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PRESSURE SENSITIVE TRANSFER SHEET

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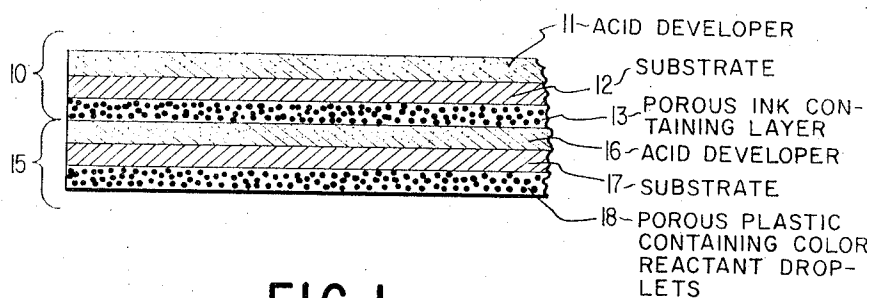


FIG. 1

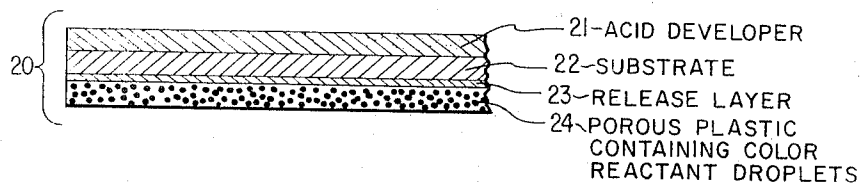


FIG. 2

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PRESSURE SENSITIVE TRANSFER SHEET

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The present invention relates to improved transfer materials of the "carbonless" type.

In recent years, considerable attention has been given to the development of "carbonless" transfer materials. One of the systems which has gained some acceptance is based upon the color-forming reaction which takes place between certain aromatic amines, referred to as color precursors, and acid developing agents, such as clays.

In one well-known type of transfer material, droplets of the aromatic amine reactant are encapsulated by a process known as coacervation and are distributed within a plastic film or matrix. This film is pressure-sensitive so that upon the application of pressure by a stylus, type bar, or the like, the capsules are ruptured releasing the contained aromatic amine in the region where pressure is applied.

Particles of clay or other acid materials are brought into contact with the released aromatic amine to form the colored reaction product. The acid developer may be provided in the form of a discrete film associated with the aromatic amine film or may be coated on a separate substrate which is pressed into contact with the substrate on which the aromatic amine is deposited.

In many of the commercial manifolding systems based upon color-forming reactions of the type just described, several sheets are bound in a manifolding pack or book. The sheets are then arranged so that an aromatic amine-containing layer is disposed in overlying, face-to-face contact, with a layer containing an acid developer.

Thus, the pressure of a stylus on the surface of the top sheet is transferred to all of the intermediate sheets and results in the expression of encapsulated droplets of the aromatic amine into contact with the acid developer producing copies on each of the intermediate sheets.

While systems of the type just described have met with some success, there are still a number of problems associated with them. One of the principal difficulties is obtaining sufficient release of the aromatic amine color precursor so that sharply defined and intense images are formed. The experience has been that relatively little of the encapsulated aromatic amine is released from the material formed by coacervation. This may be due to the nature of the encapsulation technique which surrounds each droplet of aromatic amine with a tough film which is relatively difficult to disrupt in order to release the color-forming reactant.

Therefore, in order to obtain images of acceptable sharpness and intensity, it is generally necessary to employ a high concentration of aromatic amine in the plastic coating layer, so that the small percent that is transferred will be sufficient to bring about the desired reaction.

However, this solution to the problem itself raises a secondary problem, namely, that of "rub-off." In applying large concentrations of aromatic amine reactant on the surface of the papers, it has been found that the color-forming reaction tends to proceed while the papers are in storage or while they are handled during normal use.

