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[54]	PRESSURE-SENSITIVE CARBONLESS							
	TRANSFER SHEET AND METHOD FOR							
	PROVIDING A CHEMICALLY FORMED							
	IMAGE ON AN UNTREATED SUBSTRATE							
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[22]	Filed:	Apr. 16, 1973						
[21]	Appl. No.:	Appl. No.: 351,710						
[52]								
[51]	Int. Cl							
[58]	Field of Search 117/36.2, 36.1, 36.8, 36.9							
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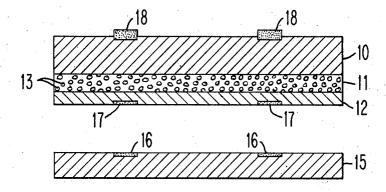
Primary Examiner—Thomas J. Herbert, Jr. Attorney, Agent, or Firm—Henry E. Otto, Jr.

[57] ABSTRACT

An encapsulated liquid reactant precursor and a coreactant therefor are supported on the under surface of a donor sheet that is placed over an untreated surface (i.e, devoid of reactant precursor and coreactant) of a receptor sheet or other substrate. Upon pressure-effected rupture of the capsules, a substantial amount of both the reactant precursor and the coreactant physically transfers to the untreated surface to provide, as a chemical reaction product, an essentially smudge-free, eradication-resistant, right-readable image on the untreated receptor surface. This donor transfer sheet and method are especially desirable where the receptor to be imaged is a data processing card or record on which a reactant and/or co-reactant coating could adversely affect processability through data processing equipment; or the receptor to be imaged has a rigid non-flat surface on which a conventional carbonless receptor coating is impractical; or where only a small area of the receptor is to be imaged.

11 Claims, 2 Drawing Figures

AFTER IMAGING



BEFORE IMAGING

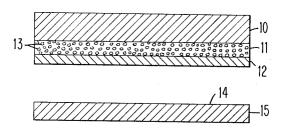


FIG. 1

AFTER IMAGING

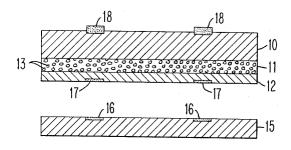


FIG. 2

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PRESSURE-SENSITIVE CARBONLESS TRANSFER SHEET AND METHOD FOR PROVIDING A CHEMICALLY FORMED IMAGE ON AN UNTREATED SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATION

U.S. patent application of Richard B. Jablonski et al., Ser. No. 275,394, filed July 26, 1972, entitled "Pressure Sensitive Recording System and Method of Providing a Split Image Therefor," assigned to the assignee of the present invention.

BACKGROUND OF THE INVENTION

This invention relates to pressure-sensitive transfer 15 sheets and methods, and more particularly to an improved transfer sheet of the so-called carbonless type which supports an encapsulated liquid reactant and a co-reactant therefor that, upon rupture of the capsules by application of localized pressure, are adapted to 20 physically transfer to an untreated surface of a substrate to provide a visible, chemical reaction product image on said untreated surface.

Numerous carbonless systems have heretofore been proposed involving encapsulated liquid dyes or reac-25 tants that, upon rupture of the capsules, create an image by release or physical transfer of the colored dye or by chemical reaction of the encapsulated reactant with a co-reactant on the same or an adjacent surface. But, insofar as is known, in all previous self-contained systems (i.e., those with both the reactant and co-reactant on the same surface), no imaging occurred on any adjacent untreated surface that was devoid of both reactant and co-reactant. In prior art self-contained systems employing an encapsulated reactant and a co-reactant, the application of localized pressure effected merely a chemical reaction product image on the reactant/co-reactant supporting surface.

The only known prior art system in which an image might be produced on an untreated surface is one wherein one of two superposed sheets is coated with an encapsulated colored marking fluid or colored dye; but in such systems, the images are formed not by any chemical reaction, but by capsule rupture and physical transfer of colored ink or dye to the untreated sheet. But systems employing colored inks or dyes have several disadvantages. For example, the capsule supporting sheet must be heavily pigmented to obscure the highly colored imaging matter. Moreover, if such inks and dyes are capable of penetrating the receptor sheet, they will also be subject to continuing migration and dissolution.

SUMMARY OF THE INVENTION

Applicants have discovered that certain non-obvious advantages over prior art arrangements are achieved by providing a pressure-sensitive donor sheet supporting on one surface thereof both an encapsulated reactant in solution and a distinctive co-reactant therefor, preferably in the form of separate coatings. When the coated surface of the donor sheet is placed face down in contact with an untreated surface of a receptor sheet or substrate and the capsules are ruptured by localized application of pressure, a substantial amount of both the reactant and co-reactant physically transfer to the untreated surface and there react to produce an essentially smudge-free, chemical reaction product image.

