Colloid & Polymer Science Colloid Polym Sci 272:1104–1110 (1994)

Synthetic process to control the total size and component distribution of multilayer magnetic composite particles

K. Furusawa[1]), K. Nagashima[2]), and C. Anzai[3])

[1]) Department of Chemistry, University of Tsukuba, Ibaraki, Japan.
[2]) Department of Industrial Chemistry, Science University of Tokyo, Tokyo, Japan.
[3]) Hoechst Gosei Co. Ltd., Shizuoka, Japan.

Abstract: A new synthetic process to prepare composite particles with multilayers, comprised of usual polymer latices, ultra-fine magnetic particles, and a polystyrene layer was examined under various solution conditions.

First, the synthetic conditions of heterocoagulates, consisted of polystyrene latices ($2a = 180 \sim 900$ nm) and $NiO \cdot ZnO \cdot Fe_2O_3$ particles ($2a = 20$ nm), were investigated as a function of medium pH, particle concentration, and particle size ratio, based on the concept of the heterocoagulation theory as applied by Harding et al. Regular heterocoagulates were generated under suitable medium and mixing conditions, and that their total size can be controlled by selecting the size of the original polymer latices used as the core.

Second, the best encapsulation condition of the heterocoagulates via emulsion polymerization with polystyrene monomer was surveyed. The encapsulation of the heterocoagulates was greatly promoted by pretreatment with oleate molecules, although there is no tendency for the encapsulation when the surfactant-free bare heterocoagulates are used as the core.

Key words: Composite particles – heterocoagulation – magnetic particles – encapsulation – seed polymerization

1. Introduction

The exceptional uniform shape and the wide diameter range of latex particles are of interest because their combination with other dispersion systems should extend their application in the field of academic research as well as industrial material development. Especially, on the synthesis of composite particles comprised of organic and inorganic substances, the adoption of monodispersed polymer latices as their one component largely expands the variety of composite particles because many techniques to prepare latex samples with different sizes and structures have already been developed.

Up to now, we have been investigating inorganic–organic composite particles using monodispersed spherical silica-amphoteric latices and α-alumina powder-ionic latices with regard to their preparation, the behavior of their generation process, and their characteristics. Through research, it was confirmed that the solution conditions of each dispersion, i.e., pH of medium, electrolyte concentration, and particle number ratio, dominate the process of heterocoagulation between those two different particles [1–3].

In the synthesis of inorganic–organic composite particles, the establishment of a method to control the orientation of each element should be regarded as an important factor, because the characteristics of the composite particles largely depend on the orientation of the component particles. Simultaneously, since the function of the composite particles is frequently determined by their size and uniformity, the development of a way to fix the particle diameter in a narrow size distribution is also indispensable. In practice, for example, when some magnetic composite particles are applied for the separation of T-cells from B-cells (grounded on the difference of magnetism

between composite particles and these cells), it can be considered that the further out the magnetic particles are in the composite particles, the more efficiently the separation proceeds. Moreover, when immune latices, on which surface some antibodies are placed, are applied for diagnosis of pathological symptoms, their shape uniformity and particle size dramatically effect the accuracy [4].

Aiming at the systematic resolution of these problems, the synthesis method and the properties of the magnetic particles were investigated adopting the concept of heterocoagulation theory; heterocoagulates were prepared from magnetic ultra-fine powder ($NiO \cdot ZnO \cdot Fe_2O_3$; $2a = 20$ nm) and four types of monodispersed negative latices with different particle diameters ($2a = 180 \sim 900$ nm) and functional groups ($-SO_3^-$, $-COO^-$). In addition, the optimum condition for encapsulating the heterocoagulates was surveyed; multilayer composite particles were prepared by emulsion polymerization in which a polystyrene layer was formed on the surface of the heterocoagulates.

