or alcohol-soluble dyestuffs commonly employed in hectograph transfer sheets do not have the property of absorbing infrared radiation and converting it to heat.

It is therefore an object of the present invention to prepare hectograph transfer sheets which function properly in the spirit duplicating process and which contain dyestuffs having the property of absorbing infrared radiation and converting it to heat.

It is another object of the present invention to produce hectograph copies in the spirit duplicating process which copies may be duplicated thermographically.

These and other objects are accomplished according to the present invention as more fully explained hereinafter.

In the drawing:

FIGURE 1 is a diagrammatic cross-section, to an enlarged scale, of an imaged hectograph copy sheet and a heat-reactive or heat-compressible copy sheet superposed and under the influence of infrared radiation, though separated for purposes of clarification.

FIG. 2 is a diagrammatic cross-section, to an enlarged scale, of an imaged hectograph copy sheet, a heat-sensitive transfer sheet and a duplicate copy sheet superposed and under the influence of infrared radiation, though separated for purposes of clarification.

FIG. 3 is a dragrammatic cross-section, to an enlarged scale, of the heat-sensitive transfer sheet and the duplicate copy sheet of FIG. 2 after irradiation and imaging of the duplicate copy sheet.

The objects of this invention are accomplished by the preparation of hectograph transfer sheets in which the transfer layer is based upon resinous materials which are at least partly soluble in alcohol, and contains a complex azine dystuff.

It has been discovered that of all the dystuffs tested the complex azine family of dyes is the only one having the property of absorbing infrared radiation to such an extent that spirit copies containing this dyestuff are heat sensitive.

However, it has also been found that certain problems are encountered in the use of these dyes. In the first place, most of them do not have sufficient alcohol solubility in spirit duplicating fluids. Therefore they are not used to any extent in the production of hectograph transfer sheets but find their greatest utility in the field of planographic printing. Secondly, these dyes, particularly the nigrosine dyes, tend to soften with heat so as to fuse and aggolomerate at elevated temperatures thereby becoming less soluble in solvents and losing their tinctorial strength. This is an important disadvantage since the transfer layer of conventional hectograph sheets is based upon wax and is applied by the so-called hot-melt method. At the temperatures used in the hot-melt method, the complex azine dye particles soften and fuse together to form agglomerates which are far too large and far too insoluble to effect the production of either legible or radiation-sensitive spirit copies.

According to this invention, transfer sheets are prepared having transfer layers which are based upon resinous materials and which are applied as solvent solutions or dispersions at ordinary room temperatures, thus avoiding the harmful effects of heat upon the dyestuff. Due to the slow solubility of the complex azines as compared with conventional spirit dyestuffs, the resinous material of the transfer layer must be one which is at least slowly soluble in the spirit duplicating fluids such as ethanol. In this way the resin in the master images functions not only as a binder for the dyestuff but also as a carrier therefor in effecting transfer of the dye to the copy sheets in the spirit process. Likewise all of the dye in the master images is made available for transfer since there is no barrier created by the binder as is the case when only spirit-insoluble waxes are used.

According to the preferred form of the present invention, the complex azine dyestuff is used in combination with large amounts of a conventional spirit dyestuff. Although the latter class of dyestuffs do not absorb infrared radiation to any degree, it has been found that their excellent solubility in the spirit fluids in some way tends to aid the solubility of the radiation-absorbent dyestuff so as to provide for the production of many more radiation-sensitive spirit copies than possible through the use of complex azine dyestuff alone.

In practicing this preferred form, the complex azine dyestuff is present in an amount ranging from about 10% by weight up to about 80% by weight based upon the total weight of the dyestuff mixture. In all cases, the amount of complex azine dyestuff in the final transfer layer after evaporation of the volatile coating solvents is at least 10% and up to 60% by weight based upon the total weight of the transfer layer.

