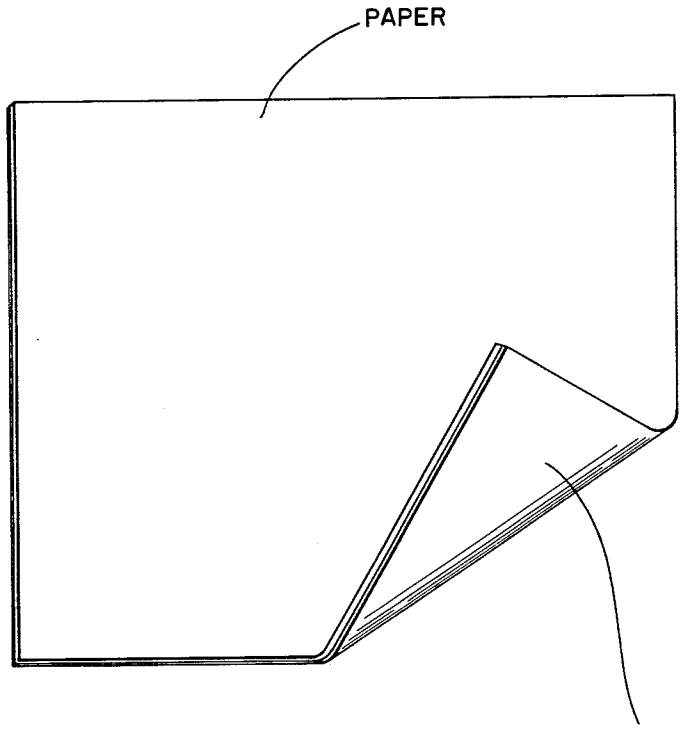
July 5, 1955 B. K. GREEN 2,712,507

PRESSURE SENSITIVE RECORD MATERIAL

Filed June 30, 1953



COATING OF MICROSCOPIC HYDROPHILIC COLLOID RUPTURABLE CAPSULES CONTAINING PRINTING FLUID

INVENTOR
BARRETT K. GREEN

BY Earl Berest
Justin S. Lawton

HIS ATTORNEYS

United States Patent Office 2,712,507 Patented July 5, 1955

2,712,507

PRESSURE SENSITIVE RECORD MATERIAL

Barrett K. Green, Dayton, Ohio, assignor to The National Cash Register Company, Dayton, Ohio, a corporation of Maryland

Application June 30, 1953, Serial No. 365,184

4 Claims. (Cl. 117—36)

This invention relates to manifold record material, and more particularly pertains to such record material which has a transfer coating thereon of microscopic gelled hydrophilic colloid capsules, each of said capsules consisting of a dense oil-impervious shell-like wall of film-forming colloid material deposited around a nucleus of an oily water-immiscible printing fluid by coacervate forces, said capsules being rupturable by printing or writing pressure applied to the record material so as to release said printing fluid for transfer to an underlying sheet.

The encapsulating material which encloses the oil droplets is a single gelled hydrophilic colloid material as contrasted with capsules made of a complex gelled gellable hydrophilic colloid material, which characterizes the encapsulating material of the microscopic oil-containing capsules with which the record material is coated, as disclosed in application for United States Letters Patent, Serial No. 365,198, which was filed on the same day as this application, by this applicant and Lowell Schleicher.

The record material of this invention also is distinguished from that disclosed in applicant Green's United States Patent No. 2,374,862, and applicant Green's and Robert W. Sandberg's United States Patents 2,548,366; 2,550,466; 2,550,467; 2,550,468; and 2,550,469, in that in the patents, instead of using microscopic oil-containing capsules in the transfer coating, the oily printing fluid was contained in droplet form in a continuous gelled hydrophilic colloid film.

In forming a continuous hydrophilic colloid film, there is a permeable condition set up whereby, even though the surface of the film is hardened by treatment that closes the surface pores, cracks may form through handling, or due to environmental conditions, which rupture the film. In such cracks the voids holding the oil are opened up because the cracks run straight through the voids. As the walls separating the voids in the film are somewhat permeable to the oil, oil may leak out, not only from the region of the cracks, but from uncracked portions of the film, leaving the film inadequate to perform its function.