2. Experimental

2.1. Materials and characterization

As an inorganic material, the magnetic ultra-fine powder $NiO \cdot ZnO \cdot Fe_2O_3$ offered by Sumitomo Chemical Co. Ltd. was used without further purification. On the other hand, four different polystyrene latices were employed as organic species. The latex-L is a standard sample offered by Japan Synthetic Rubber Co. Ltd. The other three latex samples, the latex-M, the latex-S, and the latex-SS, were synthesized by surfactant-free emulsion polymerization in our laboratory. All of these latex samples were used after sufficient dialysis in purified water and subsequent ion exchange treatment with resin grains. The particle sizes of the samples were evaluated by transmission electron microscopy (100CX; Hitachi Electronics Co. Ltd.) and by dynamic light scattering measurement (ELS-800; Ohtsuka Electronics Co. Ltd.). The diameter and functional group of each sample are listed in Table 1. The behavior of each particle in bulk was observed with a lateral type metallurgical microscope (Axio Mart 2; Carl Zeiss Co. Ltd.) and the morphology was confirmed using a scanning electron microscope (JSM-25; NEC Co. Ltd.).

Table 1. Diameter and functional groups of samples

Sample	Diameter (nm)	Functional group
Latex-L	900	$-COO^-$
Latex-M	600	$-COO^-$
Latex-S	530	$-SO_3^-$
Latex-SS	180	$-SO_3^-$
$NiO \cdot ZnO \cdot Fe_2O_3$	20	–

2.2. Measurements of ζ-potential

The electrophoretic mobilities of four kinds of polymer latices, magnetic particles and heterocoagulates were examined in 1×10^{-3} mol/dm^3 potassium nitrate aqueous solutions adjusted at various pH levels. The measurements were performed using a micro-electrophoresis apparatus (MK-2; Rank Brother Co. Ltd.) using a rectangular cell. The procedure followed the method in the literature [5]. The determined electrophoretic mobility was converted into ζ-potential using Henry's equation.

2.3. Preparation of heterocoagulates

The procedure to prepare the heterocoagulates from the latex-M and the magnetic particles is given here for illustration.

To begin with, 200 ml of pure water was added to a beaker containing 0.25 g of the magnetic powder and sonicated for 20 min with a 600 W homogenizer (T-180; Ultrasonic Co. Ltd.) at the best tuning. Meanwhile, the original latex-M dispersion was diluted with purified water to control the particle number ratio to magnetic particles at 1/4500. These two suspensions were quickly blended and ultrasonic emission was used for another 3 min to promote complete mixing. Next, the pH of the blend suspension was adjusted with nitric acid to pH 2.5 to insure that each particle acquired the opposite charge to one another. After the suspension was kept for 24 h at room temperature, the heterocoagulates, comprised of the latex-L (core) and the magnetic particles (shell), accumulated at the bottom of the vessel. The supernatant was replaced by purified water to

remove the residual magnetic particles which did not adhere to the latex surface. The product was repeatedly washed in purified water and kept in a stock bottle. Approximately 0.5 g of the heterocoagulates can be obtained by this procedure.

2.4. *Thermogravimetry*

Thermogravimetric analysis was conducted to clarify the composition of the heterocoagulates prepared from the latex-M and the magnetic particles using a thermoanalyzer (SSC/560; Seiko Co. Ltd.). The experiments were carried out using a previously described procedure [2].

2.5. *Encapsulation polymerization of heterocoagulates*

The heterocoagulates were encapsulated with a polystyrene layer via emulsion polymerization to prepare multilayer composite particles. The conditions for the emulsion polymerization are shown in Table 2. The heterocoagulates prepared from the latex-M were used as the seeds after 24 h dialysis in purified water. Approximately 0.2 g of the seed heterocoagulates was dispersed into 180 ml of water using the homogenizer, before it was moved into a special 200 ml vial with a screw cap. After that, distilled water containing a definite amount of potassium persulfate ($K_2S_2O_8$) and sodium oleate ($C_{17}H_{33}COONa$) was carefully added to the vial. The pH of the sodium oleate aqueous solution was primarily adjusted to pH 6.0 with nitric acid, because the magnetic particles on the heterocoagulates desorb from the latex surface in the alkaline medium (Fig. 2). This vial was set on the rotating disk of polymerization equipment and polymerized for 36 h at 60 °C.

