# Air stable Fe and Fe-Co magnetic fluids—synthesis and characterization

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Thermolysis of  $Fe(CO)_5$  and  $Co_2(CO)_8$ , dissolved in tetrahydronaphthalene, in the presence of aluminum trialkyl leads to uniform-sized Fe or Fe-Co nanoparticles, respectively. Subsequent treatment with very dilute oxygen forms a shell which protects the metallic or alloyed core of the particles against further oxidation. With the help of surfactants, for instance oleic acid or cashew nut shell liquid, the particles can be peptized in organic solvents like toluene or kerosene, resulting in magnetic fluids with extraordinary magnetic properties. The saturation of magnetization,  $M_{\rm s}$ , of the fluids was determined by specific magnetization. The sizes and structure of the particles were investigated by transmission electron microscopy, and Moessbauer analysis showed that the core of the particles was metallic or alloyed, respectively. The particle surface termination was studied by X-ray photoelectron spectroscopy and Auger electron spectroscopy. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: nanoparticle; magnetism; magnetic fluid; Moessbauer spectroscopy; TEM; XPS; AES; Fe(CO)<sub>5</sub>; Co<sub>2</sub>(CO)<sub>8</sub>

# **INTRODUCTION**

For technical and biomedical applications (for instance high vacuum seals or cell separation) magnetic fluids (MFs) are useful materials. Most applied MFs consist of magnetite nanoparticles dispersed in viscous organic solvents or water. However, the magnetic properties of these MFs are not sufficient for most applications. We have found a simple procedure to generate oxygen-resistant Co<sup>0</sup> particles of different sizes and narrow size distribution,<sup>1,2</sup> which can be peptized by treatment with surfactants to produce mechanically and air-stable MFs that fulfil some of the required properties. Especially for medical applications, Fe is the metal of choice because of its non-toxicity. Additionally, MFs of Fe or Fe-Co nanoparticles exhibit a higher saturation

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of magnetization,  $M_{\rm s}$ , as compared with those of Co at the same concentration and particle size.

Some attempts at the preparation of Fe and Fe-Co nanoparticles and their subsequent peptization to MFs have been described in the literature,  $^{3-8}$  starting with the thermal decomposition of the metal carbonyls in high-boiling-point organic solvents at temperatures above 180 °C. However, the particles and the resulting MFs were not air-stable and had to be handled under inert atmosphere. A one-pot preparation of MFs without isolating the metallic or alloyed particles has also been tried.9-11 This also did not succeed in producing stable MFs. Therefore we tried to transfer our Co nanoparticle synthesis<sup>1,2</sup> to the preparation of Fe or Fe-Co particles for the production of air- and mechanically stable MFs.

As mentioned above, the basis for the preparation is the synthesis of Co<sup>0</sup> particles starting from Co<sub>2</sub>(CO)<sub>8</sub> and Al(alkyl)<sub>3</sub> in organic solvents.<sup>1</sup> For the preparation of Fe particles we therefore used  $Fe(CO)_5$  and  $Al(C_8H_{17})_3$ and for the Fe-Co particles a mixture of Fe(CO)<sub>5</sub> and

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 $Co_2(CO)_8$  in different Fe:Co ratios, also in the presence of  $Al(C_8H_{17})_3$ . Because of the higher decomposition temperature of  $Fe(CO)_5$  as compared with  $Co_2(CO)_8$ , tetrahydronaphthalene was used as the solvent. Fe and Fe–Co nanoparticles were produced which could be peptized using suitable surfactants, for instance oleic acid or cashew nut shell liquid (CNSL), in different organic solvents forming air- and mechanically stable MFs [equations (1) and (2)].

$$Fe(CO)_{5} \xrightarrow{C_{10}H_{12,\Delta},Al(C_{8}H_{17})_{3}} Fe magnetic fluid (1)$$

$$Co_{2}(CO)_{8} + Fe(CO)_{5} \xrightarrow{C_{10}H_{12,\Delta},Al(C_{8}H_{17})_{3}} O_{2}, surfactant, solvent$$

