Journal of Korean Magnetics Society, Volume 5, Number 5, October 1995

PREPARATION AND PROPERTIES OF OIL-BASED MAGNETIC FLUIDS WITH THE SYNTHESIZED MAGNETITE

K. O. JANG, S. W. DOH, S. I. CHO, H. J. SHON, W. D. HUR
R & D LAB., Samwha Electronics Co., Ltd., Osan, Korea

Abstract-The oil-based magnetic fluids were synthesized using ultra-fine Fe_3O_4 powder dispersed in hydrocarbon oil. To synthesize ultra-fine Fe_3O_4, we carried out the experiments varying the pH of reacting medium and the initial concentration of Fe^{2+}. We also investigated the amount of oleic acid to obtain a stable dispersion and the proper base oil of MF for loudspeaker application. The limits of adsorbed amount of oleic acid on the Fe_3O_4 surface were approximately 35~40 percents of the total magnetite weight. As the Fe_3O_4 content increased from 0.1g/cc to 0.6g/cc, the viscosity of oil-based magnetic fluid increased from 1,063cP to 1,828cP, and its saturation magnetization at 10kOe increased from 66G to 242G. When we tested the MF sample to a commercial speaker, improvements were noted.

I. INTRODUCTION

Magnetic fluids(MF) have been used in audio-voice coil-damping, inertia-damping apparatus, bearings and seals.[1]

For the application it is necessary for the MF to have specified values of viscosity, saturation magnetization and proper base oil. The viscosity of MF is determined by the viscosity of a carrier liquid and is related to the damping effect of a speaker. The higher the viscosity of the MF, the greater the viscous damping of the moving mass. And this reduces damping factor Q and suppresses to a lower impedance in the lowest resonance frequency f_0 and improves the frequency response of a speaker. Saturation magnetization is a measure of retaining force of MF in a speaker gap. A low saturation magnetization is desirable for the mid-range and tweeter units that the vibration of voice coil is not particularly great. When the MF is used for a speaker, the base oil must have low volatility in connection with life and also should be chosen a proper one that is completely compatible with the circumference materials(bobbin, coil, adhesive etc.). [2]

This paper describes a preparation method of ultra-fine Fe_3O_4, the method of stable dispersion of magnetic particles, and a optimum base oil for loudspeaker application.

II. EXPERIMENTAL

Mixed solutions of 0.9mole/ℓ of $FeSO \cdot 7H_2O$ and 1.08mole/ℓ of $FeCl_3 \cdot 6H_2O$(Fe^{2+}/Fe^{3+} = 5 / 6) were prepared. With vigorous stirring, the concentrated NH_4OH was added to the iron salts until the value of pH was reached 9~9.5 and the solution was reacted for 10 minutes to precipitate the ultra-fine Fe_3O_4. To investigate the basic characteristics and magnetic properties of the synthesized particles, the precipitate was washed with distilled water and filtered using No. 5C paper and dried using the vacuum drying oven at 80℃ for 2 days. The physical and magnetic properties are measured by a specific surfac area analyzer(SSAA), an x-ray diffractometer(XRD), a scanning electron microscope(SEM) and a vibrating sample magnetometer(VSM).

For the preparation of oil-based MF, the mixture of oleic acid and 3N NaOH(the chemical equivalent of oleic acid to NaOH is 1 to 1) was added to the Fe_3O_4 suspension. After the addition of surfactant, the suspension was matured at 90 ℃ for 30 minutes with stirring. To remove the physical adsorption, we added a solution of 3N HCl to the suspension, adjusted