Table 2. Operating conditions of thermogravimetry

Apparatus	SSC/560 SEIKO
TG range	0 ~ 100 [%]
Program rate	10 [°C/min]
Temperature range	10 [mV]
Chart speed	20 [cm/h]
Sample pan	Pt
Reference	Pt open pan
Gas	Air [200 ml/min]

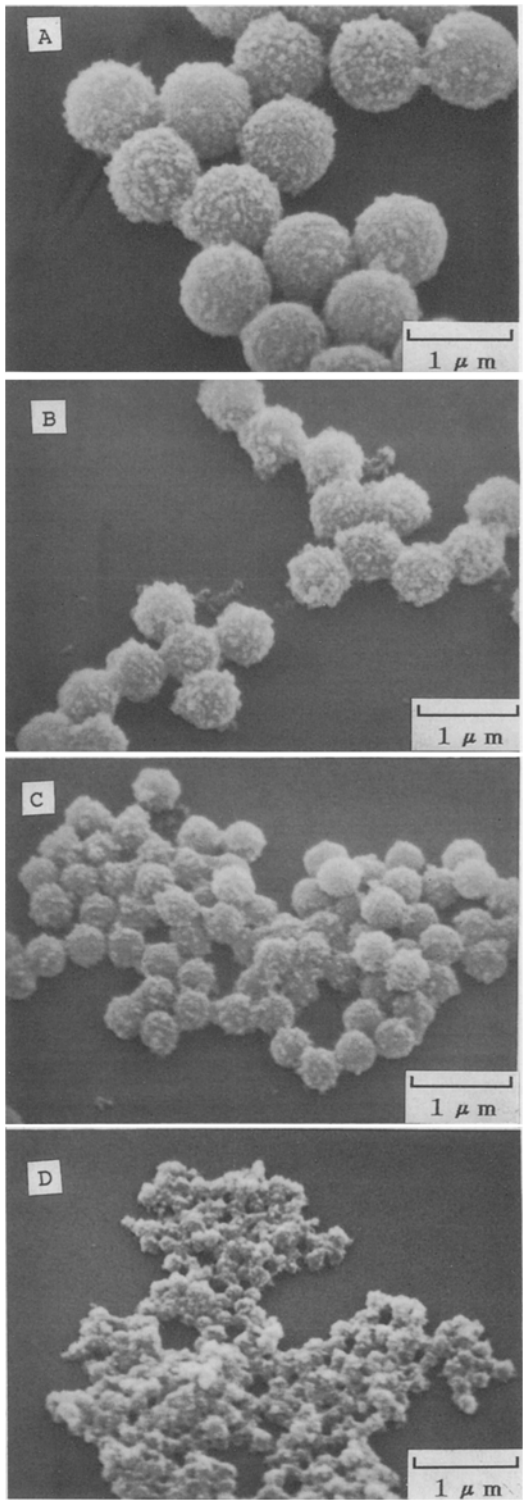

Fig. 1. Electron micrographs showing the heterocoagulates prepared from different latex samples: A) latex-L; B) latex-M; C) latex-S; D) latex-SS.

