

[54] **PRESSURE SENSITIVE RECORDING SYSTEM AND METHOD OF PROVIDING A SPLIT IMAGE THEREFOR**

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

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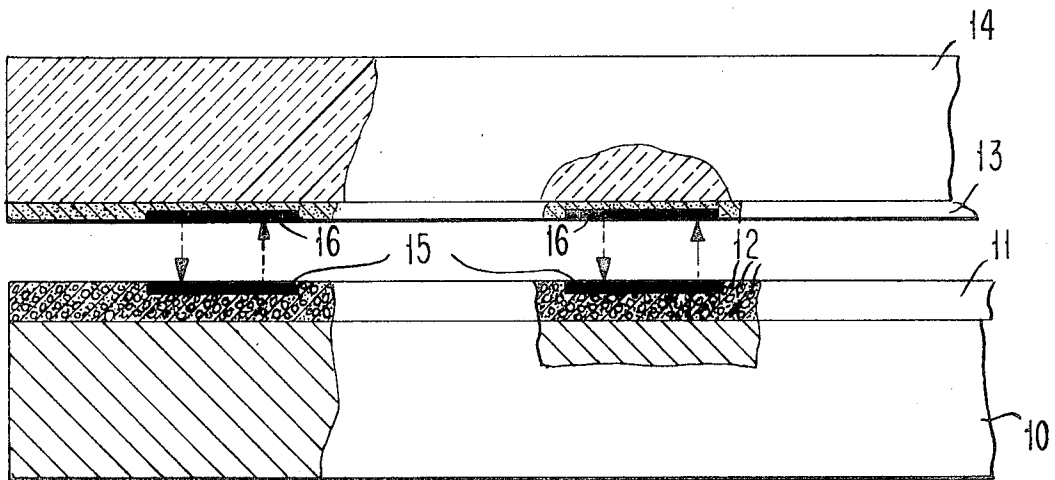
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[57] **ABSTRACT**

Corresponding images (an image and a mirror image thereof) are provided on adjacent surfaces of two sheets. An encapsulated liquid reactant precursor is supported on one of the surfaces and a co-reactant is coated on the other surface. The adhesion/cohesion characteristics of the co-reactant coating are so adjusted and selected that upon pressure-effected rupture of the particular capsules used, some of the co-reactant (as well as some precursor) physically transfer and the balance of each remains in situ and does not transfer. Substantially identical chemical reactions are thus produced concurrently on both adjacent surfaces to provide corresponding colored images thereon.

If the upper one of the sheets is translucent, as in a typical gasoline credit set, the mirror image formed on the underside thereof by one of the chemical reactions will be viewable from the top side thereof as a right-readable image upon separation of the sheets.

7 Claims, 2 Drawing Figures



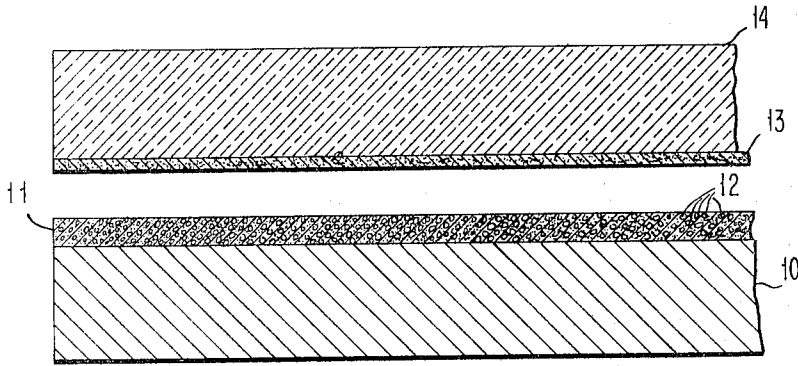
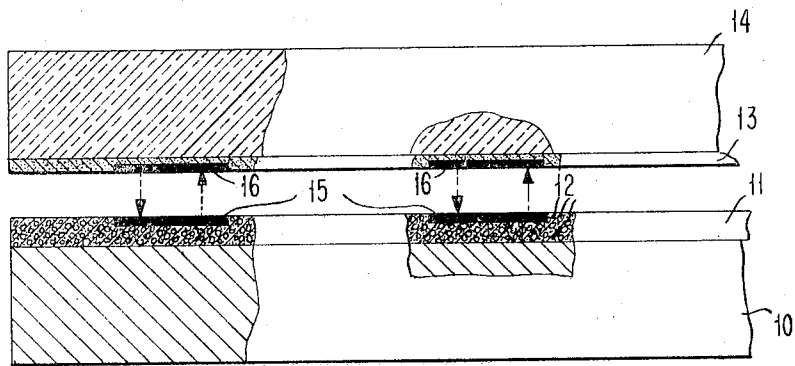


