Feb. 14, 1961 L. SCHLEICHER ET AL 2,971,916

MICROSCOPIC CAPSULES CONTAINING MAGNETIZABLE MATERIAL

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FIG. 1

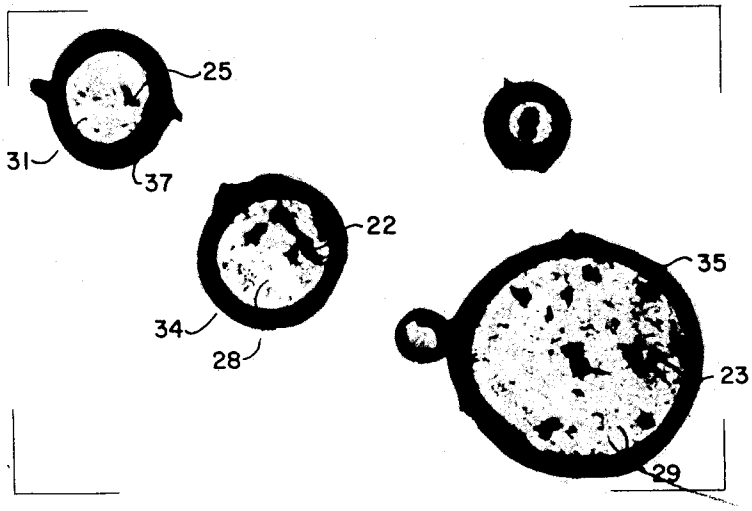

FIG. 2

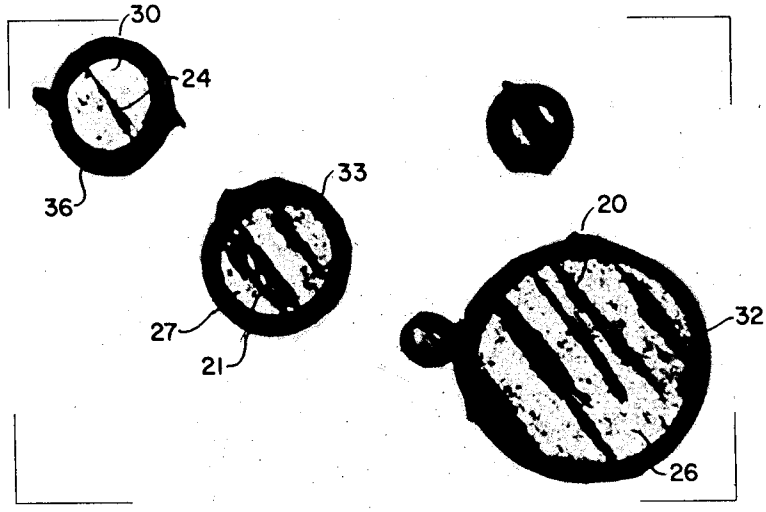

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FIG. 3

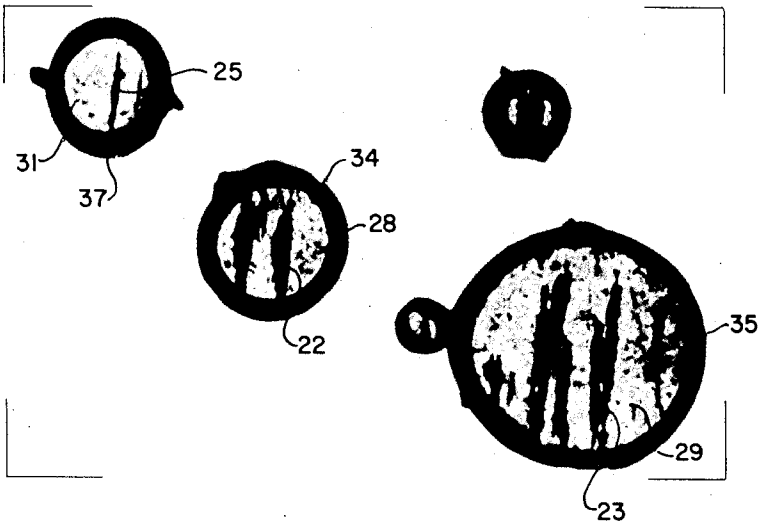
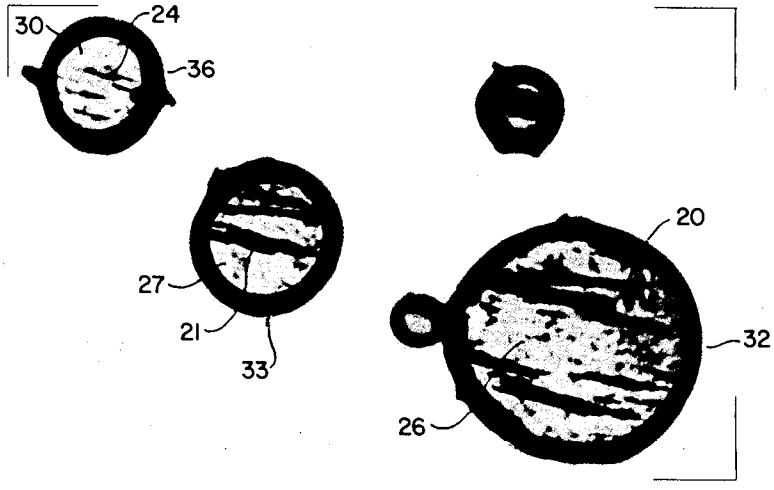


FIG. 4



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MICROSCOPIC CAPSULES CONTAINING MAGNETIZABLE MATERIAL

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1 Claim. (Cl. 252—62.5)

This invention relates to pressure-rupturable microscopic capsules having contained therein, suspended in a liquid vehicle, micro-fine particles of magnetic material.

The magnetic material may be of any desired kind. Some examples of magnetic material are black or red-magnetic iron oxide, carbonyl iron, ferro magnetic alloys, nickel and its magnetic alloys, cobalt and its magnetic alloys, or any mixture of the aforementioned. The naming of these materials is not to be deemed to limit the invention, as other solid magnetic powders will do. These magnetic powders may be permanently magnetized in the capsules, or they may be magnetized by magnetic fields applied to the capsules.

In the preferred form of the invention hydrophyllic colloid capsule walls enclose an oily vehicle, in which vehicle the magnetic particles are suspended. Among the preferred oils, because of their inertness, are chlorinated diphenyl, light petroleum fractions, or any equivalent non-polar oily solvent, which will not attack the particles of magnetic material.