Another problem encountered in the use of inter-reactive transfer materials of the type in question is one of the time, expense and difficulty of manufacturing such materials. In general, the process of coacervation or encapsulation of the aromatic amine droplets, as is now widely used, is a very exacting procedure. Coacervation requires

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special chemicals, careful control of the conditions of reaction and is relatively time consuming.

For these and other reasons, therefore, the available "carbonless" transfer materials are not entirely satisfactory.

Accordingly, the primary object of the invention is to provide improved "carbonless" transfer papers.

A more specific object of the present invention is to provide "carbonless" transfer materials capable of producing sharp and intense images, but relatively free from "rub-off," i.e., premature or accidental color formation during normal use, handling or storage.

An additional object of the present invention is to provide improved "carbonless" transfer materials and fast, efficient and economical methods for their manufacture.

The manner in which the above objects and many other highly desirable advantages are achieved will be apparent from the following detailed description of the invention and of certain preferred embodiments of the invention considered in the light of the accompanying drawing.

In the drawing, FIGURE 1 is a somewhat schematic, cross-sectional, edge view of transfer materials produced in accordance with this invention, and

FIGURE 2 is a somewhat schematic, cross-sectional, edge view of other transfer materials of the invention.

In general, the present invention comprises an improved method for producing layers containing dispersed droplets of color precursor which are readily transferred under pressure.

The invention further contemplates new methods and materials for improving and controlling transfer of a color precursor into contact with a developing agent.

The invention also comprises an improved developing agent for use in "carbonless" transfer systems.

The improved method for producing plastic layers containing dispersed droplets of color precursor comprises dissolving the precursor in an organic solvent. The resulting solution is then dispersed or emulsified in a solution of a natural or synthetic polymer or resin. This dispersion is then coated on a suitable substrate and is dried.

In some cases, it is preferable to use a dispersing agent, such as alkyl aryl sulfonates, polyoxyethylene derivatives or the like, to obtain a good dispersion. It may also be desirable to plasticize the polymer by the addition of a suitable plasticizer to the dispersion so that a layer of the desired flexibility is produced.

In a preferred embodiment, polyvinyl alcohol is employed as the film-forming matrix for production of the precursor containing layers.

Such layers give excellent transfer of the precursor under the influence of pressure with minimum "rub-off" during normal handling or storage. Many other protective matrices for the precursor droplets provide poor transfer and also tend to exude precursor at the surface, even if no pressure is applied. It may be that contractive forces within such matrix films result in the expression of the precursor droplets. Polyvinyl alcohol has a unique rubber-like consistency which retains the precursor droplets without exudation leading to "rub-off" and which also permits almost complete release or transfer under the influence of pressure.

The color precursors employed in the present invention are materials which are well known in the art and which, in themselves, are not the basis of the invention. A large number of the precursors are described in a paper presented before the Colloid Division of the American Chemical Society at Cincinnati, Ohio, on April 9, 1940, by E. A. Hauser and M. B. Leggett. The paper is entitled, "Color Reactions Between Clays and Amines" and lists many amine reactants which are useful as color precursors in the present invention.

Color precursors of this type which are now in general use include, for example, triaryl lactones, leuco methylene blues, leucoauramines, triarylmethane leucoauramines, etc.

The color precursor is then dissolved in an organic solvent. Again, the exact nature of the organic solvent is not critical to the invention and various materials are satisfactory for the purpose. Illustrative examples include, mineral oil, and other aliphatic hydrocarbon solvents, methyl cellosolve recinoleate, chlorinated polyphenyl, dibutyl phthalate, tricresyl phosphate, etc.

If the polymer is to be plasticized, any conventional plasticizer may be employed. Examples of suitable materials for this purpose include glycerol, ethylene glycol, sorbitol, etc. The plasticizer may conveniently be added to the polymer solution before or after the color precursor is dispersed in it.

In the preferred embodiment, an aqueous solution of polyvinyl alcohol is prepared by adding from about 2% to 20% by weight of polyvinyl alcohol to water and heating to about 60°–80° C. to dissolve the polymer. A few percent by weight of glycerol is then added to plasticize the polymer. The amount of plasticizer will vary depending on the molecular weight of the polymer being employed.