FIG. 1

FIG. 2



PRESSURE SENSITIVE RECORDING SYSTEM AND METHOD OF PROVIDING A SPLIT IMAGE THEREFOR

BACKGROUND OF THE INVENTION

This invention relates to pressure-sensitive recording systems and methods, and more particularly to an improved system of the so-called carbonless type wherein capsules on one sheet containing one liquid reactant are ruptured by pressure to produce a chemical reaction with a co-reactant on another sheet to provide visible images on both such sheets as a result of a partial transfer of the co-reactant as well as the reactant.

Numerous carbonless systems have heretofore been proposed involving encapsulated liquid dyes or reactants 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 in each of these systems, insofar as is known, the co-reactant never transfers. Hence, in a self-contained system (i.e., both reactants on the same surface), no imaging occurs on an adjacent surface because no co-reactant is transferred; any encapsulated reactant released to the adjacent surface thus has no co-reactant to react with to form an image. Similarly, in a two-sheet system (i.e., reactant and coreactant on adjacent surfaces), only reactant that transfers to the co-reactant coated sheet will form an image on the latter; since no co-reactant transfers, any reactant remaining in situ has no co-reactant to react with to form an image on the capsule-containing surface.

In one pressure-sensitive recording system heretofore proposed, an encapsulated colorless marking material is coated on the underside of a porous sheet having a reactive coating on its upper side. When a stylus or the like applies pressure to said upper side, the capsules rupture causing marking material to bleed up through the porous sheet and react with the reactive coating to produce a right-readable image on said top side. If and when a receiving sheet with a reactive coating is disposed adjacent the encapsulated underside of the porous sheet, a chemical reaction will also occur to provide an image on the top of the receiving sheet. Thus, when compressed, the porous sheet releases a reactant that migrates up through the sheet to make a one-way reaction with a reactive coating at the top of the sheet and a one-way reaction with the adjacent reactively coated surface of another sheet. However, the colorless marking material produces no image on the underside of the porous sheet.

In another system, an image is produced concurrently on the adjacent surfaces of two superposed sheets; but in such system the underside of a porous upper sheet is coated with an encapsulated colored marking fluid or colored dye. In such event the images are formed, not by any chemical reaction, but by capsule rupture and release of colored ink or dye in the upper sheet and oneway physical transfer of some of such colored ink or dye to the lower sheet.

While these arrangements may be interesting in theory, they have several disadvantages in practice. Any inadvertent rupture of the colored-dye-containing capsules prior to superposition of the sheets will produce undesirable marking or smearing. Also, the material used to coat the sheet must provide a low-viscosity ink

comprising a solvent capable of penetrating that sheet in such manner and in such quantity as to provide a visible colored mark or a potentially visible mark on the side opposite the coated side. The solvent must be sufficiently volatile to limit the migration. Volatile solvents are difficult to retain in capsules. Moreover, the low viscosity inks will feather out laterally, as well as vertically, as they bleed through the porous sheet; and this will impair legibility and sharpness of the resultant image on the porous sheet.

