

[54] INK SUPPLY TRANSFER MEDIUM

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[58] Field of Search 117/36.2, 36.4, 36.8, 36.1, 117/36.3

[56] **References Cited**

UNITED STATES PATENTS

3,244,549	4/1966	Farnham et al.	117/36.2
3,565,666	2/1971	Phillips	117/36.2
3,576,660	4/1971	Bayless et al.	117/36.8
3,689,301	9/1972	Scott	117/36.4
3,788,875	1/1974	Schutzner	117/36.4 X

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[57] **ABSTRACT**

An ink supply transfer medium is disclosed. The medium is of such a construction that marking pressure causes a transfer of colored ink material to any surface with which the medium is then in contact. The medium, usually in sheet form, includes a substrate and an ink supply layer with a dye decoloring layer located therebetween. The ink supply layer includes all of the reactive colorless components required to yield a colored marking ink but the components are separated and provide a potential colored mark available on occasion of component release. The decoloring layer includes a continuous polymeric barrier film with a dye decoloring reactant homogeneously dispersed therethroughout. Prior to application of marking pressure, the sheet does not include colored ink and does not appear to include colored ink transfer capabilities. After application of marking pressure, colored ink is produced and transferred and there is no trace of residual, untransferred, colored ink on the sheet.

10 Claims, 2 Drawing Figures

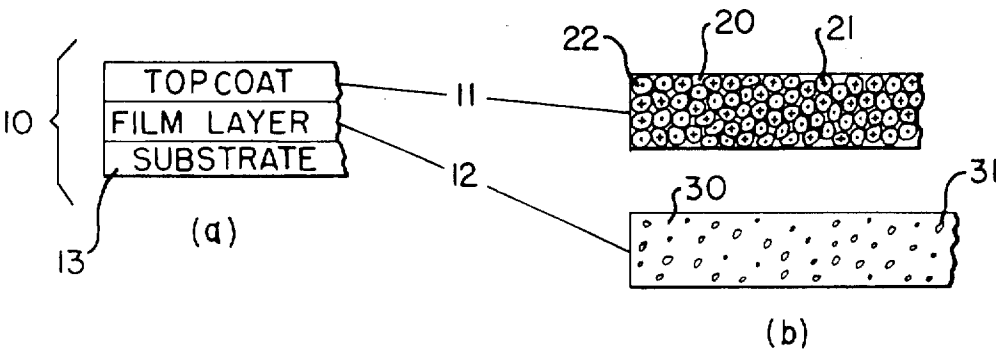


FIG. 1

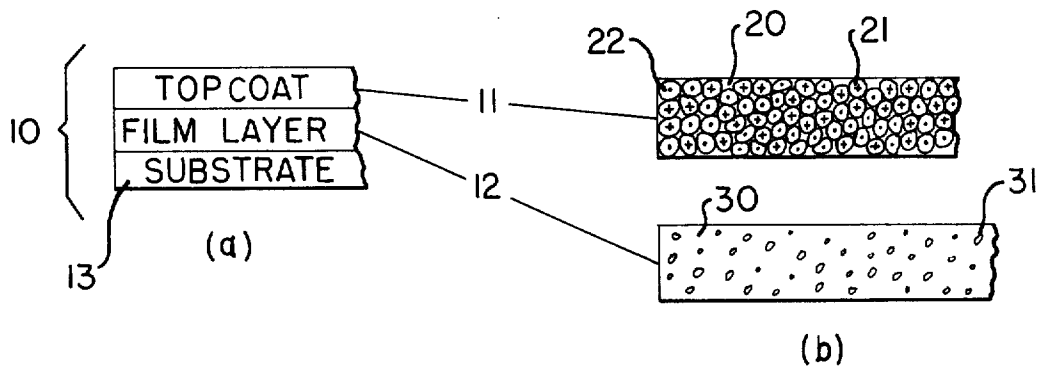
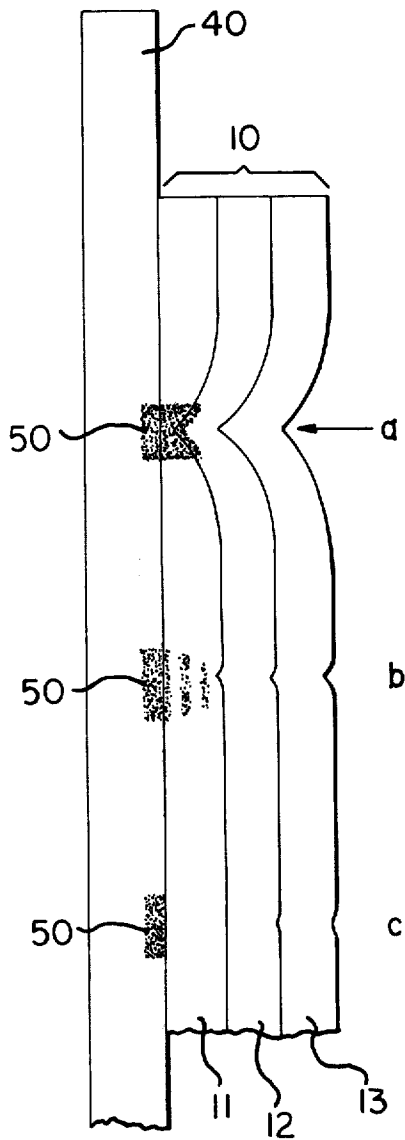