$$Fe-Co magnetic fluid \qquad (2)$$

### **EXPERIMENTAL**

#### Synthesis of the particles

#### *Fe particles*

In a 1000 ml three-necked flask fitted with a mechanical stirrer and reflux condenser, 50 g (255.2 mM) of Fe(CO)<sub>5</sub> were placed under argon flow. To this 13.53 ml (25.52 mM) of  $Al(C_8H_{17})_3$ dissolved in 500 ml tetrahydronaphthalene were added under ambient conditions. The mixture was stirred and heated up slowly to 90 °C. The temperature of 90 °C was maintained for 1 h, then increased stepwise at 10 °C/h up to 150 °C. For another 5 h the reaction was kept at this temperature until gas evolution stopped. A black precipitate was formed from the solution. The contents were cooled to room temperature and stirred for another 16 h. After this the precipitate was allowed to settle for 2 h. For 3 h the material was slowly oxidized by a gas mixture of argon and 3.5 vol% oxygen bubbled through a capillary into the reaction mixture. The precipitate was allowed to settle for 2 h. The supernatant was decanted, and the Fe particles were washed twice using 500 ml of toluene, and isolated in wet form (suspended in approximately 100 ml of toluene).

#### *Fe/Co particles (Fe–Co ratio 2:1)*

A 50 g (255.2 mM) aliquote of Fe(CO)<sub>5</sub> and 21.81 g (63.8 mM) of Co<sub>2</sub>(CO)<sub>8</sub> were placed in a three-necked flask fitted with a mechanical stirrer and reflux condenser under argon flow. A 500 ml volume of tetrahydronaphthalene was added and the mixture stirred at room temperature for 3 days under protective atmosphere. Then 20.3 ml (38.4 mM) of Al(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> were added. Subsequently the reaction mixture was slowly heated to 90 °C. Then the mixture was stepwise heated with 10 °C/h up to 120 °C, where the evolution of CO started. The temperature of 120 °C was carefully maintained for 3 h and after this brought up to 130 °C for 1 h, then to 140 °C for 1 h. Finally, the temperature was adjusted to reach 150 °C and kept there for 4 h to finalize the gas evolution After this

the mixture was allowed to cool to room temperature for 1 h. A dark particle solution was obtained also containing suspended parts of the material.

At room temperature the 'smooth oxidation step' was added by bubbling a flow of diluted oxygen gas ( $3.5 \text{ vol}\% O_2$  in argon) for 8 h through the mixture using a thin capillary. The precipitate was allowed to settle for 2 h. The supernatant was decanted, and the Fe/Co particles were washed twice using 500 ml of toluene, and isolated in wet form (suspended in approximately 100 ml of toluene).

# Extraction of the surfactant CNSL from cashew nuts (*Anacardium occidentale*)

CNSL can be prepared in the laboratory very easily using commercially available cashew nuts which dipped in liquid nitrogen for 30 min. Then they were broken manually and de-shelled. The shells were put into the mill and ground to obtain a pasty mass from which CNSL was extracted using a polar organic solvent (for instance ethyl acetate or 1:1 v/v acetone–ethanol mixture). The solvents were then evaporated to obtain CNSL (32% by weight of the nut).

The oil was subjected to both NMR and HPLC analysis to quantitatively determine its chemical constituents. From the result it was evident that anacardic acid -ene mixtures constituted 77.31% of the oil (with a triene–diene–monoene ratio of 36:21:43), cardols and 2-methyl cardols together accounted for 18.26% and cardanols accounted for 2.27%, with the reminder other lipophilic phenols.

#### **Peptization of the particles**

#### *Peptization of the Fe particles*

Fe particles should be coated with surfactant as soon as possible.

#### Peptization of the Fe particles by CNSL in toluene

To peptize the Fe particles in toluene 0.73 g (0.8 ml) CNSL was added dropwise into 12 ml suspension of the toluene-wet Fe particles, containing about 6 g Fe. In order to facilitate the particle peptization, the mixture was stirred very well and gradually heated to 60-70 °C over 15 min.

# *Peptization of the Fe particles by CNSL and LP4 in kerosene*

To transfer the Fe particles from toluene to kerosene, the Fe MF in toluene was destroyed by adding ethanol three times in 15–25 ml portions. In this way the surfactant-coated Fe particles were precipitated. Then they were washed with 10–15 ml kerosene twice. After adding a small portion (about 5 ml) of kerosene, CNSL-coated Fe particles start to peptize. For better peptization, 10 ml of kerosene containing 0.2 g LP4 (a fatty acid condensation polymer) were added and the CNSL-coated Fe particles peptized in kerosene very well. The mixture was vigorously mixed and heated to 60-70 °C for 1–2 h until all mass became homogeneous, resulting in an Fe-magnetic fluid in kerosene stabilized by CNSL and LP4.



