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METHOD OF POLYVINYL ALCOHOL SUBSTITUTION IN AQUEOUS MAGNETIC COLLOIDS

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Résumé. — On décrit une méthode pour figer la distribution spatiale des grains magnétiques dans un *ferrofluide* à base d'eau. La méthode est basée sur un remplacement progressif de l'eau par un alcool polyvinylique. Les échantillons obtenus sont solides et peuvent être étudiés par microscopie électronique. Pour un système de grains de Fe_3O_4 (diamètre 100 Å) et une fraction de volume de magnétite de 3 %, on observe des agrégats sphéroïdaux d'une taille moyenne de 0,5 μ en l'absence de champ magnétique. Pour un champ appliqué de ~ 100 G, les agrégats prennent la forme de longues chaînes.

Abstract. — A method of freezing the spatial distribution of magnetic grains in a water-base *ferrofluid* is described. The procedure is based on the progressive substitution of the water by a polyvinyl alcohol. The resulting samples are solid and can be studied by electron micrography. With a system of Fe_3O_4 grains with a diameter of 100 Å and a 3 % volume fraction of magnetite, we find spheroidal aggregates of average size 0.5 μ at zero magnetic field. At a field of ~ 100 G, the aggregates appear as long chains.

Conventional ferrofluids are made of magnetic grains (e. g. cobalt) coated by a suitable agent and suspended in a hydrocarbon. The possibility of using a water matrix instead of a hydrocarbon matrix is of some interest : water has lower evaporation rates, higher surface tension and is chemically passive.

Water base systems have been prepared and are stable [1], however, there are indications that the grains are not independent but aggregate strongly to form larger units. By placing a thin layer (100 μ) of water base ferrofluid between two glass slides in a weak magnetic field (a few gauss), it is easy to observe the formation of long chains under an optical microscope. The chains extend over a few tens of microns. This has also been observed recently by Hayes [2].

The *Bitter technique* [3] may be a simple test of the quality of a ferrofluid : a drop of a magnetic suspension is spread on a flat magnetic crystal. The magnetic domains are visualized through the agglomeration of the grains along the magnetic walls which separate two adjacent domains where the local field is higher. A ferrofluid may be used as a Bitter solution [4, 5]. If one uses the standard procedure as described above, it is observed that the ferrofluid accumulates near the domain boundaries. If, on the other hand, we confine

the ferrofluid between the crystal and a glass slide, the results are very different : a *good* ferrofluid, i. e. one which strongly counteracts the separation of the grains from the liquid, remains uniform and nothing is revealed. A *bad* ferrofluid reveals the domains with good contrast because the grains can agglomerate. Aqueous ferrofluids always delineate the crystal sharply.

These association effects are responsible for the birefringence [4, 6] and diffraction figures [7] reported for water-base ferrofluids. On the other hand, with hydrocarbon-base ferrofluids, the grains remain individually dispersed even in high magnetic fields (100 G). Some weak correlation does exist between two neighbouring grains in hydrocarbon-ferrofluids, and the resulting magnetic birefringence has been observed [4] ; chains however have never been observed.

Our aim here is to obtain information on the agglomeration in water-base colloids at a scale smaller than is seen under the optical microscope. The method amounts to gentle freezing of the solution. In a preceding note [8], we proposed a method of matrix polymerization which is convenient for fluids having an organic solvent as parent liquid. For water-base fluids, however no method was available to study directly the grain distribution at room temperature on microscopic scale. For instance, in ref. [2], only

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conjectures were proposed for the structures taking place at the grain scale.

Satisfactory results have been obtained by progressive substitution of the water by polyvinyl alcohols— $(\text{CH}-\text{CH}_2)_n$ —.

Typically a polyvinyl alcohol with an ester index of 5 [9] is added to the ferrofluid. After solution (30 mn at 80 °C under stirring) the water is slowly evaporated and a solid-like material results. The amount of added alcohol is chosen so that the final saturation magnetization (concentration of the grains) is equal to that in the original material. (If thick samples are wanted, it seems more convenient to let the liquid dry drop by drop. The sample grows slowly and one avoids the formation of inner bubbles).

The resulting material can be studied either by electron microscopy or by measurements of macroscopic magnetic properties. The magnetic anisotropy has been studied as a function of the magnetic field applied during the solidification ; the results will be published elsewhere [10].

In order to obtain electron micrographs, it is necessary to have the samples in the form of thin layers. Two methods have been used :

i) the water-base-fluid-polyvinyl-alcohol mixture obtained in the first stage is diluted in water (1 part in 10^4). A drop of this solution is spread on a copper grid. After evaporation, the sample can be directly observed. Notice that this procedure is drastically different from the simple method which consists of letting a drop of the original fluid dry. In this later case, the final concentration would be very high and the grain agglomeration not representative of the actual distribution in the fluid, while with the polyvinyl alcohol solution, the grain concentration in the final film and in the original fluid are the same.

ii) microtomy can be performed. However, there is a difficulty as the sections cannot be collected on water due to the solubility of the solid material at hand. The methods of anhydrous sectioning of ref. [11] can be used with glycerol in particular as flotation liquid. More simply, it is possible to slice the samples without any flotation liquid. Polyvinyl alcohol is a material which can be sectioned very easily. One obtains continuous sections which stick to the edge of the knife. When a section of the correct colour is obtained, the arm of the ultramicrotome is stopped and the section is collected by approaching a copper grid wet with a drop of xylene. By capillarity, the section adheres to the grid and after evaporation of xylene, the specimen is ready for observation.

Typical results are shown on plate 1 for an original aqueous base fluid [1] with $4\pi M_s = 200 \text{ G/cm}^3$. At zero magnetic field (A and B) one can see that there

Plate 1. — Micrography of the grain distribution in a water-base solidified magnetic colloid after substitution of the matrix by polyvinyl alcohol : A) in absence of magnetic field ; B) idem (enlarged scale) ; C) with 100 G applied magnetic field.

is a marked trend towards agglomeration. A certain fraction of the grains is well dispersed, but many clusters (of about a thousand grains each) are present. In (C), for a field of about 100 G, a strong chaining is revealed.

This confirms the optical observations. Plate 1 has been obtained by the drying method. Similar results have been found with the section method. It has to be noticed, however, that with the drying method, the sample shows some extra round-shaped spots. These spots (typically $\sim 10^3 \text{ Å}$ in diameter) have not been encountered with the section method. We believe that they are due to surface effects during the drying process.

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