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R. F. HELIKER ET AL

3,411,976

SELF-MARKING RECORD MATERIAL

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FIG. 1

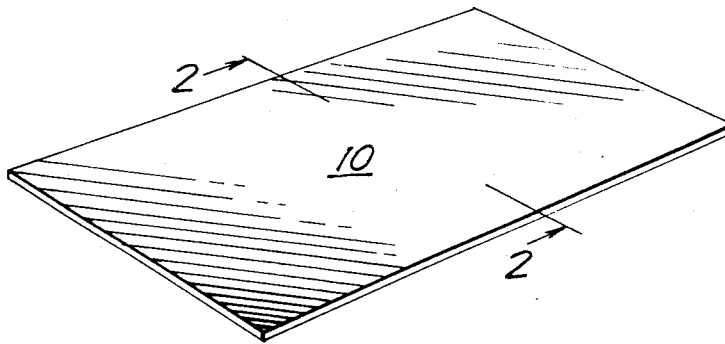


FIG. 2

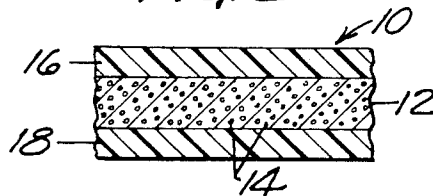
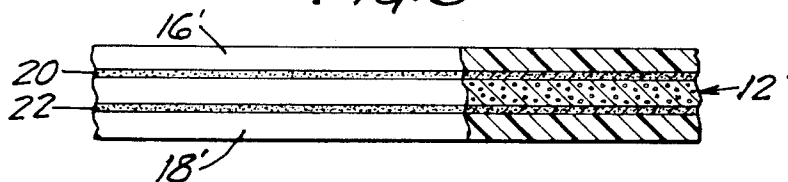


FIG. 3



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SELF-MARKING RECORD MATERIAL

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6 Claims. (Cl. 161—5)

This invention relates to self-marking sheet materials surfaced with protective plastic coatings.

There are many applications for which rugged, weatherable, dust resistant and tamperproof self-marking sheet materials are desired. For example, in so-called "clean rooms" or other industrial work areas where dust and other particle contamination must be minimized, conventional writing instruments which transfer a marking substance, e.g. lead or ink, from the writing instrument to the document to form an image are objectionable because both the marking substance and fibers or other material scraped from the document by the writing instrument result in objectionable contamination. Also, many goods such as steel parts and the like are stored outdoors by industry. Such storage requires a large quantity daily of weatherproof identification tags. Such tags have been made by first marking a paper, paperboard, or similar sheet and then coating or laminating a transparent plastic material over the surface of the sheet. Another application where a need has existed for such sheet materials include plastic coated marking bands used in hospitals for identification of patients in which moisture resistance of the sheet material is important.

Sheet material having a protective plastic coating which could be imaged beneath the protective coating later when desired and which would be both tamper resistant and weather resistant would be highly desirable for such applications. In spite of a long-felt need, such materials have hitherto been unavailable.

It is an object of the present invention to provide a protective plastic coated self-marking record material which will fill these and other needs. In accordance with the present invention a self-imaging paper or similar substrate is provided which carries normally separated image-forming reactants, at least one of the reactants being contained within tiny pressure-rupturable capsules which contain a reactant in liquid form. This substrate is surfaced on one or both surfaces with a protective plastic layer which is capable of transmitting marking pressures to localized areas of the substrate so that such pressures, when applied by a stylus, typewriter key, or the like, will cause rupture of the capsules within the substrate to release a color-forming reactant contained in the capsules, causing a color-forming reaction to occur underneath the plastic protective surfacing, thus providing a visible image in areas in which marking pressure has been applied. In one embodiment the image-making capacity of the reactants in the unmarked areas of the sheet can be destroyed by exposing the materials to ultraviolet light thus forming an imaged sheet in which no further imaging can occur.

In the drawings:

FIGURE 1 is a perspective view of a sheet material of the invention;

FIGURE 2 is a greatly magnified broken away sectional view taken through the region 2—2 of FIGURE 1; and

FIGURE 3 is a view similar to FIGURE 2, showing a further embodiment of the invention.