In the present invention the microscopic capsules, although adherent to one another and to the paper, maintain their individuality so that if cracks are made by folding of the paper or otherwise, the cracks in the coating will run between the capsules and not through them. Also, in the present invention the microscopic capsules are made impermeable to the oil by a method disclosed and claimed in applicant's co-pending application for United States Letters Patent, Serial No. 365,106, filed the same day as this application. That method will be described in this application, insofar as applicable, but will not be claimed herein.

The manifold sheet of this invention, therefore, is superior to those shown in the patents to which reference has been made, insofar as shelf-life and durability are concerned.

Therefore, it is an object of this invention to provide

a manifold sheet having a transfer film coating, on a surface thereof, which is composed of microscopic capsules of gelled hydrophilic colloid material, each of said capsules consisting of a dense oil-impervious shell-like wall of the colloid material deposited around a nucleus of an oily printing fluid by coacervate forces, and the capsules being present in such number as to be in substantial contiguity.

Inasmuch as the invention contemplates the use of color-reactant materials, which constitute the oil, or which form a part of the oil, it is another object of the invention to make such a manifold sheet in which the transfer coating is substantially colorless, but which will render colored marks upon sensitized receiving sheets.

With these and incidental objects in view, the invention includes certain novel features of structure and combinations of elements, a preferred form or embodiment of which is hereinafter described with reference to the drawing which accompanies and forms a part of this specification.

The drawing shows the manifold sheet of this invention in an enlarged and exaggerated form, so that the features may be discernible.

In the preferred embodiment of the invention there will be described a manifold sheet containing as the printing mark substance the compound 3,3 bis(p-dimethylaminophenyl) 6-dimethylamino phthalide, which is colorless and forms blue marks when coming into adsorption contact with a record material sensitized with acid claylike material such as attapulgite, or zeolite material, such as sodium aluminum silicate material, or such in which the sodium has been exchanged for hydrogen or some other metal ion, as disclosed in applicant's United States Letters Patents No. 2,581,186 and No. 2,641,557. As a secondary color-reactant in the oily printing fluid of the preferred embodiment there is provided a type of color reactant which oxidizes from a normally colorless form to a colored form when in contact with the clay materials just described, after the passage of some hours or days. This preferred compound is benzoyl leuco methylene blue. The phthalide compound, like all triphenyl methane dyes, tends to fade in time, but the secondary color reactant of the oxidizing type forms a color which is lasting. The phthalide compound reacts instantly to form a colored mark, to be supported later by the color of the oxidized secondary color reactant.

As the oily vehicle in which the color-reactants named above are carried, applicant has chosen for the preferred embodiment trichlorodiphenyl, the color reactants being used therein in amounts equal to several percent, by weight, of the total amount of the printing fluid.

As the encapsulating colloid material for the preferred embodiment, applicant has selected a gelatin, although other gellable film-forming hydrophilic colloids, such as agar-agar, will do.

The preferred method of forming the capsules includes the step of treating an aqueous sol of the colloid material having the oil emulsified therein, with a salt solution to cause the colloid material to deposit around the oil droplets, and then causing the colloid to gel. In making up the capsular material, one gallon of an oil-in-water emulsion of 20 parts, by weight, of trichlorodiphenyl containing the color reactants, and 100 parts, by weight, of a sol of 10%, by weight, of pigskin gelatin in water, is prepared, the emulsifying continuing until the drop size of the oil is from 2 to 5 microns. This material is kept at 50° centigrade to prevent the gelatin from gelling. With the temperature of the ingredients still kept at 50° C., coacervation then is induced by adding, slowly and uniformly, four-tenths of a gallon of 20%, by weight, of sodium sulphate in water. The uniform addition of this material is accomplished by continuous agitation.

To gel the coacervate, the heated coacervate mixture is poured into 10 gallons of 7%, by weight, of sodium sulphate in water at 19° centigrade, with agitation. At this point the encapsulation of the oil with the gelled hydrophilic colloid material has taken place and the further steps are to put it in condition for use as intended. The material is filtered and washed with water, the temperature being kept below the melting point of the gelatin, to remove the salt. If desired, the filtered material is hardened by combining it with 2 gallons of a 37% solution of formaldehyde in water. This hardened mass is then filtered and washed to remove the residual formaldehyde. The resulting filter cake is adjusted to the proper water content by the addition of water or the removal thereof, by ordinary means such as centrifuging or spray drying, and the material is ready for use. As this material is intended for a paper coating composition, it is kept in aqueous suspension and applied directly to the paper, which is then dried, leaving the capsules adherent to the paper and to each other in a film.