FIG. 2



INK SUPPLY TRANSFER MEDIUM

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention pertains, generally, to pressure-sensitive recording media. Such recording media include colorless but colorable components separated to prevent coloration until the components are somehow brought together. More particularly, this invention relates to pressure-sensitive recording media wherein the component separation is achieved by containing selected components within the confines of microscopically small capsules termed "microcapsules", and wherein coloration is achieved by rupturing the microcapsules and by providing an opportunity for coreaction among the various components.

This invention pertains, in part, to so-called "self-contained" pressure-sensitive recording media wherein all of the colorable components are included on or in a single sheet and wherein the application of localized pressure to that sheet causes a reactive contact among the components to yield a colored reaction product in the configuration of the pressure. This invention more specifically, in part, pertains to such self-contained media wherein at least one of the components is contained in microcapsules and wherein all of the components are located on the same side of a single sheet.

This invention pertains, in part, to pressure-sensitive recording media which are manufactured and used as manifold sets of sheets wherein colorable components are separated by being located on apposing faces of sheet juxtaposed in a manifold set. This invention more particularly, in part, pertains to such manifold sets of recording media wherein at least one of the components is contained in microcapsules which microcapsules are located on or near one of the aforementioned apposing faces. This invention additionally pertains, in part, to pressure-sensitive recording media wherein there is necessity for a transfer of colorable component material from one sheet to another to produce a mark of colored product.

This invention even more specifically and particularly pertains to pressure-sensitive recording media wherein all of the colorable components are maintained separated on or in a single sheet and at least one of the colorable components is contained in microcapsules; and wherein, on application of pressure, capsules are ruptured, a colored product is produced, the colored product is transferred as a mark to any receiving surface, and the sheet from which the colored product is transferred bears no trace of residual, untransferred colored material.

2. Description of the Prior Art

U.S. Pat. No. 3,576,660 issued Apr. 27, 1971 on the application of R. G. Bayless and D. J. Striley, discloses a self-contained pressure-sensitive record sheet which carries two kinds of microcapsules, each containing a liquid solution of one of two colorable component materials. Both of the kinds of microcapsules are located on a common surface of the sheet, and a mark is produced by rupturing adjacent capsules of different kinds. The colorable components described therein are characterized as base-reacting chromogenic material (such as Crystal Violet Lactone) and organic, polymeric, acidic material (such as oil soluble phenolic-aldehyde polymers). The record sheets disclosed therein are self-marking sheets and are not disclosed as

transfer sheets. Self-contained pressure-sensitive record sheets are further exemplified and disclosed in U.S. Pat. Nos. 3,663,256 and 3,672,935 issued May 16, 1972 on the application of R. E. Miller and B. W. Brockett and June 27, 1972 on the application of R. E. Miller and P. S. Phillips, Jr., respectively. Those two latter patents disclose both transfer papers and self-contained papers and specifically differentiate between the two. In the prior art, self-contained pressure-sensitive paper maintains a place separate and distinct from pressure-sensitive transfer paper.

U.S. Pat. No. 3,565,666 issued Feb. 23, 1971 on the application of P. S. Phillips, Jr. discloses a pressure-sensitive transfer sheet having a latex subcoat and a surface coating of microcapsules containing an oily solution of dye. The latex subcoat is described therein as a cushion to protect the capsules from rupture by casual or inadvertent contact forces and is also described as an aid to transfer of liquid by providing a barrier to absorption of capsule-released liquid solution back into the carrier sheet member. The capsule-contained liquid is only disclosed therein to be oily solutions of basic chromogenic dye reactants.