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The term "untreated surface," as used herein, means a surface that is devoid of both reactant and co-reactant.

Applicants' pressure-sensitive carbonless transfer sheet is especially useful in applications where it is undesirable or impractical to have a reactant and/or coreactant coating preapplied to the sheet on which the image is desired; e.g., tabulating cards or the like on which a chemical coating could adversely affect the ability to process the cards through data processing equipment, or articles on which the surface to be imaged is only a small fraction of the total surface of the article or is irregular in configuration. Thus, no chemically reactive coating need be preapplied to the surface to be imaged that would or might change the properties or characteristics of the said surface; and when imaged, the card has a dry, smudge-free chemical reaction product image that does not impair its machine processing ability. With applicants' formulations hereinbelow set forth, a visible mirror image of the image formed on the untreated receptor sheet is provided on the reactant/co-reactant coated surface of the donor sheet; this is useful as a security feature on legal documents, checks, etc. to produce automatically on the coated back of the document a mirror image of the right reading image imprinted on the uncoated face of the document and any alteration of which mirror image can be readily detected.

Other objects and advantages of the invention will become apparent from the following more detailed description and from the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1 and 2 are elevational sectional views, to greatly enlarged scale, of a pressure-sensitive donor sheet embodying the invention and supporting encapsulated reactant and co-reactant coatings for physical transfer to and chemical reaction on the adjacent untreated surface of a receptor sheet. FIG. 1 denotes the condition before and FIG. 2 the condition after the transfer of reactant and co-reactant from the donor sheet to the receptor sheet.

DESCRIPTION OF PREFERRED EMBODIMENT

As illustrated in FIGS. 1 and 2, a donor substrate or sheet 10 has on its under surface a reactant coating 11 that is overcoated with a co-reactant coating 12. Reactant coating 11 includes a multitude of microscopic pressure-rupturable capsules 13 containing a reactant solution comprising a chemically reactive dye precursor and a solvent. Co-reactant coating 12 comprises a color-forming co-reactant for the dye precursor and is normally colorless.

According to the invention, sheet 10 is adapted to be placed with its co-reactant coating 12 face down in intimate physical contact with the untreated somewhat absorptive surface 14 of a receptor substrate, such as a tabulating card or sheet 15. By a stylus, imprint member, or the like that exerts at least a preselected magnitude of impact or shear force, sufficient localized pressure is applied to the composite of sheets 10 and 14 to rupture the capsules 13. When these capsules rupture, the reactant solution will be released; and this solution, together with a substantial amount of the co-reactant in coating 12, will physically transfer from donor sheet 10 to the untreated surface 14 of sheet 15. The reactant solution and co-reactant thus transferred to sheet 15 chemically react to immediately produce in untreated

surface 14 a dry, right-reading, permanent image 16 corresponding to the right-reading image pattern of pressure applied to the upper surface of sheet 10.

According to a feature of the invention, the receptor surface 14 is somewhat absorptive so that image 16 is 5 actually absorbed into the surface; i.e., it is formed substantially within the receptor surface rather than applied on it, as would be the case if the image were formed solely by physical transfer of a transfer medium. This makes the image 16 essentially erasure and 10 alteration resistant, as well as smear and smudge free.

A sufficient proportion of the released reactant solution and co-reactant will generally remain on sheet 10 to chemically react in situ to produce simultaneously on the underside of donor sheet 10 a dry reaction prod- 15 are preferably applied by a conventional coating appauct mirror image 17 of the image 16 produced on sheet 15. In most instances, this mirror image will be an incidential product of the main chemical reaction that produces the right-reading image 16 on the untreated surface 14. However, in certain applications the creation 20 of such a mirror image may be useful or desirable as a security feature, in that there will be recorded on the underside of sheet 10 a mirror image 17 of the rightreading image 18 imparted on the upper side of sheet 10. This chemically formed mirror image 17 is embed- 25 ded in the underside of sheet 10, rendering it essentially impossible to alter without such attempted alteration being readily detectable. Thus, if image 17 is not a mirror image of the right-reading image 18, the observer will be alerted to the fact that image 18 has been al- 30 tered. This would be highly desirable for legal documents, such as last wills and testaments. It is also useful where checks or drafts are computer-prepared by running through a high speed printer as continuous forms, and a print-out record carbonless copy is made of the 35 indicia entered on the check; in such case, when image 18 is imprinted on the face of the check, applicants' coatings 11, 12 on the back of the check would concurrently form the security mirror image 17 and image 16 on the permanent record ply. Coatings 11, 12 may be 40 applied to the entire back surface; or, if desired, to only a restricted area.