About 10% by weight of an amine color precursor is then dissolved in a suitable solvent such as mineral oil. The amount of precursor may vary from an effective minimum of a few percent up to saturation of the solvent, generally about 15%.

The precursor solution is then dispersed in the polymer solution with the aid of about 0.25 to 5.0% by weight of a dispersing agent. Generally, about 0.5% to 1.0% of dispersing agent is sufficient.

The amount of precursor solution added to the polymer solution may vary over fairly wide ranges. Due to the excellent transfer obtained from polyvinyl alcohol, the droplets of precursor may comprise only a few percent by weight of the polymer in the dried layer, e.g., about 5%. However, this concentration may be substantially increased up to 50% or more, if desired. Generally, a concentration of from about 5% to 20% is satisfactory for the production of highly efficient transfer materials.

In forming the layers, the dispersion of the precursor solution in the polymer solution is coated on a suitable support and is dried to remove the polymer solvent, in this case water. The resulting film comprises a continuous, porous, polyvinyl alcohol layer containing dispersed droplets of the precursor solution which are readily exuded under pressure.

Referring to FIGURE 1 of the drawing, transfer elements 10 and 15 may be produced according to this invention as described above. Supports 12 and 17 of paper, plastic, metal, foil or other suitable material may be coated on at least one side to form porous, plastic precursor containing layers 13 and 18. The other surfaces of the support may be coated with films 11 and 16 comprising particles of an acid developer, such as clay, dispersed in a suitable binder, such as starch.

When a number of transfer elements, such as sheets 10 and 15, are arranged in overlying relationship with a precursor containing layer 13 in surface contact with a clay developer containing layer 16, pressure on the assembly will result in exudation of precursor at the point of pressure to produce a corresponding image.

As a further significant improvement over conventional "carbonless" transfer materials and methods, it has been found that release of the porous layer containing the precursor can be enhanced and controlled by employing specific combinations of materials.

More particularly, it has been found that significantly improved release may be obtained by using a substrate which consists of or is coated with a polymer or resin which is incompatible with the polymer or resin used in the layer in which the precursor solution is dispersed.

For example, referring to FIGURE 2 of the drawing, transfer element 20 may comprise the usual clay developer layer 211, a suitable support 22, a precursor containing layer 24 and a release layer 23, between support 22 and layer 24.

Release layer 23 is preferably a polymer which is incompatible with the film-forming polymer or resin of layer 24. Good results are obtained by incorporating the precursor in a hydrophilic film-forming material such as polyvinyl alcohol, polyvinyl pyrrolidone, gelatin, sodium, carboxymethyl cellulose, etc., and coating this material onto a hydrophobic layer, such as polyethylene, polystyrene, ethyl cellulose, cellulose acetate, vinyl acetate, etc.

It will be clear too that the substrate or support on which the precursor layer is coated may itself be a film or sheet of a film-forming polymer or resin which is incompatible with the polymer or resin of the precursor layer. This makes the use of a separate release layer unnecessary.

Due to the excellent transfer of the precursor layer obtained by use of an incompatible release layer, relatively low concentrations of precursor may be employed while still obtaining very satisfactory images. This in turn minimizes the problem of "rub-off" which is prevalent in conventional materials.

Although excellent transfer is obtained by using incompatible materials in the release and precursor layers, it is also desirable to control or modify the release in some cases to prevent premature transfer. It has been found that this can be accomplished to provide excellent transfer materials by incorporating a mutually compatible agent into either or both of the precursor and release layers.

For example, in making a transfer element according to FIGURE 2 of the drawing, release layer 23 may comprise a thin film of ethyl cellulose and precursor layer 24 may comprise a matrix of cellulose acetate. The two polymers are quite incompatible and layer 24 is ordinarily released very readily under pressure, in some cases too readily, where the material is subjected to pressures during handling and storage prior to use. To avoid premature transfer in such a case, a small amount of nitrocellulose is incorporated into layer 24, layer 23 or both.