U.S. Pat. No. 3,481,759 issued Dec. 2, 1969 on the application of D. A. Ostlie discloses a manifold set of pressure-sensitive sheets of the transfer variety wherein capsules containing a solution of one reactive color-forming component are coated in a slurry onto a sheet along with a finely-divided component coreactant which yields a product of a color which matches the capsule-carrying sheet. An adjacent, facing, sheet in the manifold set disclosed therein is coated with a component coreactant which yields a dark-colored product of high contrast when reacted with the encapsulated color-forming material. As a result, the manifold set of Ostlie provides a pressure-sensitive transfer system wherein an encapsulated colorless color reactant is disposed in the set such that capsule rupturing pressures cause formation of contrasting colored marks when the colorless reactant is transferred to an adjacent sheet and cause formation of marks having the same color as the sheet when the colorless reactant is not transferred. The disclosure of Ostlie includes no barrier film and the colorless reactant does not become a material of contrasting color until it contacts and reacts with the coreactant on a different and separate sheet surface.

SUMMARY OF THE INVENTION

This invention directly relates to a pressure-sensitive ink transfer sheet wherein there is: (i) a substrate sheet coated by (ii) a film layer of polymeric material which includes a dye decoloring material and (iii) a topcoating which includes microcapsules of one kind containing an oily solution of colorless but colorable dye material and microcapsules of another kind containing an oily solution of material reactive with the colorable dye to yield a colored product. The sheet is devoted entirely to accomplishing ink supply operated by transfer of ink material away from the sheet on capsule rupture. The film layer is provided as a barrier to absorption of liquid ink into the substrate sheet; and the dye decoloring material is included in the film layer to prevent colored marks from being left on the transfer sheet after capsule rupture. The film layer with the dye decoloring material is sometimes referred to herein as the dye decoloring layer. The topcoating, sometimes referred to herein as the ink supply layer, includes all of the

components necessary to affect a dye coloration reaction. Those components are present as liquids or as liquid solutions or dispersions and are contained in and protected by microcapsules. Microcapsules containing the various components are substantially homogeneously combined such that any minute area of the topcoating includes capsules of each kind to result, on rupture, in a coloration reaction and a supply of colored liquid ink.

In use, the topcoating layer of the instant pressure-sensitive ink transfer sheet is placed in contact with an intended ink receiving surface and the sheet is subjected to a capsule rupturing pressure. Capsules of all of the various necessary components are ruptured by the applied rupturing pressure, liquids released from the capsules are combined, a color reaction occurs yielding a colored liquid ink, and a major portion of the ink is transferred to the intended receiving surface. Whatever colored liquid ink remains untransferred, comes into contact with the dye decoloring material of the film layer and is rendered colorless. Thus, from a single application of capsule rupturing pressure, a colored liquid ink is formed on an ink supply sheet, most of the ink is transferred to mark any receiving surface and the untransferred ink is decolorized to eradicate any residual trace of ink in the supply sheet.

It is an object of this invention to provide a pressure-sensitive ink supply transfer sheet wherein the ink is present as colorless liquid component parts colorable by mutual contact. It is a further object of the invention to provide such a sheet wherein the liquid component parts are present in multitudes of individual pressure-rupturable microcapsules substantially homogeneously mixed together. It is an additional object of the invention to provide such a sheet wherein, prior to rupture of microcapsules, there is no apparent colored liquid ink supply and after rupturing of capsules a colored liquid ink is formed. Moreover, it is an object of this invention to provide such a sheet wherein colored liquid ink is available and can be transferred to any receiving surface, treated or not, without need to first provide the receiving surface with any dye coreactant or developer.

It is an object of this invention to provide a pressure-sensitive ink supply transfer sheet wherein there is a film layer of a dye decoloring material and an ink barrier material, both present and located between a substrate and an ink supply topcoating. It is a further object of this invention to provide such a sheet wherein a major portion of ink supply in a particular area is transferred by application of pressure to that area and any ink not transferred is rendered colorless by contact with the dye decoloring material. It is an additional object of this invention to provide such a sheet wherein transfer of the ink is enhanced by presence of the film of ink barrier material.

It is an object of this invention to provide a pressure-sensitive ink supply transfer sheet which does not appear to include colored ink or the capability to transfer colored ink prior to application of pressure; which, on application of pressure, transfers colored ink to any contacting receiving sheet; and which, after transfer of colored ink, has all residual traces of untransferred colored ink decolorized so that the sheet does not appear to include colored ink or the capability to transfer colored ink.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 represents a highly diagrammatic representation of a corner edge of the present invention and

FIG. 2 is a cross-sectional view of the invention in use.