The pressure-rupturable capsules 13 must be formed of a film forming material that has the requisite properties, including sufficient strength to preclude inadver- 45 tent rupture. While many materials might be satisfactory, aldehyde condensation polymers, especially urea formaldehyde condensation polymers, are especially suitable. The capsules are preferably from about 1 to 50 microns in size and formed in any suitable manner already known in the art; e.g., in the manner described in U.S. Pat. Nos. 2,730,457; 3,432,327; 3,516,846 or 3.558.341. The capsules contain a liquid reactant precursor; preferably this is in the form of a solution comprising a chemically reactive dye precursor dissolved in an appropriate solvent. A particularly suitable class of reactant precursors are dithiooxamide and its N,N'-disubstituted derivatives; of these, the N,N'-diorganosubstituted-dithiooxamides, dissolved in organic solvents, are preferred. It will be understood that the solution will preferably contain one or more additional ingredients for specialized purposes such as enhancing storage stability, speed and/or intensity of colorproducing reaction, etc.

Applicants' improvement resides, primarily, in providing a reactant coating 11 and a co-reactant coating 12 that will physically transfer to an untreated some-

what absorptive surface 14 of a tabulating card 15 or the like, and there chemically react to promptly produce a dry, eradication-resistant image of commercially acceptable intensity and durability that will not impede processing of the card through data processing machines. The combination of chemical reaction and solubility characteristics and absorption characteristics into the cardstock assures that a substantial part of the coreactant coating will transfer with the reactant solution and be absorbed; the remainder of the coating and solution will remain in situ and provide a security feature for applications, such as of the type above de-

The reactant coating 11 and co-reactant coating 12 ratus before a paper web is severed into sheets 10. Coating 11 is preferably applied, then dried as the web moves in line to a second coating apparatus that applies the coating 12. However, it will be apparent that, if preferred, the coatings 11, 12 may be applied as a composite single coating, rather than sequentially as just described.

Now that the general nature of the invention has been described, the following examples are presented as illustrative of the encapsulated reactants and the coreactants that have been used sucessfully in applicants' pressure-sensitive carbonless transfer sheet and recording system and method.

EXAMPLES 1-4

In each of the following tabulated examples 1-4, a "200 CB" (Coated Back) sheet of "Action" paper marketed by Minnesota Mining and Manufacturing Company was used to constitute the donor substrate 10 and encapsulated reactant coating 11. While the specific formulation of said coating has not been disclosed by said company, the capsules 13 forming part thereof are known to contain dithiooxamide or one of its N,N'di-substituted derivatives dissolved in an organic solvent, as taught in U.S. Pat. No. 3,481,759. Based upon a cursory analysis, the capsules are believed to contain solvents of tributyl phosphate and diethyl phthalate and reactive components of N,N-bis(2-octanoyloxyethyl) dithiooxamide coated with a binder containing a zinccarboxylate; and the capsule walls are formed of urea formaldehyde resin.

The co-reactant coatings 12 were prepared by adding the ingredients specified in Table I to a suitable solvent, such as denatured alcohol. Each mixture was then shaken for 15 minutes by a vibratory paint shaker using steel balls within the container to facilitate solution and dispersion. The resulting solution was then applied as a coating over the encapsulated reactant coating 11 and dried to remove the solvent.

The variously coated sheets 10 were then placed, with the co-reactant-coated surface face down, in intimate physical contact with the untreated surface 14 of tabulating card 15. The cards 15 were then imaged by applying localized pressure to the upper uncoated surface of the sheets 10 using well known techniques such as ball-point pens, pencils, typewriter keys, and imprinting devices employing embossed credit cards.

Table I expresses the formulations of the co-reactant coatings 12 of Examples 1 through 4 in terms of percentage by weight of the various ingredients less the volatile solvent which ultimately evaporates. The examples are listed in order of preference; i.e., Example 1 is preferred. An evaluation of these formulations with respect to image intensity, image development speed and appearance of the coated sheet 10 after imaging are also included in Table I, with the letters E, G, F, P signifying, respectively, Excellent, Good, Fair and 5 Poor.

applicants' unique ingredient transfer and chemical reaction. The sodium benzoate is not essential, but is believed to contribute to image intensity on the receptor

The formulations above listed in Examples 1-4 do not constitute all of the formulations prepared and

