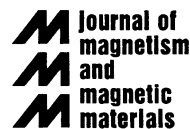




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Preparation of oxidation resistant cobalt oil colloids

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Abstract

In this work a successfully applied method is reported for the preparation of stable colloidal cobalt-based oils. The two-step process comprises thermolysis of a $\text{Co}_2(\text{CO})_8$ -toluene solution in the presence of Na-AOT or lauroylsarcosine oleic acid followed by an exchange step for the carrier liquid. In this step a second surfactant compatible with the oil carrier was used leading to a double-layer coating of the Co particles. Magnetic oil-based liquids with a saturation magnetization up to 120 mT could be prepared this way. The sedimentation stability in the presence of a strong magnetic field and the oxidation resistance are excellent. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt colloids; Synthesis; Magnetic oil; Thermolysis; Ferrofluids

1. Introduction

High saturation magnetization combined with a low viscosity is needed in many technical applications of ferrofluids. This makes Co-, Fe- or any of their respective alloys attractive candidates for the magnetic phase dispersant. However, metal-based magnetic fluids, in general, undergo a gradual decrease of susceptibility due to premature oxidation of the magnetic core material. Therefore, any preparation method has to ensure not only colloidal stability of the suspension but also a good oxidation resistance. In the past, several attempts have been made to prepare cobalt-based ferrofluids in different carrier liquids [1,2]. Toluene is the most

often used organic solvent suited for the thermolysis method. However, due to its high vapour pressure it cannot be used for long-lasting applications. Silicone oil ferrofluids employing Fe_3O_4 as the magnetic particle phase have already been prepared by aqueous phase precipitation – a method not applicable to Co or Fe [3]. No successful attempts are reported for colloidal oils on Fe/Co-basis. In this paper we report on the successful preparation of cobalt-based ferrofluids characterized by a high saturation magnetization and a low vapour pressure. The respective silicone and mineral oil carrier liquid is introduced in a two-step process.

2. Experimental details

Dicobaltoctacarbonyl $\text{Co}_2(\text{CO})_8$ stabilized with 1–5% hexane was obtained from Strem Chemicals,

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Inc. As surfactants we used dioctylsulphosuccinate sodium (Na-AOT) from Sigma Aldrich, Inc. and lauroyl sarcosin oleic acid (Korantin SH) from BASF AG. The surfactants were dried under roughing vacuum for 1 h before use. Ultrapure toluene with a nominal water content < 0.0075 mol% was obtained from Merck, Inc. In addition in the extraction step two oil-compatible surfactants have been used, Triton X-100 (Sigma Aldrich) and LP4 (ICI Inc.). In order to minimize premature oxidation effects of the metal particles during thermolysis high-purity argon gas (99.999%) was used. All chemical ingredients were handled in a glove box under argon atmosphere. As carrier liquids three different oils have been used. Silicone oil DC702 with a vapour pressure $< 1.3 \times 10^{-6}$ mbar (25°C) was obtained from Dow Corning, Inc. and graded as a mixed phenylmethyl dimethyl cyclosiloxane used in vacuum pumps. The mineral oil AP201 was obtained from Wacker Chemie, Inc. and is specified with a vapour pressure of 5×10^{-6} mbar (20°C). Finally an extremely low vapour pressure oil, Edwards L9, was obtained from Edwards, Inc. and graded as an alkylnaphthalene with a vapour pressure as low as 10^{-9} mbar (20°C). Thermolysis of the metal carbonyl was performed in a device similar to that used by Papirer et al [2]. Na-AOT and dicobaltoctacarbonyl were dissolved in toluene at room temperature. Then under continuous stirring under argon the solution was slowly heated to 110°C via an oil bath. After decomposition of the carbonyl, which usually took 3–4 h (indicated by the end of formation of carbon monoxide gas) the solution was cooled down to room temperature and mixed with silicone oil together with the second surfactant. Finally, the toluene was extracted from the solution in a rotating vacuum distillator. The resulting suspension of metal particles stabilized in silicone oil was kept under argon atmosphere in an air-tight glass container. Transmission electron microscopy (TEM) was used in order to determine the particle size of the as-prepared samples (Philips CM30). Particle size histograms were fitted (see Fig. 1) to a log-normal distribution function given by

$$f(d) = [(2\pi)^{1/2} \ln s]^{-1} \exp[-(\ln\langle d \rangle - \ln d)^2 / 2 \ln^2 s] \quad (1)$$

