

STUDIES ON POLYMERIC DISPERSANTS

I. DISPERSION OF γ -Fe₂O₃ IN NON-AQUEOUS MEDIA WITH CARBOXYLATED POLY-n-BUTYL ACRYLATES AS DISPERSANT

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ABSTRACT

Carboxylated poly-n-butyl acrylates were used as model polymeric dispersant. The effect of polymers on the dispersion of γ -Fe₂O₃ in cyclohexanone were studied through sedimentation test and rheological measurement. The polymers with strong anchoring groups at one end of the polymer chain were the most effective polymeric dispersant, which improved magnetic properties of the prepared coatings significantly.

INTRODUCTION

Stabilization of colloidal dispersion by polymer adsorption is of great scientific and technological importance. In aqueous systems, the dispersion can be satisfyingly stabilized by electrostatic interaction of the charged particles. In non-aqueous media of low dielectric constant, however, the charge stabilization is ineffective at high particle concentration^[1], practical stability can only be achieved by means of steric stabilization through polymer absorption. Sufficient bonding strength of the stabilizing polymer to the particle and full solvation of the adsorbed layer were emphasized.

It is commonly accepted that amphibious A-B block copolymers with an anchoring and a solubilizing chain are successful stabilizer for non-aqueous dispersions. As for inorganic powders, where active sites are available for strong interaction, anchoring of the polymer chain can be achieved by chemisorption of a single functional group.

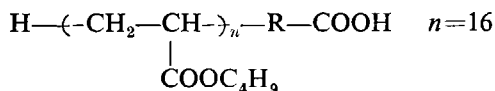
Acicular γ -Fe₂O₃ is widely used in the preparation of magnetic coatings. Due to the magnetic interaction, difficulties are usually met in dispersing the powder. An effective dispersant is therefore eagerly desired^[2]. Nakamae et al.^[3] have studied the relation between polymer adsorption and dispersion of γ -Fe₂O₃ in magnetic coatings. In this work carboxylated poly-n-butyl acrylates were studied as model polymeric dispersant for γ -Fe₂O₃ in non-aqueous media.

EXPERIMENTAL

1. Material

Carboxylated poly-n-butyl acrylates listed in Table 1 were prepared in this laboratory.

AA95BA was a random copolymer of *n*-butyl acrylate and acrylic acid (95:5 by weight). 1CBA was a carboxyl capped poly-*n*-butyl acrylate of the following structure:



2CBA (1) and 2CBA (2) were poly-*n*-butyl acrylate with two adjacent carboxyl groups at one end of polymer chain. 100BA was a homopolymer of butyl acrylate without carboxyl functional group. The $\gamma\text{-Fe}_2\text{O}_3$ powder was provided by the Guang Zhou Magnetic Materials Factory. The specific surface by N_2 adsorption was 16.8 m^2/g .

Cyclohexanone used as dispersing media was analytical reagent. Bisphenol A type epoxy resin E-51 was used as binder for the preparation of magnetic coatings, and 2-ethyl-4-methyl imidazole (EMI-2,4) was used as curing agent.

2. Characterization of the dispersion systems

Sedimentation experiments were carried out in graduated cylinders. A suspension of 2g $\gamma\text{-Fe}_2\text{O}_3$ powder in 24 ml cyclohexanone solution of dispersant (0.4 wt%) was allowed to stand at room temperature and the ultimate sediment volume was measured.

Table 1 Analysis of the polymers

Code	Molecular weight $\bar{M}_n$	Number of carboxyl groups per molecule	Location of the carboxyl groups
100BA	4300	0	—
AA95BA	4200	2.5	Pendant
1CBA	2100	1.2	Terminal
2CBA(1)	3700	1.8	Terminal
2CBA(2)	2300	2.0	Terminal

Rheological properties of the magnetic paints were determined using a rheometer (Rheotest 2 from GDR).

3. Properties of the magnetic coatings

Magnetic paints were prepared with epoxy resin E-51 as binder and EMI-2,4 as curing agent. 10g $\gamma\text{-Fe}_2\text{O}_3$, 10g E-51 epoxy resin, 1g dispersing polymer and 20 ml cyclohexanone were ball-milled. After addition of 1g EMI-2,4 the magnetic film of ca. 0.05mm thickness was cast on a polyester sheet, orientation was conducted in a 3000 Oe magnetic field. The film was cured at 120°C for 3 hrs. Longitudinal squareness S_L and vertical squareness S_V were determined and the orientation ratio S_L/S_V was calculated.