SUMMARY OF THE INVENTION

Applicants have found that these and other problems can be overcome by providing a pressure-sensitive recording system and method embodying an encapsulated reactant in solution that partially transfers and reacts with a co-reactant that also partially transfers upon rupture of the capsules so as to simultaneously produce a dry right-readable reaction by-product colored image and a dry reaction by-product colored mirror image thereof on adjacent surfaces of two sheets as a result of the two-way mutual physical transfer and chemical reaction. The encapsulated reactant and the co-reactant are supported on adjacent surfaces of different sheets. Only some of the co-reactant and some of the reactant physically transfer to the adjacent surface of the other sheet; the balance remains in situ (i.e., on the surface on which it had originally been supported), thus providing colored images by essentially identical chemical reactions on both such surfaces.

Such a pressure-responsive recording system is especially desirable in record sets, such as used for gasoline credit sales, wherein a translucent sheet overlies an opaque sheet; in such case, the encapsulated reactant would preferably be applied to the opaque sheet and the coreactant applied to the translucent sheet.

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

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1 and 2 are elevational sectional views, to vastly enlarged scale, of a pressure-sensitive recording system embodying the invention and comprising an encapsulated reactant and co-reactant coated on adjacent surfaces of different sheets, FIG. 1 denoting the condition before and FIG. 2 the condition after a mutual partial transfer of reactant and co-reactant produces chemical reactions and corresponding images on both such surfaces.

DESCRIPTION OF PREFERRED EMBODIMENT

The pressure-sensitive recording system illustrated in FIGS. 1 and 2 comprises a substrate, such as sheet 10, the upper surface of which has a coating 11 or the like.

This coating includes a multitude of microscopic pressure-rupturable capsules 12 containing a reactant solution comprising a chemically reactive dye precursor and a solvent. Above coating 11 is a coating 13 or the like which comprises a color-forming co-reactant for the said dye precursor and is carried by the underside of an overlying substrate, such as a sheet 14.

According to the invention, when sheets 10, 14 are superimposed with reactant coating 11 and co-reactant coating 13 in intimate physical contact, a concurrent partial release of the reactant solution and co-reactant coating will occur when the capsules 12 are ruptured

by application of sufficient localized pressure, for example to the upper side of sheet 14, by a stylus, imprint member or the like that exerts at least a preselected magnitude of impact or shear force. Thus, the co-reactant coating 13 transferred to sheet 10 chemically reacts with that portion of the released reactant solution which remained in situ on said sheet to produce a dry right-reading reaction by-product image 15 corresponding to the pattern of applied pressure. Meanwhile, the released reactant solution transferred to sheet 14 chemically reacts with the nontransferred portion of co-reactant coating 13 to produce simultaneously on the underside of said sheet a dry reaction by-product mirror image 16 of the image 15 produced on sheet 10. Hence, two corresponding "split" images 15, 16 will be produced concurrently on adjacent surfaces of both sheets 10, 14 by the two-way mutual partial physical transfer and chemical interaction of reactant and co-reactant.

When the pressure-sensitive recording medium is a set used for gasoline credit sales or the like, the overlying sheet 14 is preferably sufficiently transparent (e.g., translucent) so that the mirror image provided on the underside of said sheet will be viewable from the top side of the sheet as a right-reading image when the sheets 10, 14 are separated. This desirably permits the localized pressure to be applied by a noninked pressure roller via an embossed credit card, since no right-readable image need be imprinted from the credit card onto the upper surface of sheet 14.

The pressure-rupturable capsules 12 may be formed from any film forming material that is sufficiently strong to preclude inadvertent 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. No. 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 a volatile solvent. A particularly suitable class of reactant precursors are dithiooxamide and its N,N'-di-substituted derivatives; of these, the N,N'-diorgano-substituted-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 color-producing reaction, etc.