According to the present invention, the major amount by weight of the binder employed is resinous and is at least partially soluble in the spirit duplicating fluids, namely alcohol or alcohol-water mixtures. Among the resinous or plastic materials found suitable as binders are the following: cellulose plastics such as cellulose acetate, ethyl cellulose and cellulose nitrate; vinyl polymers such as polyacrylamide, polymethacrylamide, polyvinyl acetate, polyvinyl alcohol (completely hydrolyzed), polyvinyl alcohol acetate (50% hydrolyzed), polyvinyl methyl ether and polyvinyl ethyl ether; rosin modified alkyd resins such as Amberol 800, Beckacite 1111 and Lewisol 2L; mixtures of hydrocarbon copolymers such as Isopal P114RM; chlorinated biphenyl resins such as Arochlor 5460; alcohol-soluble nylon, as well as many other resin-materials which can be determined by those skilled in the art, based upon their solubility in ethyl alcohol, 2-ethoxy ethanol or mixtures of these alcohols and water.

In order to produce a resinous transfer layer having the degree of frangibility or pressure-transferability necessary according to this invention, certain materials must be added, which materials are immiscible and incompatible with the resin used. The use of such materials seems to disrupt the continuity of the resinous portion of the layer and prevents it from forming a hard, continuous, non-transferable film. The transfer layers so prepared appear to have a porous or honeycombed structure in which the resinous material forms the honeycomb or base material while the non-volataile, non-compatible material is dispersed throughout the resinous material and forms the pores or discontinuous phase. An important reason for the superior results obtained through the use of soluble resins in the present transfer sheets is thought to be that since the resinous coating is applied with solvent and contains non-volatile, non-miscible materials, the cast film on drying is porous, having minute micellular structure, permitting alcohol to penetrate through the master images and allowing more complete dye solvation. Also each dye particle is surrounded by alcohol wettable and soluble resin material thus insuring complete dye solvation.

The hectograph transfer sheets of the present invention are prepared by coating a suitable foundation such methyl isobutyl ketone, etc.

After application of the coating, the solvent is evaporated and there results the formation of a frangible, pressure-transferable hectograph layer which does not melt at elevated temperatures but becomes soft but not flowable at temperatures between 150°–450° F.

As the non-volatile non-miscible component, it has been found that any material may be used so long as it is not as paper, cellulose acetaate or Mylar, etc. with a coating composition containing a suitable resinous binder, a non-volatile, non-miscible component which is not a solvent for the resinous binder, and the hectograph dyestuff. The coating takes place at room temperature by dissolving the components in a volatile solvent which is not a solvent for the dyestuffs, coating the foundation and allowing the applied layer to set by evaporation of the volatile coating solvents.

It is important that the volatile coating solvent be a solvent for the resin and preferably also for the non-volatile, non-miscible material, and that it is a non-solvent for the dyestuffs employed. In this way, the dye particles are maintained for the most part in their concentrated undeveloped form and their potency is preserved for the production of copies in the spirit process. Suitable coating solvents include aromatic hydrocarbons such as toluene and xylene; chlorinated hydrocarbons such as chloroform and carbon tetrachloride; aliphatic ketones such as essentially compatible wtih the binder employed at temperatures in the aforementioned range. Such materials vary of course with the binder but include materials which are normally liquid or semisolid at room temperatures such as oleaginous compositions such as the animal, vegetable and mineral oils, butyl stearate, and oleic acid; or pasty materials such as lanolin, petrolatum and hydrogenated vegetable oil; or mixtures of any of the aforementioned. Also minor amounts of waxes such as beeswax and Carbowax may be employed as the non-volatile non-miscible material. The inclusion of the non-miscible material is necessary to insure the formation of a frangible, pressure-transferable hectograph layer. Excluded from the class of non-volatile, non-miscible, materials are materials which are compatible with and are partial solvents for the resins at the temperatures used, such as true plasticizers, since they prevent the release of the transfer layer from the transfer sheet because they do not allow the formation of micellular frangible films.

As the soluble, non-infrared radiation-absorbing dyestuffs which form from about 90% down to about 20% by weight based upon the total weight of the dyestuff mixture, any of the conventional hectograph dyestuffs which are soluble in spirit duplicating fluids may be employed. Suitable purple dyes include crystal violet, methyl violet and ethyl violet. Suitable orange dyes include chrysoidine, basic or acridine orange and croceine orange. Suitable green dyes include brilliant green and malachite or Victoria green. Suitable red dyes include rhodamine, magenta and safranine. The selection of other suitable dyestuffs having the described properties will be obvious to thoses killed in the art.