RESULTS AND DISCUSSION

The dispersing ability of the polymers can be examined immediately through smear test. It was conducted in the following way: 1g $\gamma\text{-Fe}_2\text{O}_3$ powder was placed in a crucible. Cyclo-

hexanone solution of the tested polymer was added dropwise while working with a small blade. The least amount of the solution needed to wet the powder was recorded. The smaller the amount of the solution needed, the more effective is the polymeric dispersant. The following order was found according to the effectiveness.

$$2\text{CBA}(1) > 2\text{CBA}(2) \gg 1\text{CBA} > \text{AA95BA} \gg 100\text{BA}$$

A parallel result was obtained by sedimentation experiments. The ultimate volume of the sediments in polymer solution are given in Table 2. The sediment in 2CBA solutions has a much smaller volume. This result denotes that a denser packing of the magnetic particle can be achieved when a 2CBA polymer is used as dispersant.

Table 2 Ultimate sediment volume of $\gamma\text{-Fe}_2\text{O}_3$ in cyclohexanone solutions

Polymer	—	AA95BA	1CBA	2CBA(1)	2CBA(2)
Sediment volume (ml/g)	4.2	3.9	3.5	2.2	2.6

Rheological property of the magnetic paints is greatly affected by polymeric dispersants. In Fig. 1 are given the rheological curves. The paint containing 2CBA has a viscosity obviously lower than those containing 100BA and 1CBA. The reduction of viscosity means the inter-particulate attraction diminishing in the presence of the polymer. The experiments indicate that 2CBAs are effective dispersant.

Magnetic properties are essential for the application of magnetic recording material.

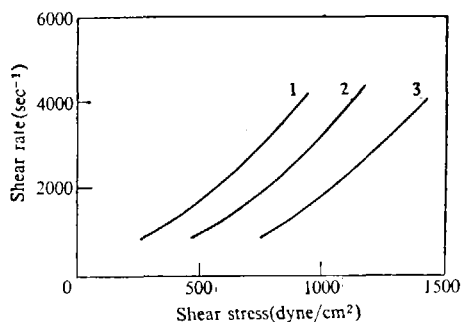


Fig. 1 Rheogram of magnetic paints after 24 hrs ball-milling
1. 2CBA(2); 2. 1CBA; 3. 100BA.

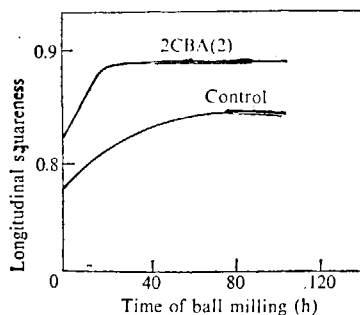


Fig. 2 Change of longitudinal squareness with ball-milling

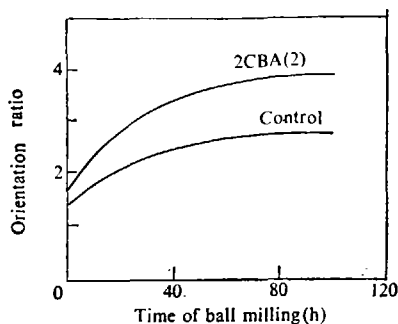


Fig. 3 Change of orientation ratio with ball-milling

They are greatly affected by the degree of dispersion of magnetic particles in the coating. The movement of acicular particles in the vehicle is hindered by agglomeration and flocculation of particles, as a result the longitudinal squareness and the orientation ratio are reduced. Thus, magnetic properties can be taken as final criterion of the level of dispersion.

Fig. 2 shows the increase of longitudinal squareness of magnetic coatings with ball-milling of the paints. For the formulations/containing 2CBA(2), the squareness reaches a limit value after 24 hrs milling whereas without polymeric dispersant the squareness approaches a lower limit after milling for more than 70 hrs. The orientations ratio changes with ball-milling of the paints in similar way (Fig. 3). It is quite evident that the dispersion of magnetic powder is much easier in the presence of 2CBA(2).

A comparison of the polymeric dispersants is given in Table 3. Magnetic properties were improved by 2CBA(2) most significantly while no improvement was given by 100BA.

Table 3 Magnetic properting of the coatings

Polymer dispersant	2CBA(2)	1CBA	100BA	Control
Longitudinal squareness	0.88	0.86	0.82	0.81
Vertical squareness	0.32	0.34	0.41	0.36
Orientation ratio	2.72	2.54	1.98	2.30

REFERENCES

- [1] Sato, T. and Ruch, R., "Stabilization of Colloidal Dispersion by Polymer Adsorption", Marcel Dekker Inc., 1980.
- [2] Kober, H. and Wimbersky, W., *Farbe und Lack*, 1978, 84 (5), 306.
- [3] Nakamae, K., Sumiya, K. and Matsumoto, T., *Prog. Org. Coat.*, 1984, 12, 143.