Journal of Korean Magnetics Society, Volume 5, Number 5, October 1995

the pH value from 5 to 5.5, coalesced magnetite powders, discharged a supernatant liquid and added water and methanol. After repeating water washing for several times, we removed electrolytes and free acid($C_{17}H_{33}COOH$) therefrom. And the Fe_3O_4 suspension which was adsorbed by the surfactant was filtered and dried using vacuum drying oven at 80℃ for 24 hrs. We added the dried Fe_3O_4 to the hydrocarbon oil and the mixture was stirred by the homogenizer for 1 hr. Thereby, we obtained a MF with good dispersibility. The properties of the MF were measured by a pycnometer, a VSM, and a viscometer (LV-DVII+). And also, to apply the MF in a loudspeaker, the thermal stability and properties of the frequency response of the MF and the temperature of voice coil were measured by TG-DTA, B & K #2012(Denmark), and ONSOKU(OMT-105) respectively

Ⅲ. RESULTS AND DISCUSSION

Fig. 1 shows the change of x-ray diffraction pattern of reaction products with the variation of pH(pH=7, 8, 9, 9.5, 10). The powder synthesized at pH=7 shows single α-FeOOH reflections. In case of pH=8, 9 and 9.5, it shows the single phase of Fe_3O_4. However, the pattern of pH=10 shows the formation of α-FeOOH.

Fig. 2 shows SEM photographs of Fe_3O_4 powder. The shape of particle represents spherical form regardless of the variation of pH.

Fig. 3 shows the variation of specific saturation magnetization of Fe_3O_4 powder as a function of pH. In case of the powder synthesized at pH=7, the evidence of strong magnetization is insufficient and no hysteresis curve was observed. The specific saturation magnetization shows maximum at pH=9~9.5, then decrease according to the increase of pH.

The mean particle diameter of Fe_3O_4 powder was determined by the BET method with the asumption of nonporous spherical particles and

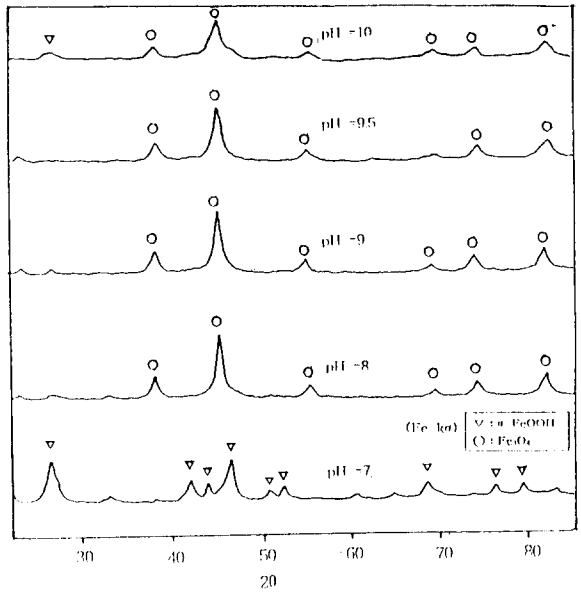

Fig. 1 X-ray diffraction patterns(Fe-kα) of the reaction products with the variation of pH (the initial concentration of Fe 0.9mole/l, the mole ratio of Fe^{2+} Fe^{3+} = 5 to 6, reaction time = 10 minutes.)

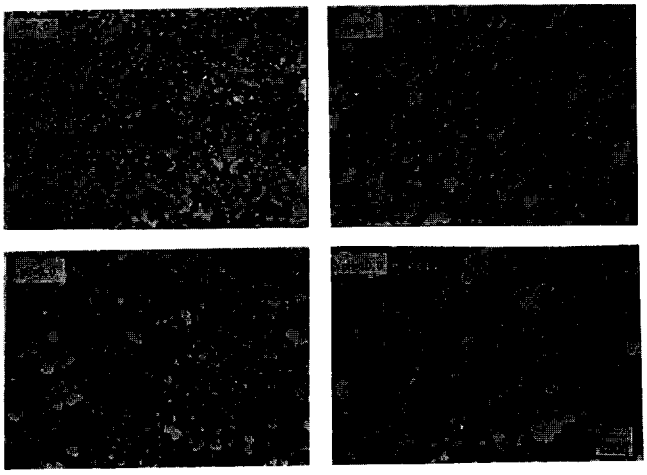

Fig. 2 SEM photographs for Fe_3O_4 powders synthesized at various pH values.

the formula[3][4].

$$D_p = \frac{6}{A_s \times D} \times 10^4$$

where, D_p is the mean particle diameter in Å, and A_s is the particle surface area in m^2/g, and D is the measured density in g/cm^3. The mean particle diameter of Fe_3O_4 is found to vary from 91Å to

106Å, and the results are summarized in Table 1.