The complex azine dyestuffs which absorb infrared radiation and convert it to heat, and which form from about 10% to about 80% by weight based upon the total weight of the dyestuff mixture, are selected from the group consisting of the indulines, the nigrosines and the aniline colors. Suitable dyestuffs from these groups include Induline 3B, CI 860; Induline 6B, CI 860; water soluble Induline sulfonates, CI 861; the nigrosines, CI 864 and 865; the alcohol soluble nigrosine chlorides, the oil-and-wax-soluble free bases of nigrosine, and the water-soluble nigrosine sulfonates; Aniline Black, CI 870; "Ungreenable" Aniline Black; N-phenyl-p-phenylenediamine Black, CI 871; and p-aminophenol Black or p-phenylenediamine Black, CI 875.

The important feature of the hectograph transfer sheets of the present invention resides in the fact that they result in the production of hectograph copies in the spirit process which carry infrared radition-absorbing images. These copies may therefore be reproduced themographically using heat-reactive or heat-compressible copy paper in the manner exemplified by FIG. 1 of the drawing. The hectograph copy sheet **10** bearing infrared radition-absorbing images **11** is superposed with a copy paper having a suitable foundation **20** and a layer **21** of heat-compressible or heat-reactive material. Examples of heat-compressible blush coated copy sheets are shown for instance in U.S. Patent No. 2,927,039 and U.S. Patent No. 2,880,110. Examples of heat-reactive, chemical-containing copy papers are shown for instance in U.S. Patent No. 2,663,657 and U.S. Patent No. 2,899,334. When the superposed sheets are subjected to infrared radition in a suitable apparatus such as a Thermofax machine, the heat generated by the images **11** penetrates to layer **21** which becomes discolored in areas **11***a* to form an exact copy of the spirit copy.

The spirit copies may also be reproduced in the manner exemplified by FIGS. 2 and 3 of the drawing whereby the production of duplicate copies is the result of a physical transfer of portions **31***a* of transfer layer **31**. In this embodiment, the spirit copy sheet **10** bearing images **11** is superposed with a copy paper **40** and a transfer sheet having a suitable foundation **30** and a non-infrared radiation-absorbing, heat transferable dye layer **31**. The dye layer may consist of a wax layer tinted with a suitable non-infrared radiation-absorbing dyestuff such as crystal violet. Under the influence of infrared radiation **50**, such as in a Thermofax machine, images **11** generate heat and cause the corresponding areas of the layer **31** to transfer to copy sheet **40** in the form of images **31***a*. A process

similar to that of FIGS. 2 and 3, is shown in U.S. Patent No. 2,769,391.

The following ingredients were thoroughly intermixed not be considered as limitative:

Example I

The following ingredients were throughly intermixed to a coatable consistency:

	Parts by weight
Ethyl cellulose N–7	5.0
Lard oil	6.6
Oleic acid	3.4
Mineral oil	5.0
Nigrosine	9.0
Crystal violet	8.0
Brilliant green	8.0
Solvent (toluol or the like)	55.0
	100.0

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

The following examples show ingredients which were mixed and coated on a suitable foundation in the same manner described in Example I.

Example II

	Parts by weight
Polyvinyl acetate	5.0
Mineral oil	17.6
Lanoline	3.2
Nigrosine	6.0
Crystal violet	13.2
Solvent (toluol or the like)	55.0
	100.0

Example III

	Parts by weight
Arochlor 5460	10.0
Beeswax	3.0
Induline	9.0
Victoria green	18.0
Carbon tetrachloride	60.0
	100.0

Example IV

	Parts by weight
Isopal Resin P 114 RM	10.0
Beeswax	3.0
Methyl violet	8.0
Aniline black	9.0
Petroleum naphtha	70.0
	100.0

Example V

	Parts by weight
Amberol Resin 800	15.0
Carbowax	1.0
Crystal violet	15.0
Nigrosine	13.0
Petroleum naphtha	56.0
	100.0

It should be understood that the foregoing examples are not to be construed as being limitative and that the principles of this invention can be carried out by using mixtures of the various resins, dyestuffs and other materials disclosed so long as the basic limitations as outlined herein are observed.