Applicants' improvement resides, primarily, in providing a co-reactant coating 13 that will partially transfer in response to localized pressure and concurrently chemically react with the particular reactant solution released from the capsules 12 to promptly produce an image of commercially acceptable intensity and durability. This involves providing a co-reactant coating 13 that not only produces the desired reaction product when it reacts chemically with the particular reactant in the capsule 12, but also exhibits proper adhesion/cohesion characteristics. That is, the coating 13 must

be of a formulation providing sufficient adhesion to the substrate 14 and cohesion within itself to prevent premature release during normal handling; it must exhibit the proper amount of adhesion to coating 12 to facilitate transfer; and yet coating 13 must have a cohesion low enough to assure that when a normal degree of localized pressure is applied, the forces of adhesion will prevail over the forces of cohesion. This combination of chemical reaction characteristics and adhesion/cohesion characteristics must assure that approximately half of the co-reactant coating will transfer and the balance will remain in situ to produce "split images" of substantially equal intensity by essentially identical chemical reactions on both adjacent surfaces. The co-reactant coating 13 is preferably applied by a conventional coating apparatus before the paper web is severed into sheets 14.

Now that the general nature of the invention has been described, the following examples are presented as illustrative of the encapsulated reactants and the co-reactants that have been used successfully in applicants' "split image" pressure-sensitive recording system and method.

EXAMPLES 1-6

In each of the following tabulated Examples 1-6, a "200 CB" (Coated Back) sheet of "Action" paper marketed by Minnesota Mining and Manufacturing Company was used to constitute the substrate 10 and encapsulated coating 11. While the specific formulation of said coating has not been disclosed by said company, the capsules 12 forming part thereof are known to contain dithiooxamide or one of its N,N'-disubstituted 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 zinc-carboxylate; and the capsule walls are formed of urea formaldehyde resin.

The co-reactant coatings 13 were prepared by adding the ingredients specified in Table I to a suitable solvent, preferably denatured alcohol such as that designated as PM 3163 and marketed by Ashland Chemical Co. Each mixture was then shaken for 15 minutes on a vibratory paint shaker using steel balls within the container to facilitate solution and dispersion. The resulting solution was then applied as a coating to an 11-pound (17x22-500) translucent paper substrate and dried to remove the solvent.

The variously coated papers were then incorporated into respective manifold sets so that the co-reactant-coated surface was face down in intimate physical contact with the encapsulated face-up coating on the 3M CB sheet. These sets were then imaged by applying localized pressure using well known techniques such as ball-point pens, pencils, and imprinting devices employing embossed credit cards.

Table I expresses the formulations of the co-reactant coatings 13 of Examples 1 through 6 in terms of percentage by weight of the various ingredients less the volatile solvent which ultimately evaporates.

Table I

Ingredients	Examples					
	1	2	3	4	5	6
Nickel (II) chloride · 6 H ₂ O	30.8	36.2	32.3	30.8	32.3	22.3

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Table I—Continued

Ingredients	Examples					
	1	2	3	4	5	6
Zinc resinate	15.4	14.6	16.2	9.2	20.8	18.5
Lithium stearate	38.4	43.8	36.1	44.6	31.5	40.7
Sodium benzoate	15.4	5.4	15.4	15.4	15.4	18.5
	100.0	100.0	100.0	100.0	100.0	100.0

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 zinc resinate provides a substance that reacts with the nickel 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; it also binds the coating to the substrate and provides coating cohesion. The lithium stearate causes a reasonably balanced split of the image between the mating sheets, provides coating cohesion and increased image intensity, and also renders the applied coating semi-opaque to increase image contrast. The three ingredients just specified are very important in assuring the split image according to the invention; whereas the sodium benzoate is considered highly desirable, though not essential, because it improves environmental image stability.

The six formulations of Examples 1–6 were found to exhibit the following functional requirements that are essential to commercial acceptability; good image visual intensity on both plies, good imaging speed, and good environmental stability. They were also found suitable for imaging by either pens or credit card im printers.