In FIGURES 1-2 is shown sheet 10 which includes an inner layer 12 of paper or equivalent fibrous material. Layer 12 carries pressure-rupturable, microscopic capsules 14, generally no larger than about 50 microns, which contain one reactive component, in liquid form,

of an image-forming reaction system. A co-reactant (not shown) for the encapsulated liquid reactant is included in the sheet material adjacent the capsules so that upon release of the liquid reactant from the capsules a reaction takes place to provide a distinctive colored image in the sheet.

Layer 12 is provided on opposite sides with coatings 16 and 18 of flexible organic polymeric film-forming material. At least one of layers 16 and 18 should be sufficiently thin and/or flexible as to be locally depressable, i.e. capable of transmitting therethrough the pressure of a stylus point applied to the film surface with a force approximating that used in writing or typing. In addition at least one of films 16 and 18 is sufficiently transparent to permit viewing of images formed in layer 12.

In the embodiment of FIGURE 3 is shown a construction wherein adhesive layers 20 and 22 are used to bond film layers 16' and 18' to fibrous sheet 12'. Such adhesive layers are required where the films 16' and 18' cannot be self-adhered to the fibrous sheet as, for example, in the case of polyethylene terephthalate films. Adhesive 20, 22 may be of a pressure sensitive type or of a heat-sealable thermoplastic type. Fibrous sheet 12 can readily be formed from an aqueous slurry of any paper-forming fibers which form a unified web, most commonly cellulosic rag and wood pulp fibers. Other fibers which may be used include "fibrils" (as defined in U.S. Patent 2,988,782 issued June 20, 1961) or other flexible sheet-forming solids such as fibers of polyacrylonitriles, polyesters and polyamides that can be deposited from a slurry to form a fibrous web on a paper-making machine. One method of incorporating the color reactive image-forming materials in sheet 12 involves mixing the capsules into the paper-making slurry before deposition on the foraminous surface of a paper machine. The co-reactant is normally in solid form and may be incorporated as a paper sizing or other treatment of the fibers.

An alternative method of forming sheet 12 involves coating the co-reactants at least one of which is activatable onto a preformed fibrous web so that the reactants are present only on one surface of sheet 12.

Capsules 14 may be formed from any film-forming material sufficiently strong to withstand necessary handling. A particularly suitable class of film-forming materials are aldehyde condensation polymers and particularly ureaformaldehyde condensation polymers. The capsules are preferably in a size range of from 1 to 50 microns and are preferably used in an amount from 5 to about 50 parts by dry weight capsules per 100 parts pulp.

Dithiooxamide (sometimes hereinafter called DTO) and its N,N'-di-substituted derivatives, as a class, when reacted with various metal cations, as well as other complexing agents, result in quite distinctive colors and thus constitute a preferred class of capsule fill materials. Particularly, N,N'-diorgano-substituted-dithiooxamides dissolved in organic solvents have been found to perform well with many of their known complexing agents, and a useful liquid fill for the capsules is one composed of about 1% to 2% solution of N,N'-dibenzylidithiooxamide (hereinafter sometimes called DBDTO) in an aromatic solvent such as xylene, preferably with some further additive or additives present to enhance speed, intensity of color reaction, to provide storage stability, or for other purposes as may be desired.

For co-reactants with DTO type color systems, solid components containing complexing agents, particularly available metal cations which form colors upon reaction with dithiooxamide derivatives, are used. These components should be in water insoluble form and may be added as suspensions to the paper slurry along with the capsules or added by other means and/or at some other

stage, for example as a coating on the dry paper. Since papers are normally sized, the metal cation providing component can conveniently be incorporated into the paper slurry as a sizing so that it may function both as a sizing and as a co-reactant for the liquid reactant. One way to carry out this procedure is to add a water soluble rosin salt such as sodium rosinate to the paper slurry along with the capsules, or prior to or after addition of the capsules, but prior to the deposition of the slurry onto the paper-making machine so that the rosin has time to find the pulp fibers in the slurry; and then add a water-soluble metal compound which insolubilizes the rosin such as nickel sulphate, chloride, or nitrate or similar salt of copper, cobalt, etc. to the slurry. This reacts with the rosin salt to form an insoluble metal rosinate sizing on the pulp fibers having available metal cations for color formation.

Nickel cations are preferred as co-reactants with the N,N'-diorgano-substituted dithiooxamide to produce rapid and vivid images, which other cations such as cobalt, copper, silver, etc. may also be used.