TABLE I

· · · · · · · · · · · · · · · · · · ·	Examples Ingredients in % by Weight of Dry Coatings				
Ingredients	•	No. I	No. 2	No. 3	No. 4
*Nickel (II) chloride hexahydrate *Sodium ricinoleate Lithium stearate *Stearic acid Sodium benzoate Anti-oxidant - alkylated polyhydroxy phenol (Santovar A, Monsanto Chemical Co.) Zinc resinate Solvent - denatured alcohol (preferably PM 3163, Ashland Chemical Co.)		20.5 20.5 10.2 20.5 10.3 7.7	15.0 35.0 16.7 25.0 — 8.3	20.0 46.2 27.6 6.2	25.0 31.3 12.5 18.7 6.3 6.2
		100.0	100.0	100.0	100.0
Evaluation Applied By		No. I	No. 2	No. 3	No. 4
Ultimate image) Imprinter Intensity) Ball Point Pen Image Develop-		G E	F G	F G	E G
met Speed Donor Sheet Aesthetic		G	G	G	G
Appearance Shelf Life		G	G	G	Ε

^{*}Essential for reaction

The formulations of these Examples provided a visible image 17 on the donor sheet 10 of sufficient intensity to be useful for security feature applications.

In the preferred formulation (Example 1), the image develops usable intensity more rapidly than that of Example 2, and donor sheet appearance is better. Both exhibit good temperature and environment stability transfer and reaction, chemically formed images of commercially acceptable intensity.

In the above formulations, it was found that the various ingredients serve the following functions: The nickel (II) chloride provides the metal cation that ultimately complexes with dithiooxamide and/or its derivatives. The sodium ricinoleate provides the anion that combines with the nickel (II) chloride to form (in part) nickel ricinoleate which is highly soluble in the solvent system included in the capsule fill of the 3M CB sheet. The lithium stearate and stearic acid facilitate release of the imaging materials from the donor sheet. The Santovar A antioxidant confers long term environmental stability to the coating. In one formulation, the amount of sodium ricinoleate is reduced and zinc resinate substituted; in this instance, the zinc resinate provides a substance that reacts with the nickel (II) chloride to form (in part) nickel resinate which is highly soluble in the solvent system included in the capsule fill of the 3M CB sheet, and it also binds the coating to the substrate and provides coating cohesion.

The ingredients just specified are important to assure

evaluated. Other formulations were prepared and evaluated which includes one or more of the ingredients 40 listed in Examples 1-4; but the evaluations made on such other formulations indicated that, for one reason or another, they would not be as suitable for commercial acceptability.

However, based upon the formulations tested, in-(i.e., shelf life) and produce on card 15, by ingredient 45 cluding those examples above enumerated, applicants have reason to believe that an acceptable ingredient transfer and chemical reaction can be achieved with formulations employing ingredients within the following ranges (all expressed in terms of percent by weight of dried coatings):

> Nickel (II) chloride hexahydrate 10 - 30Sodium ricinoleate Lithium stearate 25 - 45 total but always more stearic acid 2 - 10 0 - 12 0 - 12 Stearic acid Antioxidant (e.g., Santovar A) Zinc resinate Sodium benzoate

Although, as illustrated, the coated donor sheet 10 is described as imaging an untreated surface 14 of a tabulating card 15, it should be noted that donor sheets having the compositions above described have also been used successfully to image untreated signature panels 65 on credit cards, untreated paper sheets (e.g., bank checks, labels) and painted or coated objects. It is contemplated that, if desired, the donor sheet 10 might also be used to image porous or nonporous receptors

^{**}Added to the above ingredients to apply co-reactant coating; if PM 3163 is used, dilute with denatured alcohol at 30 to 35% concentration.

which serve as intermediaries from which the image is transferred to another surface.

It should be noted that the "split-image" formulations disclosed in the above-identified related application were tested in reactive transfer applications (i.e., 5 imaging an untreated surface), but found to be totally unsuitable.

From the foregoing, it will be seen that applicants have demonstrated that a dry, right-readable, eradication resistant, smudge free, chemical reaction product 10 image 16 can be provided on an untreated surface 14 of a receptor sheet, card or the like by a pressureeffected physical transfer of reactant and co-reactant from a donor sheet 10 to said receptor sheet, the image resulting from the chemical reaction which occurs on 15 and in the untreated surface. With most formulations, mirror image 17 of the indicia 18 imprinted on the top side of the donor sheet 10 will be formed by chemical being highly desirable for security feature applications 20 cent stearic acid; 6 percent sodium benzoate; and 6 of the type above described.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be apparent that the foregoing and other 25 changes may be made in the donor sheet, and in the specified formulations and method without departing from the spirit, scope and teaching of the present invention. Accordingly, the sheet, system and method herein disclosed are to be considered merely as illustra- 30 tive, and the scope of the invention is to be limited only as specified in the claims.