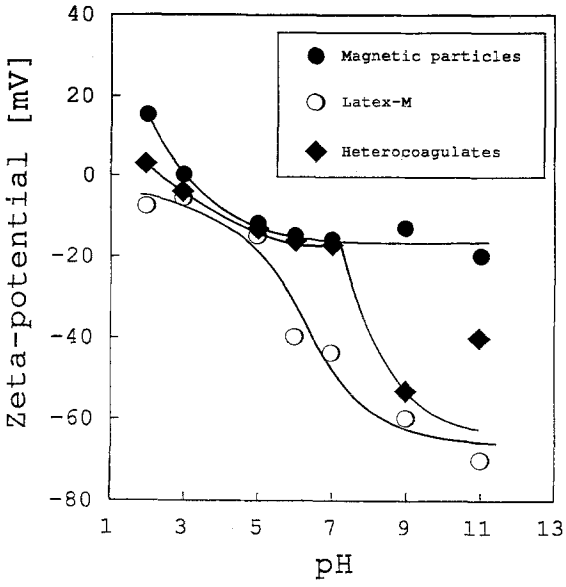

Fig. 2. Zeta-potential of $NiO \cdot ZnO \cdot Fe_2O_3$ particles (●), latex-M (○) and heterocoagulates (◆) as a function of pH at 10^{-3} M KNO_3.

3. Results and discussion

3.1. Heterocoagulation behavior and characterization

The dry powder of $NiO \cdot ZnO \cdot Fe_2O_3$ was compulsorily dispersed into ion-exchanged distilled water by intense ultrasonic emission for about 20 min. Nevertheless, the dynamic light-scattering measurement confirmed that the magnetic particles in the bulk were comprised of associated islands with the diameter of 250 nm, although the transmission electron micrographs showed the individual particle diameter to be 20 nm on average. It can be considered that this fact is due to their magnetism or to the peculiar hydrophobicity of dry powder.

Scanning electron micrographs (see Fig. 1) show four kinds of heterocoagulates provided from the suspensions of latices with different sizes and magnetic particles. All of these heterocoagulates were prepared by mixing the $NiO \cdot ZnO \cdot Fe_2O_3$ dispersion and the respective latex dispersions at pH 2.5 where the ζ-potential of the magnetic particles has the opposite sign to that of the latex particles as shown in Fig. 2. The heterocoagulates generated from the latex-L, the latex-M, and the latex-S are composed of the uniform composite particles depositing the small magnetic particles onto the large latex surfaces and all the heterocoagulates are separated as an isolated unit having an even surface. In contrast with these particles, the heterocoagulates prepared from the latex-SS are made of large irregular aggregates and the regular heterocoagulates were difficult to recognize under any mixing conditions investigated. This means that their heterocoagulation behavior does not adhere to the rule of Harding et al. [6]; larger particles are surrounded by smaller particles. Furthermore, it should be noted that the heterocoagulates took over the uniformity as the original latex particles under the suitable mixing conditions. The composite particles were formed by the heterocoagulation of the magnetic particles onto the large latex particles with a constant layer, and they exactly maintain the uniformity of the latex particles after the heterocoagulation with the magnetic particles.

In Fig. 2, the ζ-potential profile of the latex-M particles and the magnetic particles are presented as a function of medium pH, along with that of the heterocoagulates prepared by mixing their original suspensions at pH 2.5. The heterocoagulates display zero ζ-potential at pH 2.5 due to the charge neutralization between the two component particles. This suggests that the rapid sedimentation of the products after the heterocoagulation is attributed to the homoaggregation of the products rather than to the increase of their diameter or density. However, the dynamic light-scattering measurement and the transmission electron microscopy confirm that the aggregated products are re-dispersed into single particles by moderate ultrasonication without any desorption of the magnetic particles from the surfaces of the composite particles. Furthermore, Fig. 2 indicates that the ζ-potential of the heterocoagulates approaches that of the original magnetic particles in the alkaline medium. This behavior suggests that the magnetic particles, which cover the surface of the core latices in the acid and neutral pH systems, desorb from their surface in the alkaline system where the pH is above 9. This implies that the interaction between the surfaces of the two component particles changes from lateral electrostatic attraction into electrostatic repulsion according to the increase of medium pH. From these results, it can be seen that the pH of the system largely dominates the following three aspects of