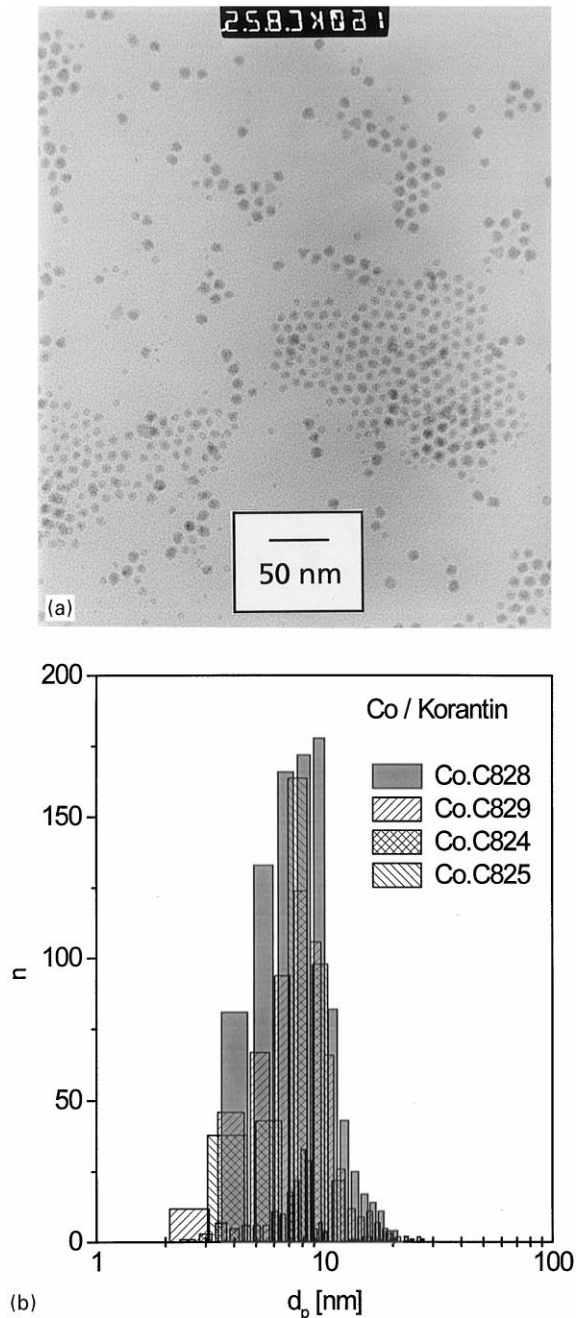


Fig. 1. Bright-field TEM image (a) and size distribution (b) of Co particles in toluene stabilized with Korantin SH. The plotted histograms of four samples were each fitted to Eq. (1) leading to $\langle d \rangle = 7.5$ nm and $s = 1.2$.

using the mean particle size $\langle d \rangle$ and the standard deviation s as fit parameters. The particle content and the saturation magnetization of the samples were determined by thermogravimetry analysis (TGA7, Perkin-Elmar) and a RF-magnetometer, respectively.

3. Results and discussion

According to the synthesis method of Hess and Parker [4] for metal nanoparticles in toluene the micelle model for particle formation is proposed. Within this model the type and particularly the molecular size of the surfactant controls the size of the micelles and consequently the mean particle diameter. Using dioctylsulphosuccinate sodium (short-chained molecule) and Korantin SH (long-chained molecule) as a surfactant in the thermolysis step we obtain cobalt particles with $\langle d \rangle = 4.2$ nm, $s = 1.5$ and $\langle d \rangle = 7.5$ nm, $s = 1.2$, respectively.

In order to obtain a magnetic oil, in a second step the toluene matrix had to be exchanged by the silicone oil or the mineral oil by using an extraction process described before. Using a second surfactant we were able to obtain cobalt ferrofluids based on silicone and mineral oils.

The measured values for the saturation magnetization J_s of the prepared Co-colloids as a function of volume content have been compared with the theoretical limit of J_s as calculated within the model of Scholten [5] for different magnetic core sizes and a surfactant layer thickness of 3 nm, which is comparable to the molecular chain length

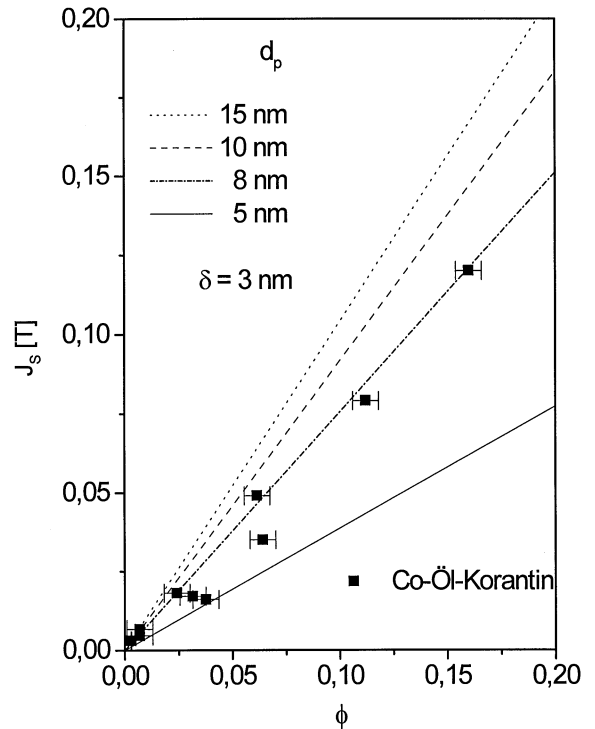


Fig. 2. Saturation magnetization as a function of the cobalt volume content obtained in the Korantin stabilized Co-oil ferrofluid. The straight lines correspond to the calculated maximum values of J_s within the Scholten model [5] for the given particle size and a fixed thickness δ of the surfactant layer (3 nm).

