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## PRESSURE RESPONSIVE RECORD MATERIALS

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This invention is a continuation-in-part of U.S. patent application Serial No. 275,197, filed April 24, 1963, now abandoned.

This invention relates to pressure-sensitive record materials useful as copy or manifold materials which do not require the use of conventional carbon papers. In particular, this invention relates to a record material base having a surface on which are adherent a profuse number of microscopic pressure-rupturable capsules of film-forming material, each capsule containing a material which will instantly react upon contact with a second material to produce a black mark.

The novel record material of this invention is an improvement in the type of record material disclosed in U.S. Patent No. 2,730,457 which comprises a surface on which are adherent a profuse number of microscopic pressure-rupturable capsules containing an oil, the oil being adapted to react upon contact with a solid material to produce a distinctive color. Printing or writing pressures applied onto said surface rupture the capsules in the locality of the pressure, releasing the color-reactive material so that it may migrate and contact a second color-reactive substance thus producing distinctively colored printing or writing marks. The novel record material of this invention is an improvement over the above-disclosed record material. The principal object of this invention is to provide a pressure-sensitive record material or a copy material on which sharp, dense, colored marks, particularly black marks, may be instantly produced by mere application of localized pressure, said black marks comprising a metal complex formed by the reaction of dithiooxamide and a heavy metal salt, the two reactants normally being held insulated from contact by reason of at least one of said reactants being contained within pressure-rupturable microscopic capsules of film-forming material, the capsules each having the reactant in a solvent as a nucleus and a dense shell-like wall deposited therearound by coacervate forces and being rupturable by printing or writing pressures.

Another object of the invention is to provide such a record material in which the mark- or image-forming reactants are present in adjacent surfaces.

Still another object of the invention is to provide such a record material in which the mark- or image-forming materials are present on the same surface.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

It is known that many heavy metal salts form stable complex compounds with dithiooxamide in a solvent medium. In general, the complexes so formed are colored to some degree, the particular color being primarily a function of the cation of the particular metal salt employed. However, where, as in the present case, black

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markings are desired, the heavy metal salt of choice is a mixture of a nickel salt and a copper salt; it has been found that the most black markings result when these salts are mixed in a ratio of 3 parts copper salt to one part nickel salt. The anion of the salt is not critical, except that it must be such as to not render the salt insoluble in the particular solvent employed within the capsules, for reasons to be dealt with in greater detail hereinafter. Since the solvents employed in this invention are organic in nature, it is generally necessary to provide anions which are also organic, such as butyrate or acetate, or anion complexes such as salicylate or acetyl acetonate. It has been found that the acetates are particularly efficacious in producing instant, dense, black markings.

This invention may be carried out by encapsulating one of the reactants and a suitable solvent in pressure-rupturable microscopic capsules, applying a profuse number of said capsules to a first surface, said first surface being in superposable relationship to a second surface containing the second reactant, said reactants insulated from contact with each other by the walls of the capsules. When pressure is applied to the superposed surfaces, as by contact with a pencil or typewriter type, the capsules in an area coextensive with the area upon which the pressure is applied will rupture, thereby releasing the reactant and solvent which will contact the second reactant to form a dense colored image coextensive with the area of the applied pressure.

It is an important feature of the present invention that the liquid employed as the solvent for the encapsulated reactant be a solvent for the co-reactant as well, whether the latter is also encapsulated or not. This same solvent then serves as a reaction medium for the two reactants at the time of rupture of the capsules. It has been found that in order to obtain instant, dense black markings using dithiooxamide and copper-nickel salts, it is necessary that the solvent be a high di-electric, highly polar organic liquid which, as noted above, is a mutual solvent for both reactants. As examples of solvents which fulfill the above criteria, mention may be made of glycerin, nitromethane, nitropropane, and nitrobenzene. The selection of additional suitable solvents will be obvious to those skilled in the art.

It has further been found desirable to control the pH of the environment in which the dithiooxamide and heavy metal salts react; while some markings may be obtained in neutral environments, it has been found that dense black marks are instantly produced where the interaction takes place in basic solution, preferably at a pH of about 10. The basic environment can be readily provided by coating or treating the copy paper with a suitable alkali, such as sodium carbonate.

The pressure-responsive record materials of this invention may be prepared and utilized in a number of ways. The invention requires dithiooxamide, a heavy metal salt, and a suitable reaction medium. At least one of the reactants must be encapsulated. When one of the reactants must be encapsulated. When one of the reactants is encapsulated, a solution of the other reactant will be applied to a surface and dried. The capsule layer and the second or copy surface will then be placed in such a relationship to each other whereby rupture of the capsules by writing pressures will release the entrapped contents and allow the reactants to coact thereby forming the dense colored image of the original mark. Alternatively, both reactants may be encapsulated and be located either in adjacent sheets in superposable relationship or on the same surface of a single sheet. The capsular material is so rugged and impervious to the reactants that it may be interspersed with a fluid suspension of a metal salt and applied to a surface as a single coating without any danger of prema-

ture image formation. Alternatively, the capsules and the heavy metal salt may be laid down as separate layers on the same surface.