The formulation that produces the optimum blend of the aforementioned functional requirements necessary for commercial acceptance was that of Example 1, which is therefore repeated below as the preferred formulation. However, it appears, based upon an evaluation of these listed examples and others, that commercially acceptable (though not necessarily optimum) co-reactant coatings may be obtained by employing the named ingredients within the ranges specified below:

Ingredient*	Preferred	Minimum	Maximum
Nickel (II) chloride 6 H ₂ O	30.8	22	37
Zinc resinate	15.4	9	21
Lithium stearate	38.4	31	45
Sodium benzoate	15.4	5	19

*Ingredients, in percent by weight, but less solvent.

While applicants do not know the precise reason why the specific formulation of Example 1 is superior to that of the others, they believe, on the basis of their findings, that it possesses the optimum balance of adhesion/cohesion forces and chemical reactivity.

As above indicated, the formulations above listed in Examples 1–6 do not constitute all of the formulations prepared and evaluated. Other formulations were prepared and evaluated which included one or more of the ingredients listed for Examples 1–6, together with nickel resinate, nickel stearate, stearic acid, and others in varying amounts; but the evaluations made on such other formulations showed that they were generally unsuitable for commercial acceptability, except for one formulation in which silica and sodium benzoate were included. However, the silica merely supplemented and

served the same function as the lithium stearate in enhancing image contrast in the translucent sheet 14, but it could not replace the lithium stearate's function of also increasing image intensity.

It should be noted, however, that applicants' pressure-sensitive recording system and method is not limited to use of the specific encapsulated reactant employed in the above-described CB sheets marketed by 3M. Applicants have successfully achieved split imaging by mutual physical transfer of reactant and co-reactant and mutual chemical reaction in carbonless systems using other commercially available encapsulated reactants. The following examples are illustrative:

EXAMPLE 7

A CB (Coated Back) encapsulated donor sheet marketed by National Cash Register Company was used to constitute the substrate 10 and encapsulated coating 11. Although the specific formulation of said coating is not known, it is believed that the capsule material and capsule content are as taught and disclosed in U.S. Pat. No. 3,427,180.

The following formulation was applied as the coating 13 on translucent sheet 14:

Ingredient	(Wet) Parts by Weight	(Dry) % by Weight
Zinc resinate	3.0	27.3
Propyl gallate	3.0	27.3
Tannic acid	1.0	9.1
Colloidal silica	4.0	36.3
Toluene	30.0	*
Denatured alcohol	10.0	*
		100.0

*Evaporated during drying.

When these coatings 11, 13 were placed in intimate contact and capsules 12 were ruptured by localized pressure in the manner already described, a split image (though not necessarily optimized) mutual transfer and chemical reaction were achieved. In this formulation, the zinc resinate serves as the binder; the propyl gallate and tannic acid serve as the co-reactant for the encapsulated precursor; and the silica facilitates a splitting of the image between the mating sheets and also renders the coating semi-opaque thereby increasing image contrast.

EXAMPLE 8

An encapsulated donor sheet currently being offered for sale in the United States by The Pilot Pen Company, Ltd., Tokyo, Japan, was used to constitute the substrate 10 and encapsulated coating 11. While the specific formulation of the encapsulated coating is not known, it is believed to be in accord with the teachings of Example 3 of U.S. Pat. No. 3,432,327.

The following formulation was applied as the coating 13 on translucent sheet 14:

Ingredient	Parts by Weight (Wet)	% by Weight (Dry)
Propyl gallate	10.0	55.3
Tannic acid	1.0	5.6
Polyvinylpyrrolidone (PVP-K30*)	1.0	5.6
Oxazoline Wax (ES-254**)	2.0	11.2
Oxazoline Wax (TX-1**)	1.0	5.6
Silica (Syloid 72 ***)	3.0	16.7
Denatured alcohol	20.0	****
Toluene	10.0	****
		100.0

*Marketed by GAF Corporation
 **Marketed by Commercial Solvents Corp.
 ***Marketed by W. R. Grace Corp.
 ****Evaporated during drying.