At FIG. 1 *a*, pressure-sensitive ink supply transfer sheet 10 comprises the substrate 13 coated by a film layer 12 and a topcoat 11. At FIG. 1 *b*, the film layer 12 is shown in schematic cross-sectional detail with a continuous polymeric matrix 30 and finely-divided dye decoloring material 31 substantially homogeneously distributed therethroughout. Alternative arrangements of the matrix 30 and the decoloring material 31 include dissolving the decoloring material 31 in the liquid system of polymer prior to its application as the matrix 30. Such an arrangement can be viewed as a system wherein the decoloring material 31 is molecularly finely-divided. Also, although not preferred, the decoloring material 31 can be substantially homogeneously distributed over the surface of matrix 30 but concentrated at or near the interface between the film layer 12 and the topcoat 11. Additionally, at FIG. 1 *b*, the topcoat 11 is shown in schematic cross-sectional detail with microcapsules containing colorless but colorable basic chromogenic material 22 and microcapsules containing colorless acid chromogenic coreactant material 21 randomly distributed and held together as a cohesive coating by binder material 20. Although it is included in the embrace of the definition of topcoat 11 that capsules of chromogenic material 22 and capsules of chromogenic coreactant 21 can be substantially segregated and located in individual layers bound together by binder material 20, such latter arrangement is not preferred.

FIG. 2 provides a schematic cross-sectional representation, in steps, of the invention in use to develop a mark. A receiving surface 40, which might be an untreated sheet of paper or some other, preferably porous, absorptive, material, is positioned in contact with the pressure-sensitive ink supply transfer sheet 10. At FIG. 2 *a*, pressure is applied to the substrate surface, as indicated, deforming the substrate 13 which, in turn, deforms the film layer 12 and forces the topcoat 11 into a compressed state thus rupturing the microcapsules. Chromogenic material and chromogenic coreactant are released from the ruptured microcapsules to yield a colored reaction product 50. At FIG. 2 *b*, pressure has been released, deformation of the transfer sheet 10 has diminished, and the untransferred portion of the colored reaction product 50 remaining in the topcoat 11 is being decolorized by material from the film layer 12. At FIG. 2 *c*, deformation of the sheet 10 has nearly disappeared and the untransferred colored reaction product 50 in the topcoat 11 has been completely decolorized while the transferred colored reaction product 50 in the receiving surface 40 remains unaffected.

The drawings of FIGS. 1 and 2 are not to scale and, to more clearly present the various facets of this invention, neither are the components within a drawing presented in a relative scale. Hatching is omitted from the cross-sectional views to more clearly depict details of the elements and details of the operation of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to an improved kind of transfer sheet wherein a colorless liquid system is carried on a

substrate sheet, a colored liquid ink is transferred from the sheet on application of pressure, and any residual untransferred liquid ink on the substrate sheet is rendered colorless without a trace. The improved transfer sheet includes three major elements.

THE SUBSTRATE

The substrate is simply a carrier for the coatings and layers and can be in the form of a sheet, ribbon, tape and the like, either flat or substantially flat or conforming or conformable to some predetermined contour. For present purposes, the word "sheet" will be deemed to embrace all of those carriers. Whatever the form of the substrate, it is essentially a two dimensional article having major length and width dimensions and only minor dimensions of thinness. The length and the width are immaterial for consideration of the present invention; but the thinness may be significant as a part of a requirement for flexibility in the substrate material. The ink supply sheet is pressure sensitive and the pressure to which it is sensitive is applied directly to the substrate and transmitted therethrough to the microcapsules of the topcoat. The substrate must be thin enough, commensurate with the kind of material from which it is made, that any effective applied pressure will be conducted through the sheet and arrive at the topcoat maintaining adequate desired or required resolution of the pressure image. The requirements that the substrate be flexible and pressure conductive demand also a certain firmness in the substrate material such that applied pressure is not lost in mere compression of the substrate but is, instead, transmitted through the substrate emerging not appreciably diminished at the other side.

To preferred material of the substrate is fibrous, absorbent and non-woven. Paper, including cellulose or cellulose derivatives, is preferred and is presently used. Such paper provides the desired flexibility when used in convenient thinnesses; and paper has been used almost exclusively in the past for manufacture of pressure-sensitive media. Other eligible substrate materials include those woven or not, fibrous or not, absorbent or not. In other words, the substrate material is not limited by previous use;—plastic film, spun polymer webbing or sheet, natural or synthetic textiles, metal foils, and the like all being eligible. The substrate can be a composite of material layers.

Thus, proper flexibility as above described is the only substantive limitation for the substrate. Thinness of a paper substrate has been found to provide indication of acceptable flexibility. In general, paper substrates can be used having a thinness of from 2.0 to about 6.0 mils, with 2.8 to about 4.2 mils being preferred. As some additional indication of acceptable flexibility, a substrate thinness of about 3.4 mils used to make the transfer sheet material of this invention will, on application of a writing pressure, permit transfer of ink from one transfer sheet to another through a face-to-back stack of about eight of the transfer sheets. While maximum substrate thinness is determined as a function of sheet flexibility, minimum substrate thinness is determined as a function of the integrity of the sheet. If the substrate is too thin, the sheet will not stand up to its intended use.

