SYNTHESIS OF TBP-BASED FERROFLUIDS

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Name of reactants were changed but no quantities are given, unlike the authors of Source #1

Also, [4] is by the same authors and contains the same picture shown here in Fig 2, taken from 1993

See below

Authors reference themselves [4], but Source #1 references *Bee et. al* from 1990.

Preparation of magnetite

Magnetite was precipitated by dissolving $FeSO_4$ and $FeNH_4(SO_4)_2$ in demineralized water and adding sodium hydroxide to this solution while stirring vigorously [4]. After sedimenting the precipitate with permanent magnet, the supernatant was removed by decantation. 2 M $HClO_4$ was then added to the black sediment and the mixture was stirred for 10 minutes. The oxidation was completed by adding $Fe(ClO_4)_3$ to the mixture and stirring it at its boiling temperature for 2 h. After sedimentation and washing with 2 M $HClO_4$, the reddish yellow sediment, S_1, contained ca. 10% solid material. S_1 dispersed by adding demineralized water and resulting black dispersion, D_1 was characterized by electron microscopy (TEM).

Reference missing. Source #1 references *Bee et al from 1990.*

Grafting magnetite with unsaturated acids

D_1 was diluted by adding demineralized water and the sol was flocculated by adding few drops of 25% NH_3, and sedimented using a permanent magnet. After washing, four times, with demineralized water new ferrophase was diluted and under mechanical stirring some unsaturated acids or their salts was added. Within a few minutes, all magnetic materials was transferred in chloroform phase. The black chloroform droplets were separated from the color less water phase and washed few times with aqueous ethanol solutions to remove excess surfactant. After room drying the particles redispersed easily in tributhylphosphate for obtaining a new ferrofluid, TBP - FF.

The FTIR spectrum of some dried products give interesting information about bonds between unsaturated acids and magnetic particles.

Thermogravimetry was performed by heating some powders from room temperature to 900 °C at a rate of 10 °C/min.

Authors reference themselves [4], but Source #2 is actually *T. Osman et al. from 2001.*

Results and Discussion

Ferrofluids are an interesting group of liquids, because they have liquid properties and act like ferromagnetic materials [4]. Many properties of the ferrofluid are similar to those of the base fluid. Since the concentration of magnetic particles is low, 3-10%, they do not affect the density, vapor pressure, pour point, or chemical properties of the liquid, but there is an increase of the ferrofluid viscosity compared with the viscosity of its base fluid [5].

Applications of ferrofluids are usually based on their controllability by external magnetic force [6].

Same reference as Source #2 this time.

http://www.library.uu.nl/digiarchief/dip/diss/1942669/full.pdf

Source #1 (pp. 18-19)

Phase behavior of mixtures of magnetic colloids and non-adsorbing polymer

Gerard Antonie van Ewijk

PhD Thesis, Uthrecht University, 2001

2.2.a *Preparation of maghemite*

Magnetite was precipitated by dissolving 2.08 g $FeCl_2$ anh. and 5.22 g $FeCl_3$ anh. in 380 ml demineralized water and adding 20 ml 25% NH_3 to this solution while stirring vigorously [10]. After sedimenting the precipitate with a permanent magnet the supernatant was removed by decantation. 40 ml 2 M HNO_3 was then added to the black sediment and the mixture was stirred for 5 minutes. The oxidation to maghemite was completed by adding 60 ml 0.35 M $Fe(NO_3)_3$ to the mixture and stirring it at its boiling temperature for one hour [10]. After sedimentation and washing with 2 M HNO_3, the reddish yellow sediment was dispersed by adding demineralized water. The resulting black dispersion, coded FF, contained 5.6 g of solid material per liter.

2.2.b *Grafting maghemite with oleic acid*

A typical experiment went as follows. 2 ml FF was diluted by adding 50 ml demineralized water. The sol was flocculated by adding a few drops of 25% NH_3, and sedimented using a permanent magnet. After washing with 50 ml water, 100 ml water was added to the precipitate. Under *mild* mechanical stirring, 2 ml oleic acid was added. Within a few minutes, all magnetic material was transferred to the oil phase. The black oil droplets were separated from the colorless water phase and washed three times with 10 ml ethanol to remove water and excess surfactant. After drying under a gentle nitrogen stream, the particles redispersed easily in cyclohexane. A representative TEM picture of the grafted particles is shown in figure 2.2.

oleic acid. Thermogravimetry was performed by heating some powder in a nitrogen stream from room temperature to 1200°C at a rate of 10°C min^{-1}. The surface area per oleic acid

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http://www.sciencedirect.com/science/article/pii/S0301679X01000172

Source #2 (p. 369)

Static and dynamic characteristics of magnetized journal bearings lubricated with ferrofluid

T.A. Osman [a,*], G.S. Nada [b], Z.S. Safar [b]

a coating on each particle [1]. Ferrofluids are an interesting group of liquids, because they have liquid properties and act like a ferromagnetic material. Many properties of the ferrofluid are similar to those of the base fluid. Since the concentration of the magnetic particles is low, 3–10%, they do not affect the density, vapor pressure, pour point, or chemical properties of the liquid, but there is an increase of the ferrofluid viscosity compared with the viscosity of its base fluid [2]. Ferrofluid properties

Applications of ferrofluids are usually based on their controllability by an external magnetic force [6]. Ferro-

The picture in Figure 2 (left) and picture M26t (right), published 10 years before (1993) by different authors, are suspected to be the same -- note the unique microscope counter number. The left picture appears stretched horizontally. Note that Aurelia Cristina Nechifor is **not** the same person as Ana-Mariana Nechifor (author from1993, left). The 1993 paper or picture are not referenced.