Examples of suitable protective plastic coating material include polyolefins, particularly polyethylene and polypropylene. Other suitable polymers include polyvinylhalides, polystyrenes, polyurethanes, epoxies, polyacrylates, polyamides, polyesters, as well as other polymeric materials which are sufficiently transparent to permit viewing of images therethrough and sufficiently flexible to provide the required local extensibility. The polymeric coatings are preferably applied in layers ranging from 1/4 to 10 mils in thickness.

The preferred method of applying coatings 16 and 18 is by hot extrusion of the polymeric material directly onto the surfaces of the fibrous web. Various other coating techniques, which will be apparent to those skilled in the art may be substituted, for example, solution coating, heat laminating, knife coating, hot roll coating, curtain coating, spraying, dipping, brushing, etc.

Self-marking papers coated with thermoplastic polymeric materials such as polyethylene may be provided with sealed edges by cutting the coated paper with knives heated to a temperature above the melting point of the polymer. Such papers are desirable in applications where exceptionally good water resistance is desired.

It has been found that the image-making capacity of the sheet materials can be destroyed by exposure to sunlight or other ultraviolet light, apparently due to a conversion of the DTO or derivatives thereof to a non-reactive form. Thus it is possible to form images in a sheet and destroy the capacity of the sheet for forming additional images by exposure to an ultraviolet light source. There is a tendency toward the images to fade upon long-term exposure to sunlight but this can be minimized by adding ultraviolet light absorbers to the plastic film. Examples of such absorbers are 2(2'-hydroxy 5'-methylphenyl) benzotriazole or benzophenones such as 2,2'-dihydroxy-4,4'-dimethoxy benzophenone. Others will be apparent to those skilled in the art. It will be understood that the absorber should be compatible with the particular polymer used in the film.

In addition to the aforementioned uses for the sheet materials of this invention a wide variety of other uses will be apparent. For example, the materials can be applied to tools or sporting equipment, such as baseball bats or golf clubs, or the like, to indicate the location of an

impact thereon. Other uses include applications where marking is desired under water.

In a specific embodiment of the invention, paper having a caliper of about 3.5 mils was provided, the paper containing about 11 parts dry weight capsules per 100 parts wood pulp and 3 parts nickel rosinate per 100 parts wood pulp. The capsules had an average diameter of about 15 microns and contained DBDTO. The paper had a weight of about 27 lbs. per ream (3000 ft.²). A 1-mil thick coating of medium density polyethylene was extruded onto each side of the paper. The finished sheet had a weight of about 54 lb. per ream (3000 ft.²). When normal writing pressure was applied to the surface of the sheet with a stylus, clearly visible violet images were produced in the sheet.

What is claimed is:

1. A protective-plastic surfaced self-marking record material, comprising a pressure-responsive self-imaging substrate carrying normally separated image-forming reactants which combine and react upon the application of marking pressure to said substrate, at least one of said reactants comprising microscopically sized pressure-rupturable capsules containing a liquid color-forming reactant, and a protective-plastic coating over said substrate comprising a locally extensible layer of transparent, flexible, plastic capable of transmitting marking pressures thereon to said substrate to cause rupture of said capsules beneath local areas to which pressure is applied.

2. A protective-plastic surfaced self-marking record material, said material comprising a substrate carrying pressure-rupturable microscopic capsules which provide a visible image on said substrate when ruptured, a protective-plastic coating surfacing said substrate and capable of transmitting marking pressures therethrough to said substrate.

3. A protective-plastic surfaced self-marking paper comprising a sheet of paper carrying pressure-rupturable microscopically sized capsules, the rupture of which causes the formation of an image in said paper, said paper being coated on both sides with a protective-plastic film, the film on at least one side of said paper being transparent, and the film on at least one side being sufficiently flexible and extensible to prevent the transmission of marking pressures applied thereon to said paper to cause rupture of said capsules beneath local areas to which pressure is applied.

4. Record material according to claim 1 wherein said plastic is a polyolefin.

5. Record material according to claim 1 wherein the walls of said pressure rupturable capsules comprise urea-formaldehyde.

6. Record material according to claim 5 wherein the liquid fill material of said capsules comprises N,N'-disubstituted dithiooxamide and said second color reactant comprises an insoluble ionizing metal salt distributed throughout said substrate.

References Cited

UNITED STATES PATENTS

2,548,366	4/1951	Green et al.	117—36.2
3,287,154	11/1966	Haas	117—36.8

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