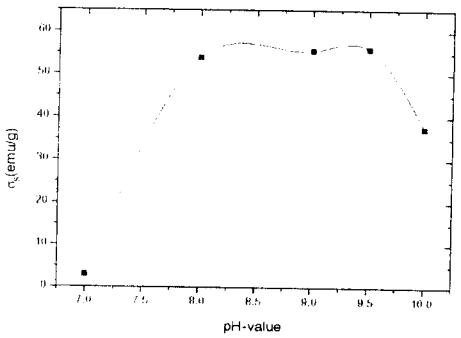

Fig. 3 The specific saturation magnetization of Fe_3O_4 powder as a function of pH

Table 1. The mean particle diameter of Fe_3O_4 powder synthesized at various pH values.

pH value	7	8	9	9.5	10
surface area(m²/g)	169.12	125.09	138.21	146.65	180.10
Mean particle diameter(Å)	99.9	99.7	96.9	106	91

Fig. 4 shows the change of x-ray diffraction pattern of the reaction products as a function of the initial concentration of Fe^{2+}(0.3, 0.5, 0.9mole/l). All the reaction products consisted of single Fe_3O_4 regardless of the initial concentration of Fe^{2+}.

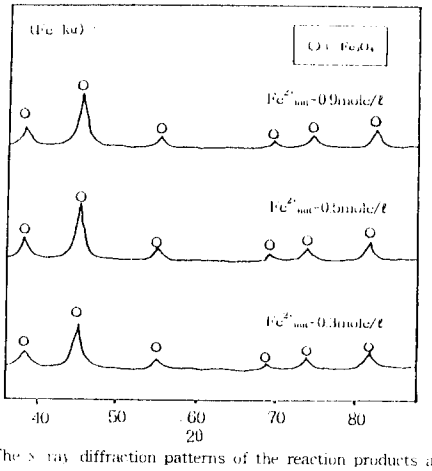

Fig. 4 The x-ray diffraction patterns of the reaction products as a function of the initial concentration of Fe^{2+}
(the mole ratio of Fe^{2+}/Fe^{3+} 5 to 6, the reaction pH = 9~9.5)

Fig. 5 shows specific saturation magnetization of Fe_3O_4 as a functon of the initial concentration of Fe^{2+}. The specific saturation magnetization varies from 55.0 to 59.8 emu/g. The mean particle diameter of Fe_3O_4 powder varied from 104Å to 127Å as shown in Table 2.

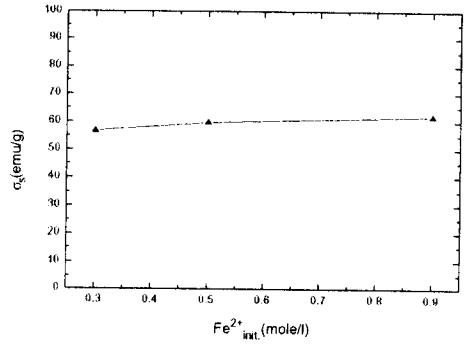

Fig. 5 Variation of the specific saturation magnetization measured as a function of the initial concentration of Fe^{2+}

Table 2. The mean particle diameter of Fe_3O_4 as a function of the initial concentration of Fe^{2+}

Fe^{2+}_{ini}(mole/l)	0.3	0.5	0.9
surface area(m²/g)	190.20	148.60	156.48
Mean particle diameter(Å)	118	104	127

Fig. 6 shows the weight loss of surfactant adsorbed on the surface of Fe_3O_4 as a function of the added amount of oleic acid. In case of R=0.3, the weight loss is about 15.4wt%. In R=0.35, there is a peak weight loss of 15.9wt% at above mentioned temperature and in R=0.4~0.5, the change of the weight loss is very small. This indicates that the amount adsorbed surfactant on the surface of Fe_3O_4 has a limitation. That value is approximately 35~40 percents of the magnetite weight.