Moessbauer investigation of the MF revealed an Fe<sup>0</sup>-Fe<sup>3+</sup> ratio of ca. 1:2 and SIGMA (specific magnetization) analysis showed a saturation of magnetization value of  $M_{\rm s} = 9.7 \, \rm kA/m$ . The Fe volume concentration was about 0.56%.

#### *Peptization of the Fe particles by Korantin SH and* LP4 in kerosene

To peptize the Fe particles in toluene, 1 ml Korantin SH was added dropwise to 10 ml suspension of the toluene-wet Fe particles. To transfer the Fe particles from toluene to kerosene, the Fe MF in toluene was destroyed by adding ethanol three times in 15-25 ml portions. In this way the surfactant-coated Fe particles were precipitated. Then they were washed with 10-15 ml of kerosene twice. After adding a further small portion (about 5 ml) of kerosene, Korantin SH-coated Fe particles started to peptize. For better peptization, 10 ml kerosene containing 0.21 g LP4 (a fatty acid condensation polymer) were added and the Korantin SH-coated Fe particles peptized in kerosene very well. The mixture was vigorously mixed and heated to 60-70 °C for 1-2 h until all mass became homogeneous, resulting in an Fe magnetic fluid in kerosene stabilized by Korantin SH and LP4.

SIGMA analysis showed a saturation of magnetization value of  $M_s = 24 \text{ kA/m}$ . The Fe volume concentration was about 1.38%.

#### *Peptization of the Fe–Co particles*

Fe/Co particles should be coated in surfactant as soon as possible.

*Peptization of the Fe–Co particles by CNSL in toluene* The toluene-wet Fe-Co particles (the suspension in toluene contained ca.10 g of Fe-Co) were peptized in toluene by adding 1.2 ml (1.32 g) CNSL dropwise. In order to facilitate the particle peptization, the mixture was stirred very well and gradually heated to 60-70 °C over 15 min.

SIGMA analysis showed a saturation of magnetization value of  $M_s = 6.36$  kA/m. The determined Fe–Co volume concentration was about 0.26%.

#### *Peptization of the Fe–Co particles by CNSL and LP4* in kerosene

To transfer the Fe-Co particles from toluene to kerosene, the Fe-Co MF in toluene (obtained as described above) was destroyed by adding ethanol three times in 15-25 ml portions. In this way the waxy CNSL-coated Fe-Co particles were precipitated. Then they were washed with 10-15 ml kerosene twice. After adding a further small portion (about 5 ml) of kerosene, CNSL-coated Fe-Co particles started to peptize. For better peptization, 10 ml kerosene containing 0.5 g LP4 (a fatty acid condensation polymer) were added and the CNSL-coated Fe-Co particles peptized in kerosene very well. The mixture was vigorously mixed and heated to 60-70 °C for 1-2 h until all mass became homogeneous,

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resulting in an Fe-Co magnetic fluid in kerosene stabilized by CNSL and LP4.

SIGMA analysis of the MF revealed a saturation of magnetization value of  $M_s = 4.81 \text{ kA/m}$ . The determined Fe-Co volume concentration was about 0.2%.

### Peptization of the Fe–Co particles by Korantin SH in toluene

The toluene-wet Fe-Co particles (suspension in toluene containing ca. 15 g of Fe-Co) were peptized in toluene by adding 3 ml of Korantin SH dropwise. In order to facilitate the particle peptization, the mixture was stirred very well and gradually heated to 60-70 °C over 15 min.

#### *Peptization of the Fe–Co particles by Korantin SH in* kerosene

To transfer the Fe-Co particles from toluene into kerosene, the Fe-Co MF in toluene (obtained as described above) was destroyed by adding ethanol three times in 15–25 ml portions. In this way the waxy Korantin SH-coated Fe-Co particles were precipitated. Then they were washed with 10-15 ml of kerosene twice. After adding a further small portion (about 5 ml) of kerosene, the Korantin SH-coated Fe-Co particles started to peptize. For better peptization, 10 ml of kerosene containing 0.5 g LP4 (a fatty acid condensation polymer) were added and the Korantin SH-coated Co particles peptized in kerosene very well. The mixture was vigorously mixed and heated up 60-70 °C for 1-2 h until all mass became homogeneous.