The brightness, gamma and white and black levels of picture M26t (right) were affected by the poor scan quality.

See next page.

Source #3 (page 3)

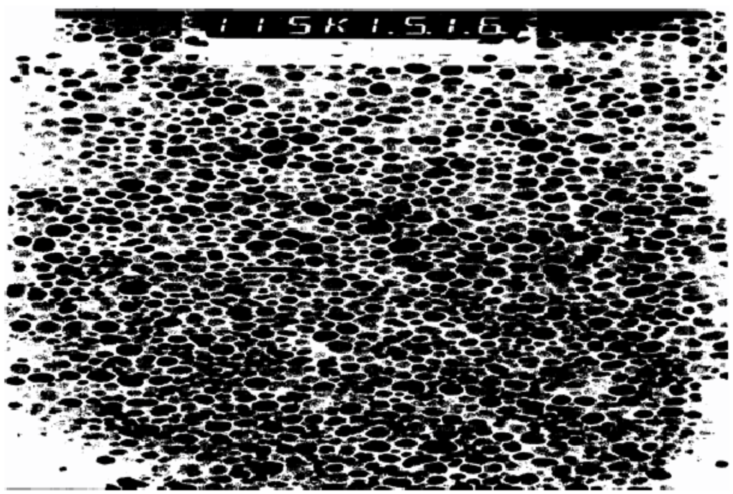


Figure 2. Magnetic nanoparticles 15-20 nm in TBP-ferrofluid

by Aurelia Cristina Nechifor and Ecaterina Andronescu (2003)

Conferinta Nationala de Chimie si Inginerie Chimica, Bucuresti 1993

TRANSPORTORI SUPRAMOLECULARI CU PROPRIETATI MAGNETICE

Ana-Mariana NECHIFOR, Eugenia TOTU, Gh. NECHIFOR si C. LUCA
CCMMM-Bucuresti; ICM-Bucuresti; U.P.B.-Facultatea de Chimie Industriala . Catedra de Chimie Analitica si Analiza Instrumentala

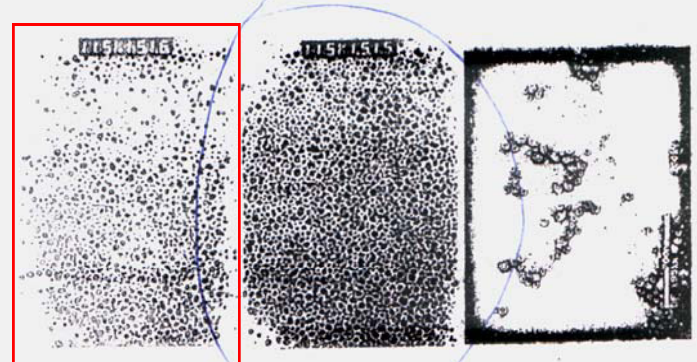


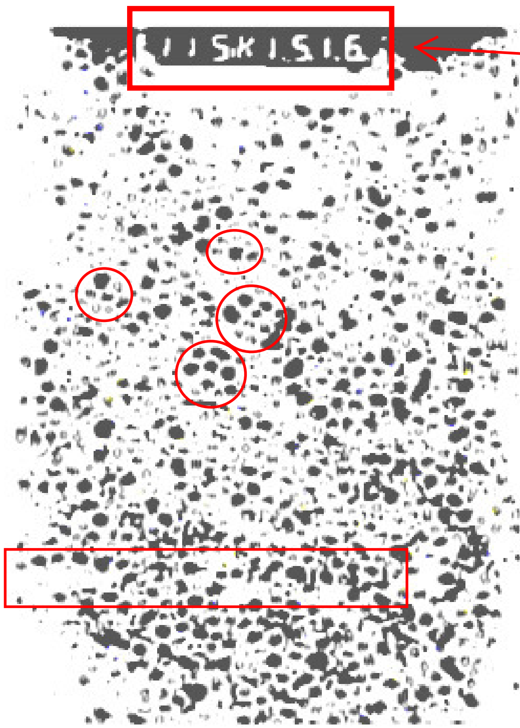
Fig.1 Microscopia electronica pentru trei probe reprezentative de particule feroferice.

1

Same two pictures again side by side. We took the left picture from the previous page (Figure 2) and shrunk it, adjusted its black and white levels, and the brightness and gamma values, to emulate the poor scan process that the M26t picture suffered. **The result suggests that the original contents of the two pictures is actually the same.**

The picture on the right was published 10 years before (1993), by different authors, and is not referenced.