If a portion of this fluid is sparsely dispersed in water and placed under a microscope, it will be seen to consist of microscopic capsules of the hydrophilic colloid material, the individual capsules being several microns in diameter and each containing a nucleus of oil. As the water content is decreased, the capsules tend to form aggregations, like bunches of grapes. When the material is of the right consistency, it is coated on paper by rollers, spray, brushes, or any other of the commonly used methods of coating paper, and allowed to dry. The material is of such a nature that the capsules are adherent to each other in the coating, and will adhere to the paper, without the addition of any other binder material.

For more details concerning the process of making the microscopic capsular material, reference is made to my co-pending application, Serial No. 365,106, regarding the process, to which attention has been drawn.

Other colorless adsorption color reactants which form color immediately on contact with acid clay-like material, such as the mentioned attapulgite, are malachite green lactone, which is 3,3 bis(p-dimethylaminophenyl) phthalide, and the ethyl and propyl homologues thereof, which form bluish green marks on the acid-like clay sensitized receiving sheet. Other comparable and equivalent materials are found in United States Patent No. 2,548,366, to which attention has been directed.

The material in the oil which produces the mark on the receiving sheet need not be a reactive material but may have an intrinsic color of itself, such as dissolved dyes, like Sudan III.

The oils which may be substituted for trichloro-diphenyl are any of the water immiscible oils, which are inert as to the other materials used in forming the capsules, such as petroleum fractions like paraffin oil, vegetable oil such as castor oil, and cottonseed oil, animal oils, such as sperm oil and lard oil, and any other various synthetic oils, such as methyl salicylate.

The coating material should be used in such quantity on the paper that when dried the coated area will be profusely supplied with the microscopic capsules, but such thickness need be no more than a fraction of a thousandth of an inch, because the size of the capsules is in terms of several microns. A four pound coating on a ream of paper 25 inches by 38 inches is satisfactory.

A sheet of ordinary writing paper, coated on one surface with the described coating composition laid with that coated surface on the attapulgite-sensitized surface of a receiving sheet, forms a manifold system which is responsive to very light printing or writing pressures, such as are ordinarily used in every-day printing and writing, so as to make clear and distinct marks on the receiving sheet, yet the coating is so durable that it will undergo rough handling without premature rupture of the capsules and is proof against the deleterious influences of the environment, either atmospheric or artificial.

The capsules may be rendered porous if the gelled material is allowed to dry without washing out the salt.

While the form of the invention herein shown and described is admirably adapted to fulfill the objects primarily stated, it is to be understood that it is not intended to confine the invention to the one form or embodiment herein disclosed, for it is susceptible of embodiment in various other forms.

What is claimed is:

1. A record material base sheet having on a surface thereof a coating consisting of a profusion of microscopic pressure-rupturable capsules having walls of gelled film-forming hydrophilic colloid material in substantial contiguity, each of the capsules consisting of an oily water-immiscible printing fluid as a central nucleus around which has been evenly deposited by coacervation forces a dense oil-impermeable shell-like coating of the colloid material, said capsules being rupturable by printing or marking pressures applied to the coated sheet.

2. Paper having coated on a surface thereof microscopic capsules having walls of gelled film-forming hydrophilic colloid material, the capsules being present in such number that they are in substantial contiguity, and each of said capsules consisting of an oily water-immiscible printing fluid as a central nucleus around which has been evenly deposited by coacervation forces a dense oil-impermeable coating of the colloid material, said cupsules being rupturable by printing or marking pressures applied to the coated sheet of paper.

3. A sheet of paper having on a surface thereof a coating that is substantially colorless, said coating consisting of a profusion of pressure-rupturable microscopic capsules having walls of gelled film-forming hydrophilic colloid material in substantial contiguity, each of the capsules consisting of a dense shell-like oil-impermeable wall of the colloid material deposited about a central nucleus of a colorless oily water-immiscible printing fluid by coacervation forces.

4. The record material of claim 3 in which the oily printing fluid consists of a water-immiscible oil vehicle in which is carried a colorless color reactant which turns to a colored form on contact with paper sensitized by having thereon acid clay-like material.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,548,366	Green	Apr. 10, 1951
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