of 3.3 nm for Korantin (Fig. 2, Table 1). In the calculations we have used the bulk value of the cobalt saturation magnetization.

The calculated maximum values of J_s for 8 nm sized Co particles stabilized with a 3 nm thick

Table 1

Volume content of cobalt particles and saturation magnetization J_s of the various oil-based ferrofluids obtained in the two-stage synthesis route as described in the text

Sample #	Carrier oil	Co-surfactant	Co-vol%	J_s [mT]
MF-37	Edwards L9	X-100	7,2	35
MF-38	Edwards L9	LP4	15,9	120
MF-39	DC702	LP4	3,6	17
MF-40	DC702	X100	no ferrofluid	–
MF-41	AP201	X100	6,9	48
MF-42	AP201	LP4	12,5	79
MF-43	AP201	LP4	13,6	100

surfactant layer are in excellent agreement with the experimental data obtained for Korantin stabilized liquids ($\langle d \rangle = 7.5$ nm from TEM measurements).

Additionally, the magnetization curves have been investigated in more detail in order to correlate the particle size distribution obtained by TEM with the magnetic behaviour of the colloid. The magnetization of polydisperse subdomain particles $M(H)$ in superparamagnetic colloids obeys the Langevin law written in the form

$$M(H) = \int f(m) L(\mu_o m H / k_B T) dm \quad (2)$$

with the Langevin function $L(\zeta) = \text{ctanh}(\zeta) - 1/\zeta$. Herein μ_o , k_B , and m denote the magnetic field constant, the Boltzmann constant, and the magnetic moment of the particle, respectively. The magnetogranulometry analysis is performed by

approximating the integral in Eq. (2) by a sum of the magnetic moments of N individual particles

$$M(H) = \sum n_i m_i L(\mu_o m_i H / k_B T), \quad i = 1, \dots, N. \quad (3)$$

The measured magnetization curve is deconvoluted, respectively. Details of the software are described elsewhere [6]. The two magnetogranulometry spectra shown in Figs. 3 and 4 are calculated using $N = 40$.

Finally, we have investigated qualitatively the effect of the surfactant double layer on the oxidation resistance of the ferrofluids by measuring the magnetic attraction in an open beaker as a function of time. For the toluene-based Co-colloids we found the magnetic attraction to decrease rapidly down to 10% of its initial value within hours whereas the Korantin/LP4 coating appeared to protect the Co-particles for months.