THE TOPCOAT

The topcoat includes capsules individually contain-

ing at least two kinds of color-forming material and, optionally, some adhesive binder material. The colorless but colorable dye material, known herein as chromogenic material, can be selected from any of several acid-activatable, substantially colorless compounds. Examples of such compounds include: phthalides such as 3,3-bis(1,2-dimethylindol-3-yl)-5-dimethylamino phthalide, 3-(p-dimethylaminophenyl)-3-(1-methylpyrrol-2-yl)-6-dimethylamino phthalide, and the like; fluorans such as 2'-formyl-6'-diethylamino fluoran, 2'-chloro-6'-diethylamino-5-(p-dimethylaminobenzylidene)amino-3'-amino fluoran, 2'-anilino-6'-diethylamino-3'-methyl fluoran, and the like; leucauramines such as N-(2,5-dichlorophenyl)leucauramine and the like; acyl auramines such as N-benzoyl auramine and the like; α , β -unsaturated aryl ketones such as dianisylidene acetone and the like; basic mono-azo dyes such as p-dimethylaminoazobenzene-o-carboxylic acid and the like; rhodamine B lactams such as N-(p-nitrophenyl)rhodamine B lactam and the like; polyaryl carbinols such as bis-(p-dimethylaminophenyl)methanol and the like; 8'-methoxy benzoindolinospiropyran such as 4,7,8'-trimethoxybenzoindolinospiropyran and the like.

The dye coreactant or developer material can be any acidic, oil-dispersible or oil-soluble, non-volatile material. Generally and most conveniently, these materials are acidic, oil-soluble, phenolic polymers such as oil-soluble phenolic-aldehyde polymers and phenolic-acetylene polymers; oil-soluble, partially or wholly hydrolyzed poly(styrene-maleic anhydride) copolymers, and poly(methyl vinyl ether-maleic anhydride) copolymers; and carboxypolyethylene. Examples of oil-soluble, non-polymeric, acidic, organic materials suitable for use in this invention are various maleic acid-roins. Polymeric color-forming reactants are disclosed in aforementioned U.S. Pat. No. 3,663,256. Although not preferred, finely-divided solid particulate materials can also be used as dye coreactants. Oil-dispersible organic polymers such as those above-specified are eligible, as are active clay and pigment particles such as bentonite, attapulgite, kaolin, talcs, feldspar, halloysite, silica gel, magnesium trisilicate, pyrophyllite, and the like.

The chromogenic materials are used, in this invention, as colorless solutions wherein the dye is dissolved in an oily, substantially water insoluble, solvent liquid. The preferred dye coreactants are, also, used as solutions in oily solvent systems. Where an eligible dye coreactant is not soluble in some selected solvent, a dispersion of the coreactant can be used; but a dispersion is not preferred. The solvent can be volatile or not and a combination of solvent materials can be used, if desired. Solvents which are volatile include toluene, petroleum distillate, perchloroethylene, xylene, and the like; and solvents which are relatively non-volatile include high-boiling petroleum fractions, partially-hydrogenated terphenyls, chlorinated biphenyls, monoisopropylbiphenyl, dioctyl adipate, dioctyl phthalate, and the like. Generally, the chosen solvent should be substantially water insoluble and should be capable of dissolving at least 0.3 percent, by weight, of the chromogenic material and, in the instance of a soluble coreactant, should preferably dissolve at least about 3-5 percent, by weight, of the coreactant. The solvent for the chromogenic material and the solvent for the

coreactant material need not be the same; but, if they are different, it is preferable that they be mutually soluble or, better, miscible, because success of the invention depends, to an extent, on rapid formation of the colored product at the time of ink transfer. The chromogenic material is generally used in solution of concentration of about 0.5 to 10 percent, by weight. The coreactant is generally used in concentration of about 5 to 40 percent, by weight, whether dissolved or dispersed.

Although it should be understood to be purely a matter of choice and selection depending, in part, upon the concentrations of reactant material in the encapsulated oil, the dry coating weight ratio of capsules containing chromogenic material to capsules containing coreactant material is from about 5:1 to 1:5, preferably 3:1 to 1:3.

The oily, color-forming, liquids are contained in microcapsules of a kind and quality which will assure that the individual reactive components will be maintained mutually isolated until color formation is desired and is prompted by capsule rupture.