In one embodiment of the invention, dithiooxamide may be dissolved in, e.g., glycerin and encapsulated in an organic polymer, e.g., a vinylidene chloride/acrylonitrile copolymer and a profuse number of thus-formed microscopic pressure-rupturable capsules applied to the underside of a first or original sheet. A second or copy sheet may be prepared by coating the first or upper surface with a heavy metal salt solution, such as a solution of nickel acetate and copper acetate, and drying. The first and second sheets are then placed in superposed relationship with the capsule layer and the metal salt layer adjacent to each other. The application of pressure, such as writing pressure, on the surface of the original or first sheet will rupture the capsules coextensive with the area upon which the pressure is applied, releasing the dithiooxamide and solvent which will react with the heavy metal salt to form a dense black image of the mark on the original or first sheets. In the above-described embodiment, a simple copy system involving only an original and one copy sheet is involved; however, it can be readily seen that by the successive addition of sheets treated on the first or upper surface with a heavy metal salt and on the second surface with a layer of microscopic capsules containing the dithiooxamide and solvent and placing the sheets in superposed stacked relationship, a large number of copies may be made thereby.

In other embodiment of the invention, the copy or second sheet may be prepared by coating the surface with a solution of dithiooxamide and drying. The solution may comprise, e.g., dithiooxamide in chloroform. The capsule layer on the superposed under-surface of the first sheet will then comprise a heavy metal salt, such as copper and nickel acetate, in a suitable solvent, such as glycerin, encapsulated in a polymer, for example, a polystyrene copolymer.

In still another embodiment of this invention, dithiooxamide and the heavy metal salt solution may be encapsulated separately. The capsules may then be intimately mixed and applied to a single surface; or they may be applied to adjacent surfaces as described above.

In yet another embodiment of this invention, a heavy metal salt may be applied to a surface and a profuse number of microscopic pressure-rupturable capsules containing dithiooxamide and a solvent may be applied to the same surface.

It may be desirable to apply a sizing to the paper to prevent the mark-forming materials from being absorbed too deeply into the paper or even striking through the paper. It may also be desirable to apply coatings to the surface of the paper also to act as barriers and to provide an adsorbent-receptive layer for the reaction product. Clays, waxes, etc., may be used for such purposes. One material which has been found to be particularly efficacious in this respect is Ludox (Du Pont brand colloidal silica), in that not only does it provide an excellent sizing, but also, being alkaline in nature, confers the desirable basicity upon the reaction environment without requiring additional alkali.

A thickener such as an organic polymer may also be encapsulated with the reactants and the solvent, in order to prevent excessive spreading of the reactants on the copy sheet or smudging of the mark, due to an otherwise excessively fluid encapsulated material. Suitable thickeners for this purpose will be apparent to one skilled in the art.

The encapsulating materials may be gelatin, a complex of gelatin and gum arabic, agar-agar, and polymers such as Saran, styrene and vinyl chloride copolymers. As the total thickness of the pressure-sensitive coating need be no greater than 0.001 to 0.002 of an inch, it may be supported on very thin paper stock. The microscopic-rupturable capsules suitable for use in this inven-

tion may be prepared by encapsulating the particular reactant and solvent in film-forming materials and applied to a surface by known methods, for example, the method disclosed in the above-noted U.S. Patent No. 2,730,457.

It can be readily seen that, by means of this invention, a number of copies of typewritten or written material may be made without the use of carbon manifold paper by placing a series of the above-described sheets in superposed relation in a typewriter. For example, the first sheet may be the original which will be contacted by the type of the typewriter. The underside of said sheet will contain the layer of microscopic capsules of dithiooxamide in a solvent. In superposed position with the capsule layer would be a copy sheet treated with a heavy metal salt on the first or upperside. The underside of said copy sheet contains a layer of microscopic dithiooxamide-containing capsules to contact a third sensitized copy sheet. By the successive addition of a number of copy sheets treated with a heavy metal salt on one side and a layer of microscopic capsules containing dithiooxamide on the underside, a reasonably large number of copies may be made thereby. Utilizing an alternative embodiment, the production of a plurality of copies may be accomplished more efficiently by means of a sheet that contains both the reactants on the same surface.

The copy sheets within the scope of this invention may be prepared by imbibing a surface with a solution of the particular reactant and drying the surface to remove the solvent.

As examples of copy sheets suitable within the scope of this invention, mention may be made of the following:

#### *Copy sheet 1*

A sheet of paper is coated with Ludox (trade name for Du Pont colloidal silica) and a dilute solution of 3 to 1 copper acetate-nickel acetate is applied to the Ludox layer and dried.

#### *Copy sheet 2*

A sheet of paper is coated with Ludox (trade name for Du Pont colloidal silica) and a solution of dithiooxamide in chloroform is applied to the sheet and dried.