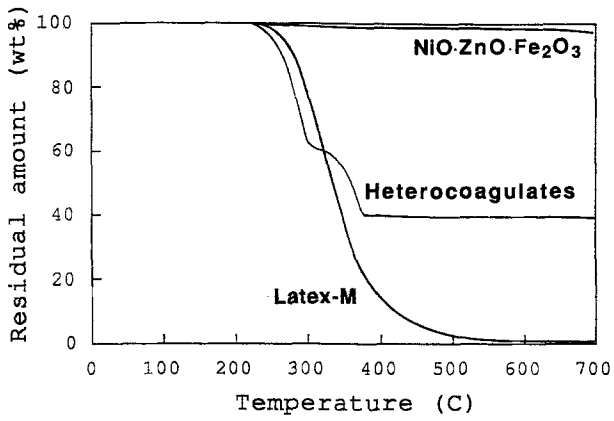

Fig. 3. Thermograms of latex-M, $NiO \cdot ZnO \cdot Fe_2O_3$ particles, and heterocoagulates.

the heterocoagulates; the generation and sedimentation in the acid system, the dispersion in the neutral pH region due to their high surface charge, and the decomposition in the alkaline system.

Figure 3 shows the thermograms of the magnetic particles, the latex-M particles, and the heterocoagulates prepared from these two kinds of particles. The measurements were carried out under the conditions shown in Table 2. The rate of mass decrease for the magnetic particles was 2.0 to 2.3% during the temperature transition from 100° to 600 °C, while the result of the latex-M was complete decomposition. The thermogram curve of the heterocoagulates exhibits a slow steady mass decrease below 200 °C, a noticeable loss around 350 °C, and a plateau above 400 °C. The residual amount above 400 °C is considered to be the weight of magnetic particles which did not decompose. As a result, the composition of the heterocoagulates is calculated to be 60.7% latex-M and 39.3% $NiO \cdot ZnO \cdot Fe_2O_3$ particles by weight percent. The application of the model proposed by Hansen et al. [7] (which assumes that the latex-M and $NiO \cdot ZnO \cdot Fe_2O_3$ are sphere particles with diameters of 600 nm and 20 nm respectively) calculates the fractional coverage of the heterocoagulates (θ) to be ca. 1.0. This high coverage is attributed to the formation of the multi-particle layers of the magnetic particles on the latex surfaces, which resulted in the peculiar adsorption mechanism; the associated magnetic particles adhere on the surface of the core latices in the heterocoagulation process as if the islands were single particles.

3.2. *Encapsulation of heterocoagulates*

Concerning the heterocoagulates, both desorption of the magnetic particles and dissolution of ion species decrease their value as bioreactors because they inactivate biological functions. Hence, the optimal condition of encapsulation polymerization, in which the heterocoagulate surface is covered with a thin polystyrene layer, was surveyed. The conditions and their results are shown in Table 3. After 24 h on dialysis, a fixed amount of the heterocoagulates prepared from the latex-M was used to examine the eight polymerization conditions set up with regard to the amount of styrene monomer, the kind of initiator, and the presence of a surfactant. An initiator

Table 3. Conditions for encapsulation polymerization of heterocoagulates (temp. 60 °C, scale 200 ml, stirring speed 30 rpm, time of polymerization 36 h)

Sample number	1	2	3	4	5	6	7	8
Seed composite [g]	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Styrene monomer [g]	0.2	1.0	0.2	1.0	0.2	1.0	0.2	1.0
KPS [g]	10^{-3}	10^{-2}	10^{-3}	10^{-2}	–	–	–	–
AIBA·2HCl [g]	–	–	–	–	10^{-3}	10^{-2}	10^{-3}	10^{-2}
Sodium oleate [g]	–	–	0.06	0.06	–	–	0.06	0.06
PRODUCT	×	×	⊙	×	×	×	△	×

KPS; potassium persulfate
AIBA·2HCl; azo-bis(isobutylamidine hydrochloric acid)
⊙; good encapsulation, △; encapsulation and new particle generation,
×; flocculation or new particle generation, or both.

