COATING OF MICROSCOPIC HYDROPHILIC COMPLEX COLLOID
RUPTURABLE CAPSULES CONTAINING PRINTING FLUID
This invention relates to manifold record material, and more particularly pertains to such record material which has a transfer coating thereof of microscopic sized hydrophobic colloidal capsules, each of said capsules consisting of a dense oil-impermeable shell-like wall of film-forming complex colloidal material deposited around a nucleus of an oily water-immiscible printing fluid by coacervate forces, said capsules being rupturable by printing or writing pressures 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 complex of gelled film-forming hydrophobic colloidal materials, as contrasted with capsules made of a single gelled hydrophobic colloidal material, which characterizes the encapsulating material of the microscopic oil-containing capsules with which the record material is coated, as disclosed in applicant Green's co-pending application for United States Letters Patent, Serial No. 365,184, which was filed on the same day as this application.

By a “complex” of gelled film-forming hydrophobic colloidal materials is meant the gelled state of a product formed by the union, in an aqueous medium, of two kinds of hydrophobic colloidal materials having opposite ionic charges in said medium, the union being brought about by the presence in charge, the “complex” having characteristics differing from the colloidal components.

The record material of this invention also is distinguished from that disclosed in applicant Green's United States Letters Patents No. 2,374,862, and applicant Green's and Robert W. Sandberg's United States Letters Patents 2,584,366; 2,550,468; 2,550,468; and 2,550,469, in that in the patent disclosures, instead of using microscopic oil-containing capsules in the transfer coating, the oily printing fluid was contained in droplet form in a continuous gelled hydrophobic colloidal film.

In forming a continuous hydrophobic colloidal 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, the 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 bending of the paper, 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 base disclosed and claimed in applicants' co-pending application for United States Letters Patent, Serial No. 365,105, 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 complex film-forming hydrophilic colloidal material, each of said capsules consisting of a dense oil-impermeable shell-like wall of the complex colloidal 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 colorless color-reactant materials, which constitute the oil, or which form a part of or is carried by 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 a properly sensitized receiving sheet.

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 having a coating containing as a primary printing substance the compound 3,3-bis(β-dimethylaminophenyl) 6-dimethylamino phthalide dissolved in oil, which produces dark blue marks immediately when coming into adsorption contact with a record material sensitized with acid clay-like material such as talc, orzite, or acid clay material such as sodium aluminum silicate material, or such in which the sodium has been exchanged for hydrogen or some other metal ion such as disclosed in applicant Green's United States Letters Patents Nos. 2,581,186 and 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. The phthalide compound, like all dyes, tends to fade in time, but the secondary color reactant of the oxidizing type forms a color which is lasting. The preferred secondary color reactant is benzoyl leuco methylene blue.

As the oily vehicle in which the color-reactants named above are carried, applicants have chosen for the preferred embodiment trichloro phenyl, 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 colloidal material for the preferred embodiment, applicants have selected a gelatin-gum arabic complex, which is formed during a process of coacervation in which the capsules are formed, although other pairs of film-forming colloidal materials will do.

In forming the oil-containing capsules of the preferred embodiment of the invention, 20 grams of gum arabic are dissolved in 160 grams of water and into that is emulsified 80 grams of trichloro phenyl containing 3 to 6 percent, by weight, of the two color reactant materials 3,3-bis(β-dimethylaminophenyl) 6-dimethylamino phthalide and the benzoyl leuco methylene blue, preferably in equal amounts. The emulsion is carried on until the drop size of the oil is from 2 to 5 microns. Next, 20
3 grams of gelatin is dissolved in 160 grams of water and mixed with the emulsion. This mixture of colloid sols is then diluted by adding water uniformly and slowly, with agitation, until coagulation occurs, the complex gum arabic-gelatin colloid material forming around the oil droplets. These colloid surrounded droplets make aggregates of from several microns in diameter up to 70 microns in diameter depending on the rate and extent of dilution. The added water should amount to about 500–550 grams. Up to this time all the ingredients are kept at approximately 50° C., which is about the gel point of the gelatin. After the gelatin material has deposited around the oil droplets forming particles, the colloid material is caused to gel by pouring it into a quantity of cold water; for instance, water at zero degrees centigrade. The mass is agitated and then let stand for one hour at not over 25° centigrade. At this point the total weight of all ingredients should be about 3960 grams. At this point the pH is adjusted to between 9 and 7, such adjustment being made with sodium hydroxide, and the material is left for 30 minutes or more in this state. The capsules are then hardened by pouring in about 20 grams of a solution of formaldehyde in water, of about 37%, formaldehyde content, and allowed to harden for ten minutes or more at 3° centigrade or lower. This material is adjusted to the right water content to form a coating composition that is to say, water may be added or taken away by filtering or centrifuging until the right coating viscosity is obtained. At this stage the coating composition is a creamy white fluid. 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 complex colloid material, the individual capsules being several microns in diameter and containing one or more droplets of oil. As the water content decreases, 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 our co-pending application Serial No. 365,105 regarding the procedure, with which attention has been directed, methods are disclosed for determining the ratio of one colloid to the other that can be used to make a complex colloid. The colloids do not necessarily have to be used in a one-to-one ratio, but such ratio is preferred.

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 or 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 or nigrosine.

The other substituents for the gum arabic or the gelatin, or both, hydrophilic colloid materials selected so that they have different ionic charges when dispersed in water, or can be made to have such different ionic charges by adjustment of the pH of the water, so that coagulation may be brought about by dilution with water as disclosed in more detail in said co-pending process application. It is necessary that one or both of the colloid materials be gellable in order that the encapsulation may be completed. The encapsulating film material contains por-
5. The record material of claim 4 in which the base sheet is paper.

6. The record material of claim 4 in which the oily printing fluid consists of an 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

2,183,053  Taylor ---------------- Dec. 12, 1939
2,410,110  Taylor ---------------- Oct. 29, 1946
2,505,487  Green ----------------- Apr. 25, 1950
2,548,366  Green ----------------- Apr. 10, 1951