The MF was first analysed by TEM regarding the mean particle size, which was found to be ca. 10 nm. The saturation of magnetization,  $M_{\rm s}$ , and the volume concentration of the obtained MF were calculated by SIGMA. The saturation of magnetization  $M_{\rm s}$  was determined to be 67.32 kA/m (= 84.6 mT) and the volume concentration was 2.8 vol% Fe-Co. For comparison the mean particle size was also investigated by SIGMA and calculated to be 9.6 nm, a value close to that observed by TEM. Mössbauer investigation of the MF revealed a  $Fe^0 - Fe^{3+}$  ratio of ca. 4:1.

#### Moessbauer spectroscopy

For <sup>57</sup>Fe Moessbauer spectroscopy, the metal powders including oil were mixed with high-purity Boron Nitride (BN) powder and glued into flat Plexiglas containers with thin windows. Sample absorbers of approximately 5–20 mg/cm<sup>2</sup> iron were made in this way for conventional transmission spectroscopy. Spectra were taken at room temperature and at liquid nitrogen (ca. 77 K) and liquid helium temperatures (4.2 K). For the latter two, the samples were mounted in a helium bath cryostat. Transmission spectra were taken over 24 h. For the samples reported here, the room temperature spectra showed no resonance absorption. This effect, due to the very small size of the nanoparticles, has been seen before<sup>12</sup> and indicates a zero recoil fraction (zero effective Lamb-Moessbauer or Debye-Waller factor). We can thus be certain that the particles at room temperature are not

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ferromagnetic, since then they would stick together more via magnetic dipole interactions, increasing the resonance fraction. The spectra at helium temperatures showed a nonzero resonance fraction and magnetic hyperfine splitting. Thus the particles can be seen as super-paramagnetic at room temperature. These spectra were analyzed using the WinNormos computer program. The calculated hyperfinefilled Bhf (Magnetic Hyperfine Field) shows a distribution of values which could be separated into two parts (subspectra). The first subspectrum was typical for iron atoms in the Fe<sup>3+</sup> high-spin state both for Bhf and center shift. The large linewidth was certainly due to the disorder typical of nanoparticles, and the presence of Fe<sup>3+</sup> indicated iron, or iron-cobalt, oxide. The second subspectrum was characterized by a distribution of hyperfine fields typical of metallic alloys. This part, denoted Fe<sup>0</sup>, was interpreted as being due to metallic iron or iron-cobalt alloy. The relative fractions of these two hyperfine field regions can be interpreted as the iron fraction in each phase, as long as equal resonant fractions are assumed in both (the usual assumption).

### **XPS and AES investigations**

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were performed in an ultrahigh vacuum apparatus which has been described in detail previously.<sup>13,14</sup> Briefly, it is equipped with a combined He\*/HeI source for metastable impact spectroscopy/ultraviolet photoelectron spectroscopy (MIES/UPS) , a commercial X-ray source for XPS and a newly installed electron gun for AES. XPS is performed with a photon impact under 80° to the surface normal, analyzing electrons emitted under 10° to the surface normal. The electron beam for AES hits the surface under 45° to the surface normal; electrons normal to the surface are analyzed. For high resolution the measuring time was several hours in both cases.

Particles peptized in kerosene were investigated using XPS by covering a silicon sample with the solution and immediately transferring it into a vacuum. Then the smoothly oxidized Fe–Co nanoparticles were applied to molybdenum foils and investigated using AES and XPS.

# **RESULTS AND DISCUSSION**

Following the procedures above, the preparation resulted in Fe and Fe–Co particles, respectively. Subsequent peptization of the metal powders by treatment with surfactants formed long-term-stable MFs in organic solvents with extraordinary magnetic properties. In all preparation steps the reaction parameters influenced the resulting MFs. Therefore the effect of the following parameters on the quality of the material was studied:

- reaction time and temperature guidance;
- influence of the aluminum trialkyl;

• molar ratio of Fe-Co in the reaction mixture for the alloyed

For the preparation of the magnetic material, both Fe and Fe–Co particles, the reaction time and temperature guidance must be carried out in the way described above. Changing the procedure, for instance other reaction time or temperature, causes unwanted non-magnetic by-products of unknown composition and consequently the yield of magnetic material decreases. In particular, the reaction time of 5 h at 150 °C for the magnetic Fe particles and 3 h at 120 °C for the formation of the alloyed material is of major importance.