Microcapsules having walls of any containing capsule wall material are eligible so long as the capsule wall material does not react with the color-forming coreactants and does not otherwise interfere with the color-forming reaction. Microcapsule wall materials eligible for use in this invention preferably include hydrophilic polymeric materials, either natural or synthetic, and can, specifically, be selected from among any of the following: gelatin, gum arabic, polyvinyl alcohol, albumen, alginates, zein, casein, methyl cellulose, carboxymethylcellulose, carrageenan, partially or completely hydrolyzed maleic anhydride copolymers such as poly(ethylene-co-maleic anhydride) and poly(vinylmethylether-co-maleic anhydride) and poly(styrene-co-maleic anhydride), polyvinyl pyrrolidone, and the like.

The microcapsules can be of any minute size which is desired or required for a particular use. If very large capsules are used, any record mark made by pressure rupture of the capsules will exhibit poor resolution; and if very small capsules are used, transfer properties of the system will be hindered. Capsules of an average diameter from about 2 to 30 microns, with about 4 to 12 microns preferred, are eligible for use. The capsules should contain about 75 to 95 percent by weight of liquid internal phase contents;—80 to 90 percent being preferred.

The process by which the microcapsules are made is not important to the present invention. Any process can be used which will result in capsules fitting the requirements of the invention. Examples of encapsulating processes which yield acceptable microcapsule products are included in U.S. Pat. Nos. 2,800,457; 3,041,289; 3,533,958; 3,726,803; and 3,755,190. The preferred processes are conducted in aqueous manufacturing vehicles and involve complex coacervation of at least two oppositely electrically-charged water soluble polymeric materials. For the sake of completeness, an encapsulating process will be included in the examples, following.

The binder adhesive material is any adhesive, but preferably hydrophilic, used in small amount to hold the microcapsules as a cohesive layer mass and to adhere the microcapsules to the subjacent film layer. The adhesive material can be any, or a combination of, materials such as starch, polyvinyl alcohol, gum arabic, p-

oly(vinylmethylether-co-maleic anhydride), and the like. When microcapsules are manufactured in a liquid vehicle, it has been found that there is often adequate residual capsule wall material uncomplexed and uncombined into the capsule walls to serve as the adhesive binder material. The limits of binder adhesive material are not particularly important except that when too little is used, the topcoat may not exhibit adequate integrity; and when too much is used it might serve as a barrier to capsule rupture and ink release. It should be noted that some capsule wall materials have naturally adhesive characteristics and can be coated without binder to yield serviceably coherent layers. In the case of capsule walls with naturally adhesive characteristics the capsule wall material is regarded as, and serves as, binder adhesive material.

THE FILM LAYER

The film layer includes finely-divided dye-decoloring material in a continuous matrix binder of polymer. The film layer is a coating located on one surface of the substrate. The film layer is adjacent to and in contact with the substrate on one side and the topcoat on the other side. The continuous matrix binder is a substantially nonabsorbent polymeric material which, in its dry, coated, state is water insoluble and is substantially unaffected by most of the oily organic solvents present in the microcapsules of the topcoat. The preferred matrix binder materials are latexes and, among the most preferred latexes, are those including poly(ethylene-co-vinylacetate), polyvinyl chloride, polyvinylidene chloride, poly(styrene-co-butadiene), polyacrylate copolymers, polyvinyl acetate, and the like. Other eligible binder matrix materials include polyvinyl alcohol, starch, casein and the like.

The eligible dye-decoloring materials are preferably substantially water insoluble to enable combination with the binder matrix; although, to the extent that a water soluble dye-decoloring material can be retained in a coated film of binder, a water soluble dye-decoloring material can be used. The dye-decoloring material is finely ground to an average particle size of about 0.1 to 10, preferably 0.5 to 2 microns, if insoluble, and is combined into a coating composition of the binder matrix material;—the composition usually having an aqueous liquid base. If soluble and dissolved in the liquid base, the dye decoloring material is molecularly finely-divided. Eligible dye-decoloring materials can be any which have the effect of decoloring the colored reaction product which results from combination of chromogenic material and a color-forming coreactant. The dye-decoloring materials also desensitize uncolored chromogenic material to block or prohibit any color reaction with a color-forming coreactant. Dye-decoloring materials include solid, oil soluble, organic bases such as: organo-phosphates; polyethylene glycols; quaternary amines, guanidine derivatives, amidines, and the like.