The addition of the mutually compatible, release controlling agent is preferably made to layer 24. It has been found that up to about 2% of this agent provides a transfer element exhibiting good adhesion between the precursor layer and the release layer prior to use and excellent transfer under writing pressure.

Further improvement in "carbonless" transfer materials of the present type is also contemplated in this invention and may be achieved by the use of a developing agent which comprises pyrogenic colloidal silica (SiO_2) having extremely fine particle size, on the order from 0.015 to 0.020 micron, average particle diameter, and having external surface area in the range from 175 to 225 square meters per gram and a purity of 99.0% on a moisture-free basis. This material is quite unlike conventional clays, silica gels, silica aerogels and other precipitated silicas. Pyrogenic colloidal silica shows reduced "rub-off" when compared to conventional attapulgite clays which are presently used in many acid developing layers, such as layers 11 and 21 of transfer elements 10 and 20 illustrated in the drawing.

Pyrogenic colloidal silica having the characteristics previously described produces precise character development corresponding to the point of pressure and impact and is much superior in this respect to conventional clays. As with other acid developers, the pyrogenic colloidal silica may be employed in various binders of hydrophilic or hydrophobic character, such as gelatin, starch, sodium carboxymethyl cellulose, cellulose acetate, ethyl cellulose, vinyl acetate, polystyrene, polyvinyl pyrrolidone, etc.

Pyrogenic colloidal silica is a commercially available material obtainable from the Cabot Corp., under the name of "Cabosil." It is made by the vapor phase hydrolysis

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of silicon tetrachloride at 1100° C. "Cabosil" differs from aerogel and hydrogel silica in that it has a surface area of about 200 M²/gm., super-fineness of over 11 x 10¹⁵ particles/gm., a moisture content of less than 2% under normal conditions and superior clarity.

The above described invention will perhaps be better understood in view of the following detailed examples illustrative of preferred methods for preparing the improved "carbonless" transfer materials of the present invention.

Example 1

A solution is prepared by dissolving 10% by weight of an aromatic amine color precursor in mineral oil. A second solution is then prepared by dissolving 20 gms. of polyvinyl alcohol and 7 gms. of sorbitol in 100 gms. of water.

About 10 parts by weight of the precursor solution is dispersed in 150 parts by weight of the polyvinyl alcohol solution. A thin film of the resulting dispersion is coated on a paper substrate and is dried to remove the water.

The surface of the resulting layer of polyvinyl alcohol containing dispersed droplets of the precursor solution is placed in contact with a film containing 20% by weight of pyrogenic colloidal silica having an average particle diameter in the range of from 0.015 to 0.020 micron, a surface area of from 175 to 225 square meters per gram and a purity of 99.9% on a moisture free basis.

Example 2

A paper substrate is coated on one surface with an aqueous solution of water soluble starch containing about 20% by weight of the starch of pyrogenic colloidal silica. The coating is dried to leave a continuous film of starch containing the dispersed particles of developer.

The other surface of the substrate is coated with a thin film of cellulose acetate deposited from a solution of cellulose acetate in acetone. The acetone is evaporated to leave a dry, thin coating of cellulose acetate.

About 10 parts of commercially available aromatic amine red color precursor, X4406, are dissolved in about 90 parts Aroclor 1248, a commercially available polychlorinated polyphenyl plasticizer. About 10 parts of the resulting precursor solution is then dispersed in about 100 parts of a 50% solution of ethyl cellulose in acetone.

The resulting dispersion is coated onto the film of cellulose acetate as a layer having a thickness of a few mils. The solvent is then evaporated leaving a porous film of ethyl cellulose containing dispersed droplets of the precursor solution.

Several sheets of the foregoing type are assembled in the form of a manifolding pack with the precursor layer of one sheet facing the developer layer of another. A pencil is then used to write on the surface of the uppermost sheet and this produces excellent images by pressure transfer on each sheet in the pack.