Table 4. Conditions for encapsulation polymerization of heterocoagulates. (temp. 60 °C, scale 200 ml, stirring speed 30 rpm, time of polymerization 36 h)

Sample number	9	10	11	12	13	14	15
Seed composite [g]	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Styrene monomer [g]	0.2	0.2	0.2	0.2	0.2	0.2	0.2
KPS [g]	10^{-3}	10^{-3}	10^{-3}	10^{-3}	10^{-3}	10^{-3}	10^{-3}
Sodium oleate [g]	0.003	0.006	0.03	0.06	0.12	0.30	0.60
PRODUCT	×	×	⊙	⊙	△	×	×

⊙; good encapsulation, △; encapsulation and partially no reaction, ×; flocculation or decomposition.

which provides a positive terminal group, azo-bis(isobutylamidine hydrochloric acid) was employed, while potassium persulfate was selected as a negative-terminal initiator. Moreover, sodium oleate aqueous solution was adopted to promote hydrophobicity of the magnetic particles on the heterocoagulate surfaces. As seen in the line of Product on Table 3, it is considered that the best condition in the list is the system No. 3 where ideal encapsulation was virtually accomplished. Under the conditions of the system No. 1, No. 2, No. 5, and No. 6, bridging flocculation among the seed particles or the generation of independent latex particles occurred in the course of the polymerization. Similarly, in the system No. 4, No. 7, and No. 8, the flocculation and new particle generation were observed although a part of the seed particles were encapsulated. As a result, it can be considered that sodium oleate is indispensable for the encapsulation of the heterocoagulates, and that potassium persulfate is a suitable initiator for this system.

Furthermore, as pointed out in Table 4, under similar conditions to the system No. 3 (the same amount of seeds, potassium persulfate, and styrene monomer), the encapsulation polymerization was carried out at various sodium oleate concentration ranges from 0.003 to 0.60 g/200 ml. Below the concentration of 0.01 g/200 ml, the seed particles aggregated soon after the vials were equipped, while above 0.1 g/200 ml, desorption of the magnetic particles from the seed particle surface occurred. Consequently, the concentration of sodium oleate has to be adjusted in the range from 0.01 to 0.1 g/200 ml for the encapsulation. This fact suggests that the adsorption state of oleate ion onto the seed particle surface largely affects the process of encapsulation polymerization.

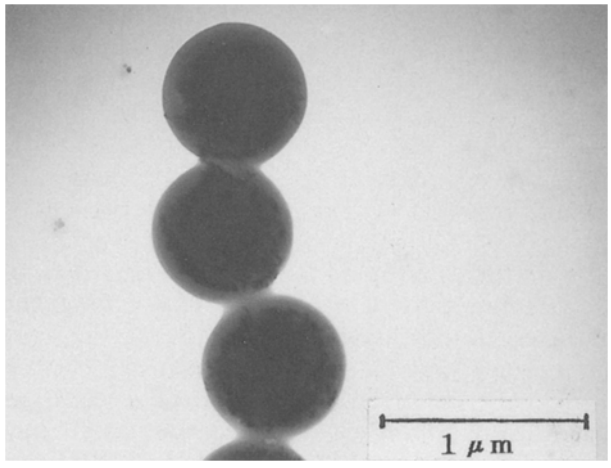

Fig. 4. Microphotograph showing the multilayer composite particles after the encapsulation polymerization.

Figure 4 is a transmission electron micrograph of the encapsulated composite particles whose surface was covered with a thin polymer layer, and it shows smoother surface than that of the seed particles (Fig. 1).

4. Conclusion

Figure 5 shows the preparation process of the multilayer magnetic composite particles.