In this formulation, the propyl gallate and tannic acid serve as the co-reactant for the encapsulated precursor; the polyvinylpyrrolidone and to some extent the waxes serve as the binder; and the waxes and the silica facilitate splitting of the image, with the silica also serving to enhance image contrast.

An acceptable (though not necessarily optimized) split image reaction was observed when the coatings 11, 13 were placed in intimate contact and the capsules 12 were ruptured by localized pressure in the manner already described. The images made using a ball-point pen were dark and formed rapidly, although those made with a credit card imprinter resulted in a somewhat less intense image than desired on the encapsulated donor sheet 14. This coating was found to exhibit reasonably good environmental stability.

From the foregoing it will be seen that applicants have demonstrated that a pressure-induced mutual two-way partial transfer of reactant and co-reactant from adjacent surfaces will provide, by essentially identical chemical reactions on both said surfaces, a legible image and a mirror image thereof; and that when the mirror image is thus provided on the underside of a translucent sheet, it may be viewed as a right-readable image from the top of such translucent sheet. This desirably eliminates the need for imprinting with an inked roll or the like on the upper sheet of a two-sheet set.

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 various changes may be made in the pressure-sensitive recording system and in the specified formulations and method without departing from the spirit, scope and teaching of the present invention. Accordingly, the system and method herein disclosed are to be considered merely as illustrative, and the scope of the invention is to be limited only as specified in the claims.

What is claimed is:

1. A pressure-sensitive recording system comprising one sheet having a surface supporting a multitude of microscopic pressure-rupturable capsules containing a reactant solution comprising a chemically re-

active dye precursor and a solvent, and a different sheet having a surface supporting a partially releasable co-reactant adapted, upon application of a localized pressure to the sheets and consequent rupture of the capsules while the surfaces are superimposed in intimate contact, to cause some of the co-reactant and some of the capsules and reactant solution to remain in situ on their respective supporting surfaces and the remainder of each to physically transfer to the adjacent supporting surface of the respective other sheets, thereby to cause essentially identical chemical reactions to occur between precursor and co-reactant concurrently on said surfaces for simultaneously providing at least one right-readable image on one of said surfaces and a mirror image thereof on the other of said surfaces,

the particular one of said sheets having said other of said surfaces being sufficiently transparent so that upon separation of the sheets the mirror image will be viewable as a right readable image from the reverse side of such particular sheet without bleed through of reaction product to said reverse side.

2. A system according to claim 1, the reactant solution comprising a precursor taken from the class of dithiooxamide and its N,N'-di-substituted derivatives, and the co-reactant comprising by weight, when dried, about 22-37 percent nickel (II) chloride; about 9-21 percent zinc resinate; about 31-45 percent lithium stearate; and about 5-19 percent sodium benzoate.

3. A system according to claim 1, wherein the co-reactant comprises by weight, when dried, essentially about 55 percent propyl gallate; 6 percent tannic acid; 6 percent polyvinylpyrrolidone; 16 percent oxazoline wax; and 17 percent silica.

4. A system according to claim 1, wherein the co-reactant comprises by weight, when dried, essentially about 27 percent zinc resinate; 27 percent propyl gallate; 9 percent tannic acid; and 37 percent colloidal silica.

5. A system according to claim 1, wherein the solution comprises a precursor taken from the class of dithiooxamide and its N,N'-di-substituted derivatives, and the co-reactant comprises nickel (II) chloride, zinc resinate, lithium stearate and sodium benzoate.

6. A system according to claim 1, wherein the co-reactant comprises by weight, when dried, 22-37 percent nickel (II) chloride; 9-21 percent zinc resinate; 31-45 percent lithium stearate; and 5-19 percent sodium benzoate.

7. A system according to claim 1, wherein the solution comprises a precursor taken from the class of dithiooxamide and its N,N'-di-substituted derivatives, and the co-reactant comprises by weight, when dried, essentially about 31 percent nickel (II) chloride; 15 percent zinc resinate; 39 percent lithium stearate and 15 percent sodium benzoate.

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