#### *Copy sheet 3*

A copper acetate-sodium carbonate solution is applied to a sheet of paper and dried.

As examples of encapsulated reactants suitable for use within the scope of this invention, mention may be made of the following:

#### *Capsular material 1*

Dithiooxamide is dissolved in glycerin and encapsulated in Saran. The capsular material is then coated on sheet of paper.

#### *Capsular material 2*

Dithiooxamide is dissolved in nitro-methane and encapsulated in gelatin-gum arabic. The capsule material is then coated on a sheet of paper.

#### *Capsular material 3*

Copper acetate and nickel acetate are dissolved in glycerin and encapsulated in Saran. The capsular materials are then coated on a sheet of paper.

As an example of a pressure-responsive record material within the scope of this invention wherein both reactants are encapsulated, mention may be made of the following:

Dithiooxamide is dissolved in glycerin and encapsulated in Saran.

Copper acetate-nickel acetate is dissolved in glycerin and encapsulated in Saran. The capsulator materials are then intimately mixed and the mixture applied to a surface.

The foregoing disclosure has described the use of dithiooxamide and heavy metal salts in pressure-respon-

sive record materials to produce dense, colored marks. It should also be understood that the term "dithiooxamide" is intended to include substituted dithiooxamides, particularly the N,N'-disubstituted derivative such as N,N-dimethyldithiooxamide and N,N - dibenzyl dithiooxamide which also complex with heavy metal salts to produce colored precipitates. However, in the interest of producing the blackest most dense markings in the systems described herein, it is preferred that unsubstituted dithiooxamide be employed.

Since one of the reactants is imbibed into a surface and dried, and the second reactant and the reaction solvent are encapsulated in an impermeable material, the novel pressure-responsive record materials of this invention are not easily smudged or blurred by physical handling and also possess a high degree of shelf-life stability.

Since certain changes may be made in the above products without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. Pressure-sensitive record material comprising a sheet of paper on a surface of which are reactants comprising a copper salt-nickel salt mixture, dithiooxamide, a high di-electric, highly polar organic liquid which is a solvent for both of said reactants as a reaction medium, and an alkali, said reactants normally being held insulated from contact by reason of at least one of said reactants and said reaction medium being contained within microscopic pressure-rupturable capsules of polymeric materials, the walls of each capsule being impervious to the reactants contained therein, whereby writing and marking pressures, alone, on said record material permit instant coaction of the reactants to form black marks at points of pressure.

2. The record material of claim 1 in which said dithiooxamide is encapsulated in said pressure-rupturable capsules.

3. The record material of claim 1 in which an adsorbent-receptive layer is applied to said surface.

4. The record material of claim 1 in which said alkali is present in sufficient quantity to provide a pH on said sheet of about 10.

5. The record material of claim 1 wherein said alkali is alkaline colloidal silica.

6. The record material of claim 1 wherein said copper salt-nickel salt is encapsulated in said pressure-rupturable capsules.

7. The record material of claim 2 wherein said copper salt-nickel salt mixture is a 3 to 1 mixture of copper acetate and nickel acetate.

8. Pressure-sensitive record material comprising a sheet of paper on a surface of which are reactants comprising a copper salt-nickel salt mixture, dithiooxamide, a high di-electric, highly polar organic liquid which is a solvent for both of said reactants as a reaction medium, and an adsorbent-receptive layer comprising alkaline colloidal silica, said reactants normally being held insulated from contact by reason of each of said reactants being separately contained with said reaction medium within pressure-rupturable capsules of polymeric materials, the walls of each capsule being impervious to the reactants contained therein, whereby writing and marking pressures, alone, on said record material allow the reactants instantly to coact to produce black marks at points of pressure.

9. The record material of claim 8 wherein said capsules are intimately mixed prior to being applied to said surface.

10. The record material of claim 8 wherein said pressure-rupturable capsules are applied in adjacent layers to said surface.

11. Pressure-sensitive record material comprising at least a first and second surface in superposed relationship, said first surface comprising alkaline colloidal silica and a first reactant and said second surface comprising a second reactant dissolved in a high di-electric, highly polar organic liquid which is a solvent for both said first reactant and said second reactant, said second reactant and said liquid being contained within pressure-rupturable capsules of polymeric material, said reactants normally being held insulated from contact with each other by reason of at least said second reactant being contained within said pressure-rupturable capsules, the walls of said capsules being impervious to both of said reactants, said reactants comprising dithiooxamide and a mixture of copper acetate and nickel acetate, whereby writing and marking pressures on said record material instantly produce dense, black marks at points of pressure on at least said first surface.

12. The record material of claim 11 wherein said first reactant is applied to said first surface in a solution and dried.

13. The record material of claim 11 wherein each of said reactants is separately contained within pressure-rupturable capsules, and each of said reactants is dissolved in the same di-electric, highly polar organic liquid within said pressure-rupturable capsules.

No references cited.

50 MURRAY KATZ, *Primary Examiner.*