Example 3

The method of Example 2 is repeated but 0.5% of nitrocellulose by weight of the ethyl cellulose is added to the precursor-ethyl cellulose dispersion before it is coated onto the cellulose acetate film.

Example 4

The method of Example 2 is repeated but 2.0% of nitrocellulose by weight of the ethyl cellulose is added to the precursor-ethyl cellulose dispersion before it is coated onto the cellulose acetate film.

Example 5

Ten parts of X4406 color precursor are dissolved in 90 parts of methyl cellosolve oleate.

Fifty gms. of polystyrene are dissolved in 50 gms. of a mixed solvent consisting of 40 parts methyl ethyl ketone, 20 parts n-butanol, 20 parts ethyl acetate, 15 parts methyl cellosolve and 5 parts toluene.

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Ten gms. of the precursor solution are then dispersed in 100 gms. of the polystyrene solution.

This dispersion is coated onto a substrate of cellulose acetate foil and is dried.

The layer formed upon drying of this coating is then pressed against a surface coated with a clay developing agent and writing pressure on the other surface of the foil produces at the interface an excellent red image corresponding to the points of pressure.

Example 6

The procedure of Example 5 is repeated, but 1.0% of nitrocellulose by weight of the polystyrene is added to the dispersion before it is coated onto the cellulose acetate foil.

As will be seen from the above examples, the high boiling solvent in which the color precursor is dissolved may be a plasticizer for the plastic matrix in which the precursor solution is dispersed.

The volatile solvent in which the plastic material is dissolved may be a volatile organic solvent or mixture of such solvents or may be water.

The incompatibility of plastic materials for the purpose of this invention refers to the adhesion existing at an interface between the plastics when one is coated on the other. If writing or typing pressure, or even lighter pressures, is sufficient to cause release of one plastic coating from the other, the materials are considered incompatible.

The mutually compatible release controlling agent may be added to the release layer, the porous layer or both in an amount of up to about 2% by weight of the plastic in the porous layer. As previously noted, the addition is preferably made to the dispersion which forms the porous layer.

Any natural or synthetic material capable of forming a flexible or plastic film may be used as the plastic materials of this invention. A wide variety of synthetic and natural polymers and resins are suitable for use in the invention including numerous vinyl polymers, cellulose derivatives, polyesters, such as Mylar, and various copolymers.

The principles of the invention may readily be adapted to the production of transfer materials having the structure of the elements illustrated in FIGURES 1 and 2 of the drawing. Obviously, other elements comprising single transfer layers, transfer layers coated with or mixed with a developer and incorporating still further modifications may also be produced in accordance with the invention.

It will be obvious to those skilled in the art that many details of the present method and products may be altered without departing from the spirit or scope of the invention as expressed in the following claims.

What is claimed is:

1. A transfer element for use in a pressure sensitive carbonless transfer printing system comprising

(a) a substrate, at least one surface of which is a plastic cellulose acetate material while the other surface has an acid clay developing agent coated thereon,

(b) a layer of porous plastic material selected from the group consisting of ethyl cellulose and polystyrene coated onto said cellulose acetate wherein droplets of a solution of an amine color precursor are dissolved in a high boiling organic solvent in the pores of said porous plastic material, and

(c) up to 2% by weight of mutually compatible nitrocellulose added to the plastic material to control the degree of release of said porous plastic droplet containing layer from said cellulose acetate surface.

2. The transfer element of claim 1 wherein in (c) the nitrocellulose is added to the porous ink containing layer.

3. The transfer element of claim 1 wherein said mu-

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tually compatible nitrocellulose material is added to the plastic cellulose acetate substrate material.

4. The transfer element of claim 1 wherein the acid clay developing agent is comprised of particles of pyrogenic colloidal silica having an average particle diameter of from 0.015 to 0.020 micron, a surface area of from 175 to 225 square meters per gram, and a purity of 99.9% on a moisture-free basis.

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MURRAY KATZ, *Primary Examiner.*