The dried film layer should include from about 5 to 75, preferably 25 to 50 percent, by weight, of dye decoloring material. The thickness of the film layer is a matter for the discretion of the practitioner; but, as a general rule, the film layer should be adequate to supply about 0.10 to 0.35 parts, by weight, of dye-decoloring material for each part, by weight, of microcapsules in the topcoat and about 25 to 100 parts, by weight, of dye-decoloring material for each part, by

weight, of chromogenic material. An eligible range of weight ratios for dye-decoloring material to microcapsules is 0.0125 to 0.75 and an eligible range of weight ratios for dye-decoloring material to chromogenic material is 2.0 to 200. In the preferred practice, the dye-decoloring material is substantially homogeneously dispersed throughout the film layer. These estimates of the desired amount of dye-developing material are provided only as guides to initial practice and are not intended to be definitive. The estimates are calculated from the following parameters: (a) About 100 to 300 grams of para-phenylphenol/formaldehyde coreactant can be used per ream of substrate area and the coreactant can be assumed to have an equivalent weight of about 400-600; (b) About 10 to 30 grams of chromogenic material can be used per ream of substrate area and the chromogenic material can be assumed to have a molecular weight of about 600; and (c) about 0.5 to 4 moles of dye-decolorizer is preferably used per mole of coreactant and one typical and eligible dye-decolorizing material (triphenyl phosphate) has a molecular weight of about 325. The eligible mole ratio of dye-decolorizer to coreactant is about 0.1 up to about 10. The values of material amounts to be used are, of course, variable with conditions and particular product specifications as well as altered and alterable with the use of different active materials in different concentrations for different intended effects.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The following components are prepared for a pressure sensitive ink supply transfer sheet which is the preferred embodiment of this invention:

(I) Oily liquid solution of chromogenic material is prepared by dissolving 3 of Crystal Violet Lactone in 197 grams of monoisopropylbiphenyl.

(II) Oily liquid solution of color forming dye coreactant is prepared by dissolving 33 grams of a resin of para-phenylphenol/formaldehyde in a mixed solvent system of 56 grams of monoiso-propylbiphenyl and 111 grams of a high boiling aromatic naphtha, such as a material which is 99 percent, by volume, aromatic exhibiting an initial boiling point of about 230°C, an end point of about 278°C and an A.P.I. (American Petroleum Institute) gravity of about 10.3 determined at 15°C. The resin can be prepared as disclosed in U.S. Pat. No. 3,672,935 wherein: 170 grams paraphenylphenol; 65 grams 37, weight percent, aqueous formaldehyde; 10 milliliters 37, weight percent, aqueous hydrochloric acid; 1 gram oxalic acid; and 40 milliliters water are refluxed at about 100°C for 2 hours after which the resin mass is separated and distilled in reduced pressure to a temperature of about 125°C.

(III) Both of (I) and (II), as capsule internal phases, are encapsulated using substantially identical microencapsulating techniques as follows: 200 grams of an internal phase liquid (either (I) or (II) above) is emulsified into 200 milliliters of 10 percent, by weight, aqueous solution of acid-extracted, high Bloom strength, pigskin gelatin adjusted with sodium hydroxide to pH 6.5. Emulsification is continued and the emulsion is heated until a drop size of about 2-3 microns and a temperature of about 50°-55°C are reached.

With the agitation and the temperature maintained, 200 milliliters of 10 percent, by weight, aqueous solution of gum arabic is added, the emulsion is diluted by

slow addition of about 700 milliliters of water, the pH is adjusted to about 9.5 using sodium hydroxide and 14 milliliters of 5 percent, by weight, aqueous solution of poly(vinylmethylether-co-maleic anhydride) (PVM/MA) is also added. A PVM/MA, of the kind used, is available from General Aniline and Film Corporation, New York, New York, 10020, under the trademark designation "Gantrez AN".

Still maintaining agitation and temperature, about 17 milliliters of 14 percent, by weight, aqueous solution of acetic acid is added to reduce the pH to about 4.5.

When (I) is the internal phase, the emulsion is chilled to about 15°C by contact with an ice bath. When (II) is the internal phase, the emulsion is chilled to about 37°C and then slowly cooled to about 30°C, while maintaining the agitation, over about the next 30 minutes. The emulsion of capsules containing (II) is then, also, chilled to about 15°C.

Systems of capsules of each of (I) and (II), at 15°C, are stirred for 4 hours after addition of 10 milliliters of 25 percent, by weight, aqueous glutaraldehyde solution after which stirring 20 milliliters of 5 percent, by weight, aqueous solution of PVM/MA is added. The pH of the system of capsules containing (I) is raised to about 9.5. Capsules prepared by this process are aggregates of individual liquid droplets and have an average capsule diameter of about 8 to 15 microns.

(IV) A topcoating composition is prepared by combining 50 grams of the capsule system containing (I), 150 grams of the capsule system containing (II), 18 grams of a 20 percent, by weight, aqueous solution of starch and 50 grams of water. A starch of the kind used is available from A. E. Staley Manufacturing Co., Decatur, Illinois, 62525, under the trademark designation "Stayco A".