What is claimed is:

1. A pressure-sensitive carbonless transfer sheet having a surface supporting a multitude of microscopic 35 pressure-rupturable capsules containing a reactant solution comprising a precursor taken from the class of dithiooxamide and its N,N'di-substituted derivatives, and a solvent and also supporting a co-reactant for the reactant solution, which co-reactant comprises nickel 40 (II) chloride, sodium ricinoleate and stearic acid,

the reactant solution and co-reactant being adapted, upon application of a localized pressure to the sheet and consequently rupture of the capsules while said surface is in intimate contact with an- 45 other surface devoid of reactant and co-reactant, to cause a substantial portion of the co-reactant and reactant solution to physically transfer to said other surface to cause chemical reactions to occur between the precursor and co-reactant for rapidly 50 providing a dry, chemically formed image on such

- 2. A sheet according to claim 1, wherein upon application of such localized pressure to another surface of the sheet opposite the first-mentioned surface, the re- 55 mainder of the co-reactant and reactant solution will remain in situ and chemically react to provide on the first-mentioned surface a chemically formed mirror image of the image formed by application of pressure to such other surface.
- 3. A sheet according to claim 1, wherein the coreactant comprises, by weight, when dried, about 10 -30 percent nickel (II) chloride; 15-50 percent sodium ricinoleate; 25-45 percent stearic acid and lithium stearate as a combined total, but for any percentage selected there being more stearic acid by weight than lithium stearate; and 2 - 10 percent anti-oxidant.

4. A sheet according to claim 1, wherein the coreactant consists by weight, when dried, of essentially about 21 percent nickel (II) chloride; 21 percent sodium ricinoleate; 10 percent lithium stearate; 20 percent stearic acid; 10 percent sodium benzoate; 10 percent zinc resinate; and 8 percent anti-oxidant.

5. A sheet according to claim 1, wherein the coreactant consists by weight, when dried, of essentially about 15 percent nickel (II) chloride; 35 percent sodium ricinoleate; 17 percent lithium stearate; 25 percent stearic acid; and 8 percent anti-oxidant.

6. A sheet according to claim 1, wherein the coreactant consists by weight, when dried, of essentially about 20 percent nickel (II) chloride; 46 percent sodium ricinoleate; 28 percent stearic acid; and 6 percent anti-oxidant.

7. A sheet according to claim 1, wherein the coreactant consists by weight, when dried, of essentially about 25 percent nickel (II) chloride; 31 percent sodium ricinoleate; 13 percent lithium stearate; 19 per-

8. In a pressure-sensitive recording system, the combination of

one member having a substantially flat surface supporting a multitude of microscopic pressurerupturable capsules containing a reactant solution comprising a precursor taken from the class of dithiooxamide and its N,N'di-substituted derivatives, and the co-reactant comprises nickel (II) chloride, sodium ricinoleate and stearic acid, and

another member having a somewhat absorptive surface which is devoid of reactant and co-reactant, the reactant solution and co-reactant being adapted, upon application of a localized pressure to said members and consequent rupture of the capsules while said surfaces are superimposed in intimate contact, to cause at least some of the reactant solution to partly dissolve at least some of the coreactant and physically transfer from the flat surface to the absorptive surface and be absorbed therein sufficiently to cause the chemical reaction that occurs between precursor and co-reactant to provide in the absorptive surface a chemically formed image that is immediately dry and essentially smudge-free and erasure resistant.

9. The system according to claim 8, wherein said members are flat sheets that are superimposed with said flat surface in face-down contact with said absorptive surface to cause the image formed in said absorptive surface to correspond identically to the pattern of applied localized pressure when such pressure is applied to a surface of said one member opposite said flat surface.

10. The system according to claim 8, wherein the localized pressure is applied to said members by imprinting a right-readable image on a different surface of said one member opposite the flat surface, and the reactant solution and co-reactant react chemically to provide on said flat surface a mirror image of the right-readable image, the mirror image being provided concurrently with and as a part of the same chemical reaction that provides the image in the absorptive surface, the image in the absorptive surface being right readable.

11. A system according to claim 8, wherein the coreactant comprises, by weight, when dried, about 10-30 percent nickel (II) chloride; 15-50 percent sodium ricinoleate; 25-45 percent stearic acid and lithium stearate with a preponderance of stearic acid; and 2-10 percent anti-oxidant.