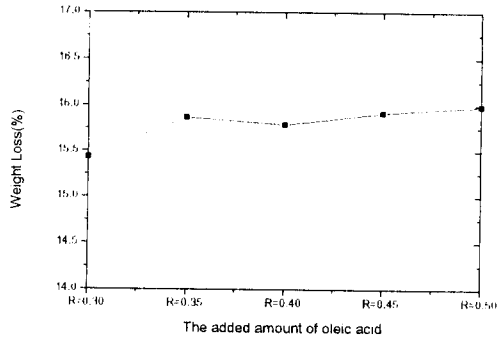

Fig. 6 Weight loss of Fe_3O_4 adsorbed surfactant as a function of the added amount of oleic acid which is measured by TG-DTA. (solid content=0.1g/cc, pH=9.2, Fe_3O_4=20g)
where R=weight ratio of the added amount of oleic acid to Fe_3O_4

In order to develop a proper base oil for the MF, the weight loss of polybutene and spindle oil

Journal of Korean Magnetics Society, Volume 5, Number 5, October 1995

were measured by TG-DTA and the results are shown in Fig. 7. The viscosity of polybutene and spindle oil were almost the same as 1,000cP. In case of polybutene oil, the temperature of weight loss is ≃ 160℃. However, the weight loss of spindle oil starts at a temperature of 200℃. and the spindle oil is evaluated to be more suitable than polybutene oil.

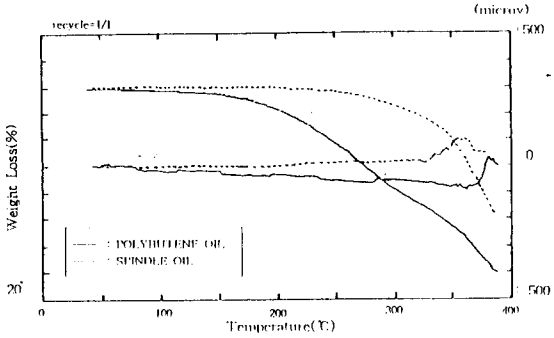

Fig. 7 Thermal analysis of polybutene and spindle oil

Fig. 8 and Fig. 9 shows the variation of saturation magnetization and the viscosity of MF as a function of the added amount of Fe_3O_4 adsorbed surfactant, respectively. In Fig. 8, the M_s increases from 66G to 242G according to the increase of Fe_3O_4 from 10wt% to 60wt%. Therefore, the value of saturation magnetization of the fluid can be adjusted by changing the particle concentration in it.

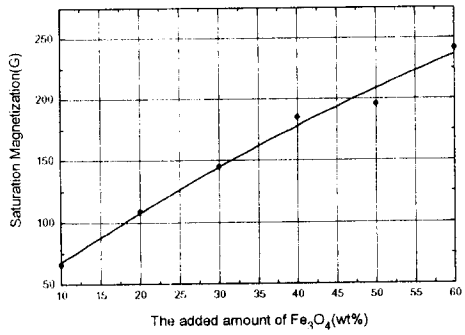

Fig. 8 Variation of the saturation magnetization of spindle oil based MF as a function of the added amount of Fe_3O_4 adsorbed surfactant.