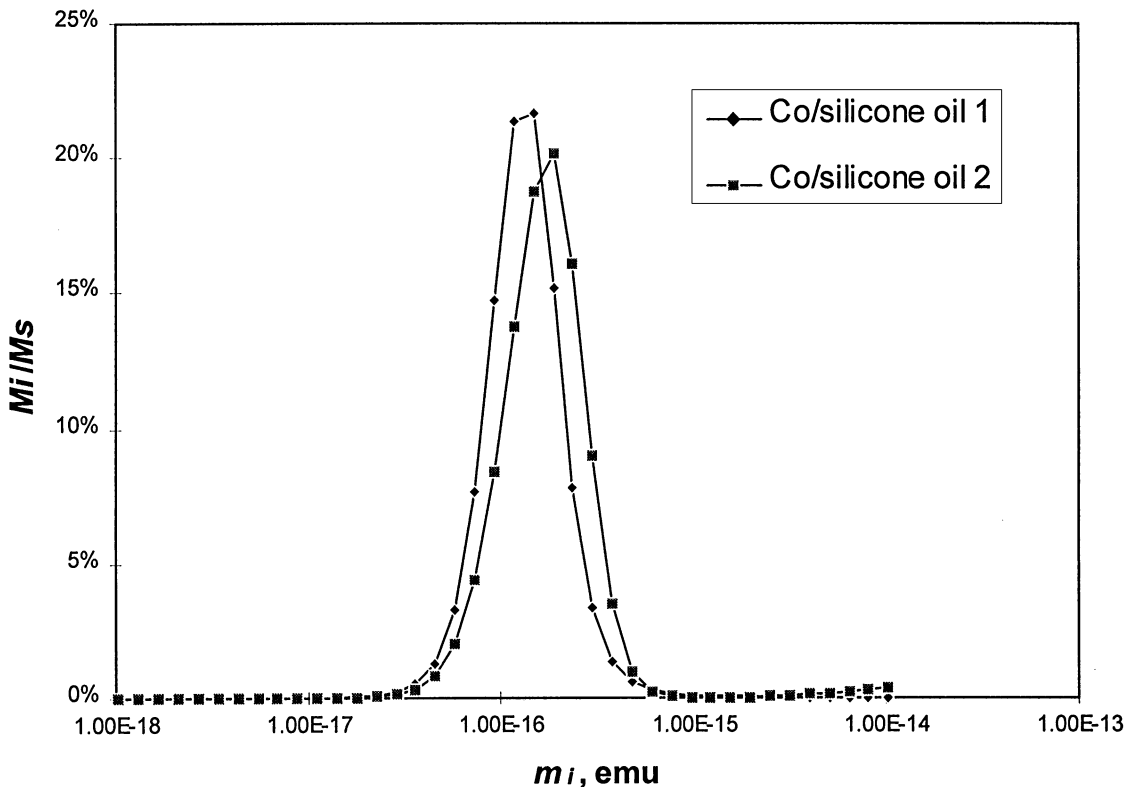


Fig. 3. Distribution of the magnetic moments of Co-particles for two different Co/silicone oil batches derived from the respective RF-magnetization measurements using Eq. (3).

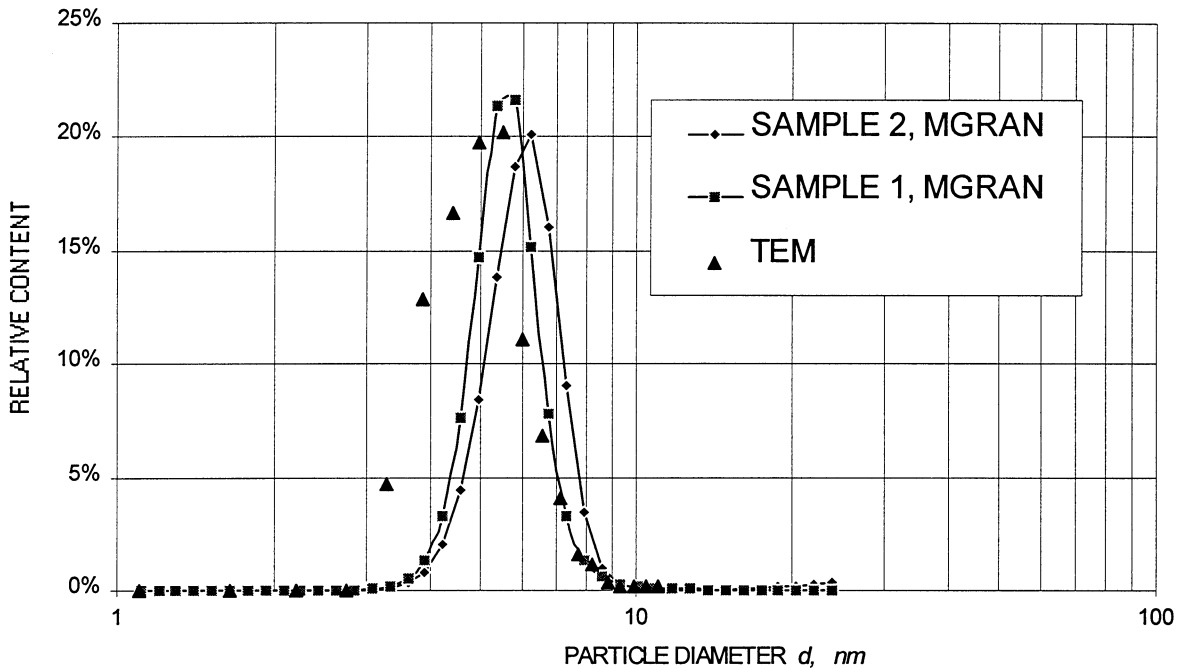


Fig. 4. Particle size distribution of Co/silicone oil ferrofluids obtained from the magneto-granulometry method (solid lines) and from TEM images (◆).

4. Conclusions

We have shown that magnetically stable cobalt fluids based on low vapour pressure silicone and mineral oil can be prepared by thermolysis followed by a liquid exchange step employing two surfactants consecutively. The saturation magnetization J_s of the as-prepared ferrofluids outperforms those of commercially available magnetite-based liquids considerably. In a sealed condition the liquids display long-term stability. On the other hand, exposure to air after months still leads to a gradual degradation of magnetic properties due to oxidation of the cobalt particles. A strong dependence on the type of surfactant combination is observed. Further work on the coating procedure is necessary for increasing the oxidation resistance.

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