# Influence of the aluminum trialkyl

• surfactant and stability of the dispersion.

The aluminum trioctyl is necessary for the synthesis of the nanoparticles, because the organo aluminum compound acts as a catalyst for the thermal decomposition of the metal carbonyls, as can be deduced by IR spectroscopy in the case of  $\text{Co}_2(\text{CO})_8$ .<sup>15</sup> The Fe(CO)<sub>5</sub> decomposes in tetrahydronaphthalene in the region of 180–200 °C, whereas under catalysis by Al(Oct)<sub>3</sub> the decomposition is already finished at 150 °C. This decrease in the decomposition temperature enables the preparation of Fe–Co-alloyed nanoparticles, because an experiment at 200 °C without Al(alkyl)<sub>3</sub> resulted only in Co particles with a small amount of Fe particles which were not alloyed.

### **Oxidation step**

oxidation step;

material;

The 'smooth' oxidation of the particles is a delicate step. Because of the very air-sensitive Fe particles, oxidation must be carried out over a long time (3 h) with very dilute oxygen (maximum 3.5 vol% in argon). Too short an oxidation time (1 h) results in air-sensitive metal particles and, conversely, too long an oxidation time (8 h) yields totally oxidized Fe in the particles, as can be deduced from Mössbauer spectra. The



**Figure 1.** TEM image of the Fe particles (metallic core, black; shell, gray).

oxidation step and the stabilization of Co nanoparticles has been studied in detail.<sup>16</sup> For Fe nanoparticles we expect the same mechanism. Figure 1 shows the TEM image of the Fe nanoparticles after the 'smooth' oxidation. The metallic core and the shell of the particles are clearly visible.

Similar results were found by the TEM analysis of the Fe–Co particles. In the TEM image of the Fe–Co particles in Fig. 2, the metallic core and the oxidized surface of the particles can easily be identified.

# Molar ratio of Fe–Co in the reaction mixture for the alloyed material

For use as precursor material for MFs, the Fe<sub>2</sub>Co alloy is best because of its high saturation of magnetization  $(M_{\rm s} = 1910 \text{ kA/m} = 2400 \text{ mT})$ . However, the metals have different electrochemical potentials, which means that Fe will be more easily oxidized than Co. Therefore, we have tested the influence of the molar ratio  $Fe(CO)_5 - Co_2(CO)_8$ in the reaction mixture for the preparation of the alloyed material Fe<sub>2</sub>Co. A molar ratio of 4:1 (Fe:Co = 2:1) results in an alloy which contains only about 40% metallic Fe. The rest of the Fe is oxidized to Fe<sup>3+</sup>, which forms the shell of the airstable particles (see Fig. 2). A molar ratio of 8:1 (Fe:Co = 4:1) reaches the desired composition of ca. 67% metallic Fe in the alloy (see Table 1). Interestingly, a higher concentration of Fe carbonyl in the reaction mixture (ratio 83:17) also leads to the desired alloy. It seems that the Fe<sub>2</sub>Co alloy is more stable in the particles than in other compositions with a higher Fe concentration.

#### Surfactants and stability

The most common surfactants for the peptization of magnetic nanopowders in organic solvents like toluene, kerosene or vacuum oil are Korantin SH (*N*-oleoyl sarcoside, from BASF AG), LP-4, a fatty acid condensation polymer (from ICI Ltd), AOT (sodium dioctyl sulfosuccinate, from SERVA), or oleic acid (from Aldrich). The natural product CNSL, an anacardic



Figure 2. TEM image of the Fe–Co particles (metallic core, black; shell, gray).

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**Table 1.** Concentration of Fe<sup>0</sup> in the alloyed Fe/CO particles

Molar educt ratio Fe-Co	Mössbauer analysis: Fe <sup>0</sup> (in the particles)
66:34	$40.2\%\pm3\%$
75:25	$44.3\%\pm2\%$
80:20	$68.8\%\pm1\%$
83:17	$65.2\%\pm1\%$

acid ene mixture used in India as a cheap washing agent, has also been tested as a surfactant.