(V) The film layer coating composition is prepared by, first, grinding 50 grams of triphenyl phosphate (the dye decoloring material of this example) for about 15 minutes with about 250 milliliters of water in a water-cooled attritor charged with stainless steel balls; and, next, combining about 45 grams of the triphenyl phosphate grind with about 35 grams of a polyvinylidene chloride latex of 45 percent, by weight, non-volatile material. A latex of that kind and in that concentration is available from A. E. Staley Manufacturing Co., Decatur, Illinois 62525, under the trademark designation "Polidene 930".

To prepare the ink supply transfer medium, paper having a weight of 13 pounds per 500 sheet ream (17 × 22 inch sheets) is selected as the substrate and the film layer composition (V) is coated onto the substrate using a wire-wound, number 12, Mayer rod, and dried. The film layer is estimated to be about 2-3 pounds per ream. The topcoating composition (IV) is coated onto the film layer using a wire-wound, number 20, Mayer rod and dried. The topcoating is estimated to be about 3-6 pounds per ream.

It is noted that incidental or accidental rupture of capsules on this sheet does not result in extraneous marks because the film layer effectively maintains a colorless state in untransferred ink. Transfer prints are made on receiving surfaces by stamping or stylus pressure or by impact, as with a typewriter. After capsule rupture and ink transfer, the residual ink is decolorized or maintained uncolored by action of the film layer components. The transfer sheet of this invention is also useful as a replacement or substitute sheet in prior art

carbonless copy paper systems which utilize capsules of chromogenic material coated onto the back of one sheet and the coreactant color-former coated onto the face of an adjacent sheet. The transfer sheet of this invention provides a supply of chromogenic material and it can color with its own coreactant or the coreactant of the adjacent sheet;—it thereby being compatible with coreactant-coated sheets. Other useful receiving surfaces include wood, cloth, various papers, plastics and metals etched or otherwise modified to receive ink, leather and the like. In short, an eligible receiving surface is any surface on which an ink mark can normally be made by ordinary means.

What is claimed is:

1. A pressure-sensitive ink supply transfer medium comprising:
 - a. substrate of flexible, pressure conductive, material;
 - b. film layer, on the substrate, of
 - i. continuous polymeric matrix binder and
 - ii. dye decoloring material in the amount of between about 5–75 percent, by weight, of the film layer
 - c. topcoat, on the film layer, of
 - i. microcapsules containing a chromogenic material and
 - ii. microcapsules containing a dye coreactant.
2. The medium of claim 1 wherein the substrate is a paper sheet.
3. The medium of claim 1 wherein the microcapsules containing chromogenic material and the microcapsules containing dye coreactant are homogeneously mixed together.
4. The medium of claim 1 wherein the weight ratio of dye-decoloring material to chromogenic material is between about 2.0 and 200.
5. The medium of claim 1 wherein the mole ratio of dye decoloring material to coreactant material is between about 0.1 and 10.
6. The medium of claim 1 wherein the weight ratio of dye decoloring material to microcapsules in the top-

coat is between about 0.0125 and 0.75.

7. The medium of claim 1 wherein the dye decoloring material is substantially homogeneously dispersed throughout the matrix binder.

8. The medium of claim 7 wherein the dye decoloring material is finely-divided and substantially water insoluble.

9. A pressure-sensitive ink supply transfer medium comprising a substrate, an ink supply layer, and a dye decoloring layer between the substrate and the ink supply wherein, the substrate is a flexible, substantially two dimensional, pressure-transmitting material, the ink supply layer includes a substantially homogeneously mixed mass of microcapsules containing a liquid solution of substantially colorless but colorable dye material, and microcapsules containing a liquid solution of dye coreactant material, which dye decoloring layer includes a continuous polymeric barrier matrix between the substrate and the ink supply layer and the finely-divided dye decoloring material in the amount of between about 5–7 percent, by weight, of the film layer substantially homogeneously distributed throughout the matrix.

10. A pressure-sensitive ink supply transfer medium comprising:

- a. substrate of flexible, pressure conductive, material;
- b. film layer, on the substrate, of
 - i. continuous polymeric matrix binder and
 - ii. dye decoloring material constituting 5 to 75 percent, by weight, of the film layer
- c. topcoat, on the film layer, of
 - i. microcapsules containing a chromogenic material in a weight ratio of dye-decoloring material to chromogenic material of 2.0 to 200 and
 - ii. microcapsules containing a dye coreactant in a mole ratio of dye-decoloring material to coreactant material of 0.1 to 10.0

wherein the weight ratio of dye-decoloring material to microcapsules in the topcoat is 0.0125 to 0.75.

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