Source #3 (page 3)



Note the same counter number *115K1.5.1.6* on both pictures. This is the unique microscope picture counter (increments every time a picture is taken).

The picture on the left is from 2003. The one on the right is from 1993, by different authors and is not referenced.

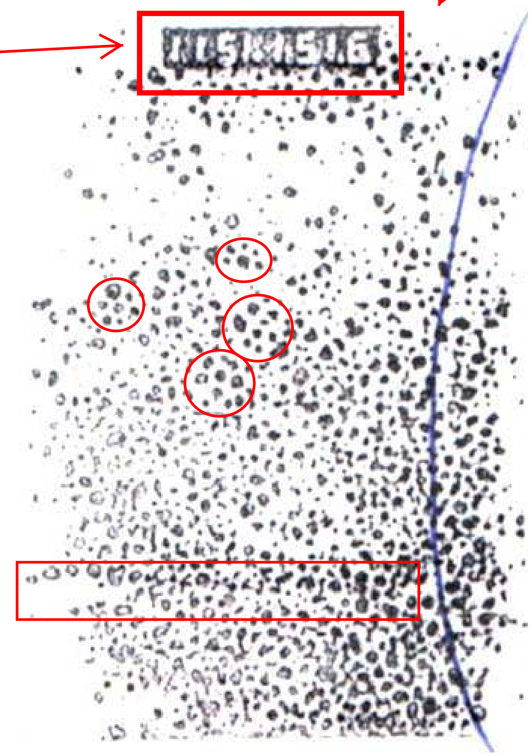


Figure 2. Magnetic nanoparticles 15-20 nm in TBP-ferrofluid

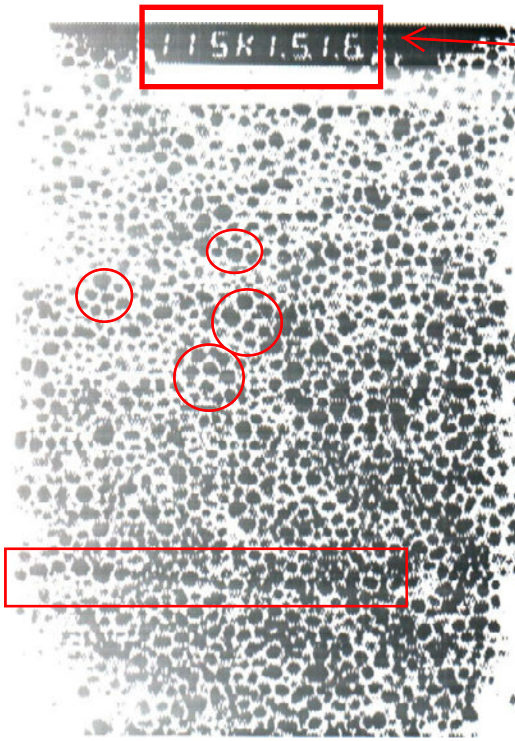
M26t

2

Same two pictures again, with different post-processing of the left picture. Again, **the result suggests that the original contents of the two pictures is actually the same.**

The picture on the right was published 10 years before (1993), by different authors, and is not referenced.

Source #3 (page 3)



Note the same counter number 115K1.5.1.6 on both pictures. This is the unique microscope picture counter (increments every time a picture is taken).

The picture on the left is from 2003. The one on the right is from 1993, by different authors and is not referenced.

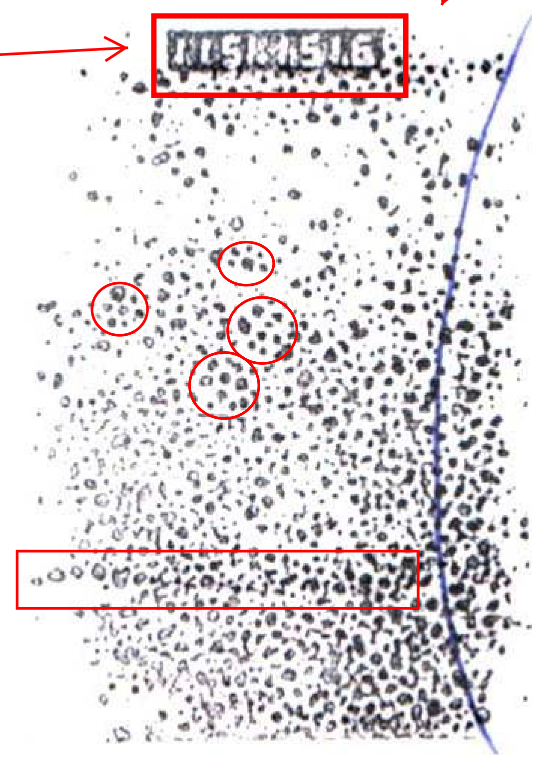


Figure 2. Magnetic nanoparticles 15-20 nm in TBP-ferrofluid

M26t