Figure 3 shows XPS investigations on peptized particles. Besides the contributions corresponding to the organic components C and O, Fe can be clearly identified. In contrast, Co may not be identified at all. Corresponding to our sensitivity, we found a detection limit for Co to be at least less than 2% of Fe. Investigations on the smoothly oxidized particles prepared on Mo samples (data not shown) showed Co contributions: a ratio of about Fe  $2p_{1/2}$  – Co  $2p_{1/2} = 1.4$  was observed. The observed Fe2p1/2 peak corresponded to Fe in an oxidized state, probably Fe<sub>2</sub>O<sub>3</sub>. Co appeared to be nonmetallic, although the peak area analysis was quite difficult. Metallic Fe was not observed. AES measurements (also not shown here) showed comparable results. All observations suggested the following picture: the nanoparticles are covered by an oxidic shell which consists, at least mostly, of Fe oxide. Co oxide was not observed. Ar<sup>+</sup> sputtering partly removed the particle shell. Subsequent XPS measurements predominantly showed metallic Fe and metallic Co from the core of the particles.

Both the Fe and Fe–Co MFs were also investigated by Mössbauer spectroscopy to determine the portion of  $Fe^{3+}$  and the degree of alloying in the Fe–Co particles. After deconvolution of the spectra of the iron MF into one of  $Fe^{0}$  and another



**Figure 3.** XPS spectra of the peptized Fe-Co particles in kerosene.

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**Figure 4.** Mössbauer spectra of the Fe–Co MF at T = 4.2 K (and the separated subspectra). In this example, both hyperfine distributions were assumed Gaussian. The sub-spectrum with the larger line splitting represents Fe<sup>3+</sup> while that for the smaller splitting represents Fe<sup>0</sup>.

one of  $Fe^{3+}$ , it was found that ca. one-third of the Fe was in the state of  $Fe^{0}$ . In the same way the spectra of the Fe–Co MFs were separated. As mentioned above, in the Fe–Co MFs, ca. 80% of the Fe was alloyed with Co and only ca. 20% of the Fe was oxidized, forming the shell of the particles. This shows clearly that it is possible to prepare stable Fe–Co MFs as well as Fe MFs. An example is shown in Fig. 4. The assumed Gaussian shape is arbitrary, but essentially identical results were obtained from a histogram distribution analysis.

Figure 5 shows the magnetization curves of the MF obtained at room temperature after the peptization of Fe–Co nanoparticles with CNSL in toluene. Because of the



**Figure 5.** Hysteresis of Fe–Co MF (solvent, toluene) at room temperature.

Table 2.	Physica	properties	of the	prepared MFs
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**Figure 6.** Hysteresis of Fe–Co MF (solvent, kerosene) at room temperature.

type of instrument, magnetic field cooling and zero field cooling measurements could not be done. As can be seen in the figure, the hysteresis drops sharply and there is no remanence, which means that the size distribution of the superparamagnetic nanoparticles must be very small. The saturation of magnetization,  $M_{\rm s}$ , was determined to be 6.36 kA/m, which implies a volume concentration of 0.26%.

The magnetization curves of a more concentrated MF are shown in Fig. 6. The superparamagnetic Fe-Co particles were peptized with Korantin SH in kerosene. The results of the SIGMA analysis are: small size distribution; saturation of magnetization,  $M_{\rm s}$ , 67.3 kA/m; volume concentration, 2.81%; average particle size, 9.7 nm. In Table 2 the physical data of the prepared MFs are summarized. An inspection of Table 2 shows that the metal and alloy particles peptized with CNSL or a mixture of CNSL and LP4 form stable MFs in organic solvents, as with the most common surfactant Korantin SH. The MFs have magnetic properties comparable to those prepared with Korantin SH. Also the long-term stability can be deduced from the magnetic measurements in which the Fe-Co MF was analysed after 4 days and 26 days. The decrease of  $M_{\rm s}$  in 3 weeks was only 67.3-66.5 kA/m which is slightly more than 1%.