The viscosity of the MF also increases from 1,063 cP to 1828cP according to the increase of the added amount of Fe_3O_4 from 0 to 60 wt%.(see Fig. 9)

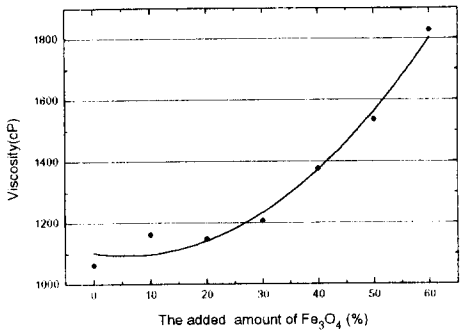

Fig. 9 Variation of viscosity according to the added amount of Fe_3O_4 adsorbed surfactant

Fig. 10 shows the frequency response curve of a speaker when the MF was applied to a commercial 5 cm dome tweeter operating in the frequency range of 20 Hz to 20 kHz. The properties of the MF used in the experiments were M_s=100G and η=1,000cP with spindle base oil. The dome tweeter shows a good transient response because of the excellent damping effect of MF. Without MF, the dome tweeter suffers from a poor transient response.[5]

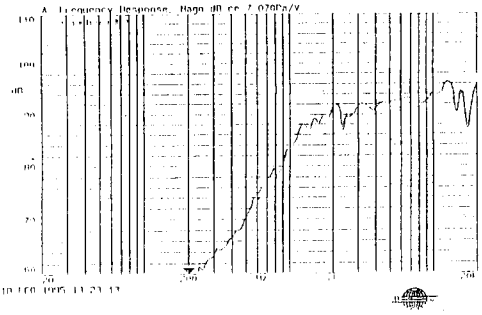

Fig. 10 The frequency response curve for 5 cm dome tweeter

Fig 11. represents the voice coil temperature with MF as a function of input power for 5cm dome tweeter. The temperature of voice coil increased from 57℃ to 196℃ according to the increase of imput power from 5 to 25W. Without MF, the voice coil has a higher temperature than the voice coil with MF. A typical high frequency loudspeaker drive with MF, however, can withstand three times the power input before the coils burn out.[6]

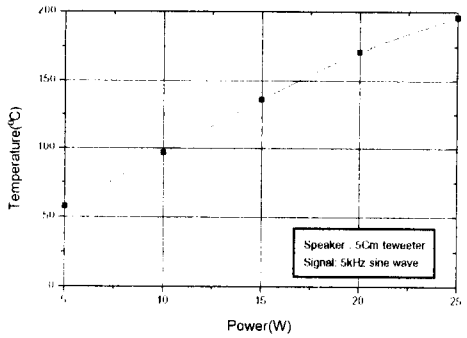

Fig. 11 Voice coil temperature with MF as a function of input power for 5 cm dome tweeter.

Ⅳ CONCLUSION

A preparation method of MF for loudspeaker application was investigated. In this method, the optimum conditions to synthesize ultra-fine Fe_3O_4 were Fe^{2+}/Fe^{3+} = 5 / 6, pH for magnetite precipitation = 9~9.5, and Fe^{2+}_{init} = 0.9mole/l. To obtain a stable dispersion, the limit of adsorbed amount of oleic acid on the Fe_3O_4 surface was approximately 35~40 percents of the magnetite weight and the optimum base oil was spindle oil. The efficiency of dome tweeter was improved by appling the MF developed in the experiments.

REFERENCES

[1] K. Raj and R. F. Moskowitz, IEEE Trans. Magn, MAG-16(1980) 358

[2] Synucgu, Kamiyama, Oyogijutsu Syuppan pub.(Japan), (1987) 184.

[3] J. H. Magee et al., J. Ceramic Bulletin, Vol. 50, No 12 (1971) 966.

[4] You-wei DU et al., J. Magn. Magn. Mat., 31-34 (1983) 896.

[5] K. Raj et al., J. Magn. Magn. Mat. 85(1990) 233.

[6] R. L. Bailey, J. Magn. Magn. Mat. 39(1983) 178.