As much as 50% by volume of the magnetic powder, as compared to the oil, may be included within the capsule walls. The oily vehicle may also have included therein dyes and pigments for purposes to be stated later on.

The microscopic capsules have been made from individual diameters of 3 microns to 150 microns, although this is not to be deemed to limit the diametrical size of these magnetic-material-containing capsules.

These capsules may be used in connection with printing by magnetic means. If a sheet of record material having a magnetizable coating is magnetized in spots to represent data, the capsules provided by this invention, if applied to the coating, will cling to the magnetized spots. The sheet may then be placed on a receiving sheet of paper and pressure applied. The capsules will rupture leaving an imprint of the data on the receiving sheet by virtue of the intrinsic color of the magnetic powder or by virtue of any dye or pigment carried by the oily vehicle.

With these and incidental objects in view, the invention includes certain novel features, a preferred form or embodiment of which is hereinafter described with reference to the drawings which accompany and form a part of this specification.

Of the drawings:

Figs. 1 to 4 inclusive each show the same array of capsules, as viewed under a microscope wherein the magnification was of the order of 1000 diameters, the larger capsules being of the order of 150 microns and the smaller capsules of the order of 50 to 75 microns in diameter. In Figs. 1 to 4 the orientation of the magnetic material within has been changed by use of a magnetic field to four different directions, showing the mobility of the magnetic material within the capsules.