1) The heterocoagulates were produced from the magnetic ultra-fine powder and the polymer latices with various sizes and functional groups. In this case, the particle size ratio and the ξ-potential of the two components should be noted in order to prepare the heterocoagulates whose fractional coverage is ca. 100%. The prepared heterocoagulates take over the uniformity of the

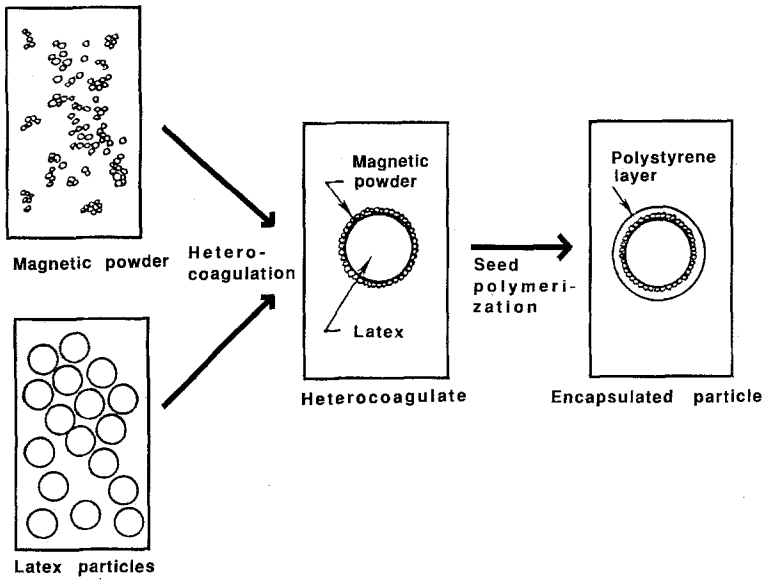

Fig. 5. Schematic picture showing the process of synthesizing the multilayer composite particles.

latex particles adopted as the core. However, in the alkaline system above pH 9, the magnetic particles desorb from the surface of the core latices.

2) Using the heterocoagulates as the seeds, the optimum condition of encapsulation polymerization with styrene monomer was surveyed. In this case, it is indispensable to promote the hydrophobicity of the heterocoagulate surface with oleate ions. With the proper control of their adsorption state, the encapsulation is promoted efficiently.

3) As is seen in Fig. 5, the size of multilayer composite particles can be controlled by the diameter of the core latices which are applied primarily. This method realizes the localization of the magnetic particles on the outside of the composite particles covered with a thin polystyrene layer, therefore, they can give full function to the surrounding system.

Acknowledgement

The authors gratefully acknowledge the cooperation of the sample providers and the collaborators: Sumitomo Chemical Co. Ltd. for the magnetic ultra-fine powder $NiO \cdot ZnO \cdot Fe_2O_3$; Japan Synthetic Rubber Co. Ltd. for the latex-L; Prof. Dr. Kijiro. Kon-no, Department of Industrial Chemistry, Science University of Tokyo, for his cooperation in the off-campus research at University of Tsukuba; and to all students, past and present, who have been concerned with this work.

References

1. Furusawa K, Kimura Y, Tagawa T (1986) J Colloid Interface Sci 109:69
2. Furusawa K, Anzai C (1987) Colloid Polym Sci 265:882
3. Furusawa K, Anzai C (1992) Colloids and Surfaces 63:103
4. Rembaum A, Yeni SPS (1979) J Macromol Sci Chem A13:603
5. Wiersema EH, Loev AL, J.Th.G. Overbeek (1966) J Colloid Interface Sci 22:78
6. Harding RD (1972) J Colloid Interface Sci 40:164
7. Hansen FK, Matijevic E (1978) J Chem Soc Faraday Trans, 1, 76:1240

Received May 27, 1993;
accepted November 17, 1993

Authors' address:

Professor Dr. Kunio Furusawa
Department of Chemistry
University of Tsukuba
1-1-1 Tennodai
Tsukuba-shi
Ibaraki 305,
Japan