Therefore we can summarize that the Fe and Fe–Co particles prepared as described above can be peptized in common organic solvents as well as in kerosene or vacuum and mineral oil with suitable surfactants to produce airstable MFs, and that the CNSL is as good a surfactant for

Metal or alloy			Magnetization, M <sub>s</sub>		
	Surfactant	Solvent	(kA/m)	(mT)	Volume concentration (%)
Fe	CNSL/LP4	Kerosene	9.70	12.19	0.56
Fe	Korantin SH/LP4	Kerosene	24.02	30.18	1.38
Fe-Co	CNSL	Toluene	6.36	7.99	0.26
Fe-Co	CNSL/LP4	Kerosene	4.81	6.04	0.20
Fe–Co	Korantin SH	Kerosene	67.32	84.60	2.81

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the peptization of Fe metal or Fe-Co alloy nanoparticles as conventional products like Koranthin SH or LP4.

#### CONCLUSIONS AND OUTLOOK

 $Fe(CO)_5$  and  $Co2(CO)_8$  are suitable precursors for the aluminum trialkyl-catalyzed synthesis of Fe and Fe-Co nanosized particles, which may be peptized in organic solvents to MFs with extraordinary magnetic properties. The particles have a narrow size distribution which will be conserved during the 'smooth' oxidation process and the subsequent peptization. Besides the well-known surfactants such as Koranthin SH or LP4, natural CNSL was tested as a novel surfactant for metallic nanoparticles, with good results.

Future work will be focused on the peptization of metallic particles in polar solvents like alcohol or water in high concentrations for biomedical applications.

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### REFERENCES

1. Bönnemann H, Brijoux W, Brinkmann R, Matoussevitch N, Waldöfner N. DE 10 227 779.6 to Studiengesellschaft Kohle mbH 2002

- 2. Bönnemann H, Brijoux W, Brinkmann R, Matoussevitch N, Waldöfner N, Palina N, Modrow H. Inorg. Chim. Acta 2003; 350: 617.
- 3. Schlecht L, Bergmann F, Oestreicher E. D.B.P. 862 204 to BASF 1952.
- 4. Huber DL, Martin JE, Venturini EL, Provencio PP. Abstract Particles 2004. Particle Synthesis. Characterization. and Particle-Based Advanced Materials, Orlando, FL, 2004; 76.
- 5. van Wonterghem J, Mørup S, Charles SW, Wells S, Villadsen J. Phys. Rev. Lett. 1986; 55: 410.
- 6. Kilner M, Hoon SR, Lambrick DB, Potton JA, Tanner BK. IEEE Trans. Magn. 1984; MAG-20: 1735.
- 7. Lambrick DB, Mason N, Harris NJ, Russell GJ, Hoon SR, Kilner M. IEEE Trans. Magn. 1985; MAG-21: 1891.
- 8. Lambrick DBN, Mason N, Hoon SR, Kilner M. J. Magn. Magn. Mater. 1987; 65: 257.
- 9. Scholten PC. J. Magn. Magn. Mater. 1983; 39: 99.
- 10. Nakatani I, Furubayashi T, Takahashi T, Hanaoka H. J. Magn. Magn. Mater. 1987; 65: 261.
- 11. Berkowitz AE, Walter JL. J. Magn. Magn. Mater. 1983; 39: 75.
- 12. Stahl B, Ellrich J, Theissmann R, Ghafari M, Bhattacharya S, Hahn H, Gajbhiye NS, Kramer D, Viswanath RN, Weissmüller J, Gleiter H. Phys. Rev. B 2003; 67: 014 422-1.
- 13. Maus-Friedrichs W, Wehrhahn M, Dieckhoff S, Kempter V. Surf. Sci. 1990: 237: 257.
- 14. Maus-Friedrichs W, Dieckhoff S, Wehrhahn M, Kempter V. Surf. Sci. 1990: 253: 137.
- 15. Bönnemann H, Brand RA, Brijoux W, Brinkmann R, Hofstadt HW, Matoussevitch N, Waßmuth B. Abstract 2004; Kolloidale magnetische Flüssigkeiten: Grundlagen, Entwicklung und Anwendungen neuartiger Ferrofluide, Benediktbeuern, Germany, 2004; 1.
- 16. Rudenkiy S, Frerichs M, Voigts F, Maus-Friedrichs W, Kempter V, Brinkmann R, Matoussevitch N, Brijoux W, Bönnemann H, Palina N, Modrow H. Appl. Organometall. Chem. 2004; 18: 553.