First, the method of making the capsules shown in the drawings will be described, and it may be considered the preferred method. The magnetic material 20 to 25,

inclusive, shown in the figures of the drawings, are chains of magnetic iron oxide particles, the individual magnetic material particles being of the order of one micron in diameter. The fluid vehicle is trichloro-diphenyl, which bears the reference numerals 26 to 31 inclusive in the various figures of the drawings. The capsule walls which have been given the reference numbers 32 to 37, inclusive, are of a complex of gelatin and gum arabic, which being treated by the process to be described, is oil-impermeable. The liquid vehicle has dissolved in it certain wetting and dispersing agents. The particular wetting and dispersing agents used in making the capsules shown in the drawings are oleic acid, zinc stearate, and dioctylphthalate.

In making these capsules shown in the drawings, the liquid with the magnetic iron oxide suspension is prepared first in the following manner:

Mill thoroughly together
160 grams of trichloro-diphenyl
30 grams of black magnetic iron oxide of an average particle size of one micron
1 gram of oleic acid
1/10 gram of zinc stearate
1 gram of dioctylphthalate

until the agglomerate size of the magnetic iron oxide particles averages about three microns. Next, a first solution of pigskin gelatin in water is made, the gelatin having its isoelectric point at pH 8. The solution is made and kept at a temperature of approximately 135 degrees Fahrenheit. The first solution contains 20 grams of the pigskin gelatin and 160 grams of water. Next, a second solution is made, consisting of gum arabic in water at 135 degrees Fahrenheit, there being used 20 grams of gum arabic and 160 grams of water. Both of the colloid solutions are adjusted to pH 6.5.

The previously prepared magnetic oxide-containing mixture is emulsified into the gelatin solution until the drop size is of the order of 10 microns; that is to say, the drop size of the oil phase. Next, the solution of gum arabic is added to the emulsion, still keeping the temperature at approximately 135 degrees Fahrenheit. About 400 grams of the resulting mixture is placed in a container, in a water bath at 135 degrees Fahrenheit, and water at 135 degrees Fahrenheit is added to bring the total volume to one liter. The water-diluted mixture then has its pH adjusted downwardly to approximately 4.7, to bring about coacervation, so that the colloid material will deposit in oriented fashion around each of the oil droplets containing the magnetic particle suspension. This phenomenon of coacervation is clearly explained in application for United States Patent Serial No. 365,105, filed June 20, 1953, by Barrett K. Green and applicant Lowell Schleicher of this application. This application was allowed as of November 26, 1956, and issued July 23, 1957, as United States Patent No. 2,800,457. Into the resulting coacervate mixture is added 2.7 cubic centimeters, of a 37% solution of formaldehyde in water. The foregoing additions of materials to each other is done with constant stirring, to keep the mixtures uniform. While still being stirred, the coacervate mixture is lowered in temperature to near 32 degrees Fahrenheit, approximately, so the deposited colloid material will gel to form capsule walls around each of the included oil droplets. Next, ten grams of a 5% aqueous solution of the polyvinyl-methyl ether of maleic anhydride is added, with continued stirring for a period of several hours, maintaining the temperature below 50 degrees Fahrenheit, to prevent the capsules from agglomerating in the hardening step described next. The capsules are complete at this time, but are dispersed in a substantially colloid-free excess of water. So the capsules will withstand temperatures higher than the ordinary melting point of

the colloid, the pH is then adjusted to 9 or 10 with sodium hydroxide to cause the formaldehyde to react with the colloid to harden it. This dispersion of capsules and the aqueous medium can be coated directly on paper and dried, the individual capsules maintaining their integrity and each having within it the magnetic powder, as described. If desired, the water in which the capsules are dispersed may be eliminated by spray-drying in a hot atmosphere, the resulting product being a very fine powder containing the discrete capsules with the magnetic oxide floating in the included vehicle.

The capsules shown in the drawings and the described method of making them have not included the addition of coloring matter to increase the marking color of the capsule because to do so would have rendered it impossible to show the magnetic material in the drawings. Any

oil soluble dye or oil dispersible pigment can be used as an addition agent to the vehicle in which the magnetic iron oxide is suspended.

What is claimed is:

A microscopic capsule having a wall of hardened organic colloid material enclosing an oily liquid containing a dispersion of magnetic powder.

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