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. The process of preparing a hectograph transfer element having thereon a frangible resinous transfer layer which is transferable to a master sheet under the effects of imaging pressure to form master images having the ability of producing highly infrared radiation-absorbing, thermographically-reproducible duplicate images on a copy sheet in the spirit duplicating process, which comprises coating at ordinary room temperature a suitable foundation with a hectograph ink composition comprising a resinous binder material which is at least partly soluble in spirit duplicating fluids, a non-volatile oily material which is a non-solvent for said resinous binder material, a concentrated undeveloped mixture of dyestuff particles comprising from about 10% to about 80% by weight of an infrared radiation-absorbing dyestuff having poor spirit-solubility and selected from the class of complex azine dyestuffs consisting of the nigrosines, the indulines and the aniline colors, and from about 90% to about 20% by weight of a non-infrared radiation-absorbing hectograph dyestuff from another class and having good solubility in spirit duplicating fluids, said azine dyestuff being present in an amount equal to from about 10% to about 60% by weight based upon the total weight of the frangible transfer layer, and a volatile organic solvent for said resinous binder material which is a non-solvent for said dyestuff mixture whereby the latter is maintained in the form of concentrated undeveloped particles, and evaporating said volatile solvent to form said frangible hectograph transfer layer on said foundation.

2. The process of claim **1** in which the resinous binder material comprises a spirit-soluble vinyl resin.

3. The process of claim **1** in which the resinous binder material comprises a spirit-soluble cellulose plastic.

4. A hectograph transfer element comprising a suitable foundation carrying a frangible resinous hectograph layer which is transferable to a master sheet under the effects of imaging pressure to form master images having the ability of producing highly infrared radiation-absorbing, thermographically-reproducible duplicate images on a copy sheet in the spirit duplicating process, said layer comprising a resinous binder material which is at least partly soluble in spirit duplicating fluids, a non-volatile oily material which is a non-solvent for said resinous binder material, and a concentrated undeveloped mixture of dyestuff particles comprising from about 10% to about 80% by weight of an infrared radiation-absorbing dyestuff having poor spirit-solubility and selected from the class of complex azine dyestuffs consisting of the nigrosines, the indulines and the aniline colors, and from about 90% to about 20% by weight of a non-infrared radiation-absorbing hectograph dyestuff from another class and having good solubility in spirit duplicating fluids, said azine dyestuff being present in an amount equal to from about 10% to about 60% by weight based upon the total weight of the hectograph transfer layer.

5. A hectograph transfer element according to claim **4** in which the resinous binder material comprises a spirit-soluble cellulose plastic.

6. A hectograph transfer element according to claim **4** in which the resinous binder material comprises a spirit-soluble vinyl resin.

References Cited by the Examiner

UNITED STATES PATENTS

2,138,836	12/38	Brower.
2,454,700	11/48	Holik.
2,492,163	12/49	Locke.
2,800,077	7/57	Marron.
2,810,661	10/57	Newman et al.

(Other references on following page)

UNITED STATES PATENTS

2,872,340	2/59	Newman et al.
2,984,582	5/61	Newman et al.
3,036,924	5/62	Newman.

FOREIGN PATENTS

563,932	7/58	Belgium.
873,178	7/61	Great Britain.

OTHER REFERENCES

Apps: Printing Ink Technology, pub. 1958 by Leonard Hill (Books) Ltd., London. Only pages 392, 393, 396 and 398 made of record.

DAVID KLEIN, *Primary Examiner.*

ROBERT E. PULFREY, WILLIAM B. PENN, R. A. LEIGHEY, *Examiners.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,207,621 September 21, 1965

Douglas A. Newman et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 35, for "is" read -- it --; column 2, line 21, for "aggolomerate" read -- agglomerate --; column 3, line 15, for "resin-" read -- resinous --; line 43, beginning with "methyl isobutyl" strike out all to and including "as it is not" in line 50, and insert the same after "ketones such as" in line 69, same column 3; same column 3, line 70, for "wtih" read -- with --; column 4, line 26, for "thoses killed" read -- those skilled --; lines 44 and 48, for "radition-", each occurrence, read -- radiation- --; line 57, for "radition" read -- radiation --; column 5, line 3, strike out "The following ingredients were thoroughly intermixed" and insert instead -- The following examples are illustrative only and should --; line 33, for "Lanoline" read -- Lanolin --.

Signed and sealed this 10th day of May 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents