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The Interaction of Pigment with Polystyrene Latex Particles Prepared Using an Amino-Acid-Type Amphoteric Emulsifier

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An emulsion polymerization of styrene in the presence of an amino-acid type amphoteric emulsifier (N^{ϵ}-lauroyl-N^{α},N^{α}-dimethyllysine (DMLL)) was carried out at pH 7.0. The stability of mixed dispersions containing the latex particles prepared with DMLL and titanium dioxide (TiO_2) was then discussed as a function of the pH in a mixed dispersed solution. The zeta-potential of the synthesized latex particles was significantly dependent on the pH and showed the existence of an isoelectric point (IEP) at pH 4.5. On the other hand, TiO_2 particles had their IEP at pH 8.5. Below pH 4.5 and above pH 8.5, the mixed dispersions of the synthesized latex particles and TiO_2 particles were well-dispersed because of their electric repulsion. In the range of pH 4.5—8.5, where the latices were negatively charged, while the TiO_2 were positively charged, at low concentrations of the latex particles the mixed suspension was dispersed, but with an increase in the number of latex they heterocoagulated and were then redispersed at high concentrations of the latex particles. The mechanisms of these processes are discussed.

Latices are added to various pigments in order to achieve many industrial objectives, for example, increases in weatherability, storage stability, and pigment compatibility, and good resistance against alkaline reagents and water. Further, latices play two important roles as film formers and binders. Therefore, it has become a very important problem to study the interaction of pigments with latices.

There have been many reports on mixed dispersion systems containing latices and inorganic pigments by measuring the turbidity, the sedimentation velocity, the sedimentation volume, the viscosity, the particle size, and the surface potential.[1–7] In general, the surface charge of the latex particles prepared using a conventional anionic emulsifier is hardly dependent at all on the pH of their suspended solution, and they have a negative charge everywhere over the pH. On the other hand, normal pigments which are used for coating or painting are almost all dependent on the pH, since H^+ or OH^- acts as a potential determining ion. The pigment particles have a positive charge below the isoelectric point (IEP) and have a negative charge above the IEP. Therefore, in the pH range below the IEP, the mixed aqueous suspension of the latex particles and pigment particles is composed of a loose three-dimensional network structure with an electric force of attraction between the positively charged inorganic pigment and the negatively charged latex particles.

We have previously reported the surface properties of styrene latex prepared by emulsion polymerization in the presence of N^{ϵ}-lauroyl-N^{α},N^{α}-dimethyllysine (DMLL) as an amphoteric emulsifier, and have found that the latex particles exhibit characteristic properties: they change their surface potential with their pH, and they have an isoelectric point, since the ionic form of the DMLL molecules adsorbed onto the latex surfaces alters with the pH.[8] However, there have been only a few reports relating to the interaction of inorganic pigments with latices prepared by using amphoteric surfactants.

In this work, the effect of the addition of latex particles prepared with DMLL to inorganic pigments on mixed dispersion systems was investigated in respect with the pH of their suspended solutions.

Experimental

Materials. $C_{11}H_{23}CONH(CH_2)_4CH[N(CH_3)_2]COOH$ (DMLL) supplied by the Ajinomoto Co., Ltd., was purified by repeated recrystallization from mixture of hexane and 2-propanol (7:3) and then carefully dried in vacuo before use. The purity of the sample was confirmed by the absence of a minimum in its surface tension vs. concentration curve.

The styrene monomer (Wako Pure Industries, Ltd.) was distilled under a nitrogen atmosphere and was stored in a refrigerator under nitrogen. The potassium peroxodisulfate ($K_2S_2O_8$) used as an initiator was of an analytical grade, supplied by Wako Pure Industries, Ltd.

Titanium dioxide (TiO_2 (rutile)), with a surface treated by Al_2O_3 and supplied by Teikoku Kako Co., Ltd., was used. The characteristics of this pigment are indicated in Table 1. The specific surface area of the pigments was measured using a Shimadzu GAS CHROMATOGRAPH GC-7A connected with a Shimadzu SORPTOGRAPH ADS-1B and was determined by applying the BET theory to the nitrogen adsorption at the temperature of liquid nitrogen.

Table 1. Characteristics of TiO_2 Particles

Pigment	Density	Particle size	Specific surface area
	g cm^{-3}	nm	m^2 g^{-1}
TiO_2 (rutile)	4.2	326.8	19.1

Procedure. An isoelectric region of the DMLL solution has been determined using the method described in a previous paper.[8]

Preparation of Latex Particles. The emulsion polymerization was performed in a one-liter glass reactor, fitted with a metal screw and a thermometer. The emulsion polymerization recipe is shown in Table 2. First, water and emulsifier (DMLL) were added to the reactor at room temperature, and then styrene monomer was added to them. The reaction flask was immersed in a constant-temperature bath adjusted to 60±1 °C under a nitrogen atmosphere, and the mixture was stirred at 250 rpm. After the temperature had risen to 60 °C, an aqueous solution of $K_2S_2O_8$ (0.1 g/50 cm^3) was added to the contents of the reactor, resulting in the final initiator concentration (0.1 g/300 g of the mixture). The polymerization time was taken as 3 h. The particle diameter of the synthesized latex particles was determined by means of Transmission Electron Microscopy and by the use of a particle sizer. The molecular weight distribution of polystyrene in the latices was determined by use of a GPC. The number of latex particles per cubic decimeter of the aqueous solution (N) was calculated by means of the particle size and the conversion, which was estimated by means of the (polystyrene latex/styrene monomer) ratio.

Interaction of Pigment with the Latex. The mixed systems of polystyrene latex and TiO_2 were prepared by the following method: First, a known weight of TiO_2 was put into 27 cm^3 of a 10^{-3} mol dm^{-3} sodium chloride aqueous solution in a sedimentation tube. This suspension was dispersed by the use of supersonic waves for an hour, and then 3 cm^3 of a styrene latex suspension was added to it. The mixed suspensions were adjusted to various pH values. After 48 h of standing, the turbidity of the suspension collected from the top portion of the sedimentation tube was measured with a turbidimeter (SEP-PT 501, Nippon Precision Optical Instrument Co., Ltd.).

The zeta-potentials (Zp) of the latex particles and TiO_2 were measured at 25 °C by means of an electrophoresis apparatus [Laser Zee TM Model-500 (PEN-KEM, Inc.)]. The amounts of latex particles adsorbed onto the surface of the TiO_2 particles were determined by means of the difference between the weight of the latices before and after the adsorption.

All of the suspensions for measuring the particle size, the electrophoresis, and the turbidity were prepared with a 10^{-3} mol dm^{-3} sodium chloride aqueous solution in order to keep the ionic strength as constant as possible. The pH of the suspension was adjusted by the addition of sodium hydroxide or hydrochloric acid.

Table 2. Emulsion Polymerization Recipe

Ingredient	Gram
Styrene	50
Water	250
Potassium peroxodisulfate	0.2
N^{ϵ}-Lauroyl-N^{α},N^{α}-dimethyllysine(DMLL)	6.0

Results and Discussion

Characterization of DMLL. DMLL has both acidic and basic groups in the same molecule, and can change its ionic form depending on the pH value of its aqueous solution. DMLL aqueous solutions have a wide isoelectric region ranging from pH 4 to 9: the cationic structure predominates below pH 4, and the zwitterionic one occurs in the range of pH 4—9, whereas the anionic one exists mainly above pH 9.[8–11]

Characterization of the Latex. In the emulsion polymerization of styrene in the presence of DMLL at pH 7.0, it was confirmed that the final latices were stable. The number-average particle diameter (D_n) and its polydispersity (D_w/D_n), as measured by Transmission Electron Microscopy, the z-average particle diameter (D_z) and its polydispersity (Q fac.), as measured by a particle sizer, and the weight-average molecular weight (M_w) and the distribution of the synthesized latex (M_w/M_n) are summarized in Table 3. From the two polydispersities, which give an indication of the breadth of the particle size distributions, it can be seen that the particle size of latex formed with DMLL has a relatively narrow distribution and that the latex consists of rather monodispersed microspheres.

Zeta-Potentials of the Latex and TiO_2. The

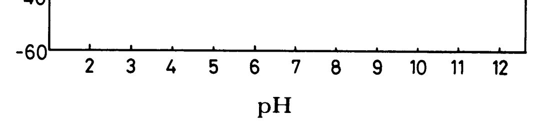

Fig. 1 The change in zeta-potentials of latex particles synthesized with DMLL and TiO_2 particles.

Table 3. Characteristics of the Latex Particles Prepared in a DMLL Solution

Particle size			
Dn/nm	Dw/Dn	Dz/nm	Q.f
48.4	1.07	59.9	0.05
Molecular weight			
Mw(×10^6)		Mw/Mn	
1.94		5.24	

change in the zeta-potentials of the latex particles and TiO_2 as a function of the pH is shown in Fig. 1. All the curves had an extended S shape, and the zeta-potentials were largely dependent on the pH.

The latex particles had an isoelectric point (IEP) at pH 4.5. They were positively charged below IEP, while they were negatively charged above it. This variation in the zeta-potential of the latex particles with the change in the pH of the solution is attributable to DMLL molecules adsorbing onto the surface of the latex particles.

TiO_2 had a positive charge below pH 8.5, and its zeta-potential became negative with an increase in the pH. TiO_2 had an isoelectric point at pH 8.5.[12)]

The Mixed System of Polystyrene Latex and TiO_2. The change in the turbidity of the mixed suspension with the particle number (*N*) of the latices at a constant pH (3.0, 5.0, 11.0) is shown in Fig. 2. Here, the amount of TiO_2 added was 10.0 mg. In this figure, a high turbidity means a good titania dispersion and a low one for flocculation. On the measurement of the turbidity, TiO_2 particles were clearly detected, but hardly any latex particles were detected.

At pH 3.0, the turbidity even slightly increased upon the addition of a number of the latex particles, indicating that the mixture of TiO_2 and the latex particles is well-dispersed throughout the range of the number of latex particles (*N*). At pH 11.0, since the turbidity was constant throughout the range of *N* values, the mixed suspension was also well-dispersed.

Figure 3 shows the zeta-potentials of TiO_2 particles in the mixed suspension as a function of the *N*. At pH 2.5 and 3.0, *Zp* was constantly positive. At pH 10.0 and 11.0, *Zp* was constantly negative. Since the latex particles and TiO_2 particles are both positively charged below pH 4.5, the good dispersion of their mixed suspension occurs by means of the positive mutual electric repulsion between hetero particles.[13)–15)] Similarly, above pH 8.5 it is understood that the mixtures are well-dispersed as a result of the mutual electric repulsion between these negatively charged particles.

At pH 5.0, as may be found from Fig. 2, at a low concentration of the latex particles the mixed suspensions are in the dispersed state, but with an increase in the number of latices they are heterocoagulated until they redisperse at a high concentration of the latex particles. At this pH, the polystyrene latex particles have a negative charge, while TiO_2 particles are positively charged.

In order to evaluate in more detail the interaction between the latex and TiO_2 with a different charge, the changes in the turbidity of the mixed suspension with N were measured at the constant pH values of 5.0, 6.0, and 7.0: These results are also shown in Fig. 2. At these pH values (pH 5.0, 6.0, and 7.0), the flocculation and the redispersion of the mixed suspensions were also observed. In the pH range of 4.5—8.5, the mixed aqueous suspensions of the latex particles and pigment particles were composed of a loose three-dimensional network structure. It may be found from Fig. 3 that the particle number of the latex at which the flocculation occurs shifts toward lower numbers of latex particles (*N*) with an increase in the pH.

The changes in the zeta-potential of the mixed suspension at a constant pH (5.0, 6.0, 7.0) with log *N* are shown in Fig. 4. The zeta-potential of TiO_2 altered from positive to negative with the increase in *N* and showed a zero point of charge. The particle number of the latex (*N*) at the zero point of the charge shifted toward a lower *N* with an increase in the pH. It was confirmed that the particle number of the latex at the zero point of charge was in good agreement with that at the flocculation of the mixed suspension.

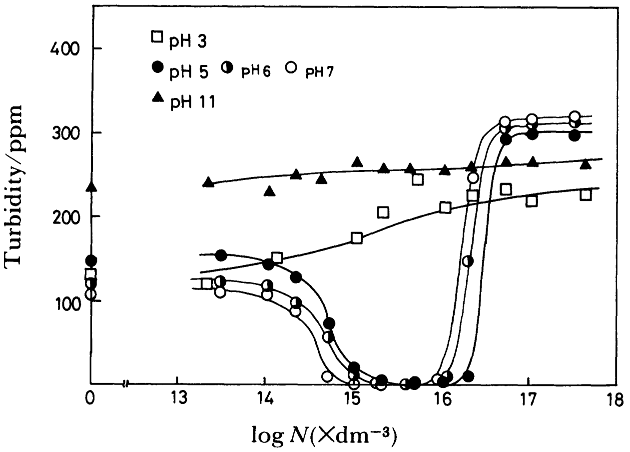

Fig. 2. The change in turbidities of mixed suspensions of latex particles and TiO_2 particles with number of latex particles added at various pH.

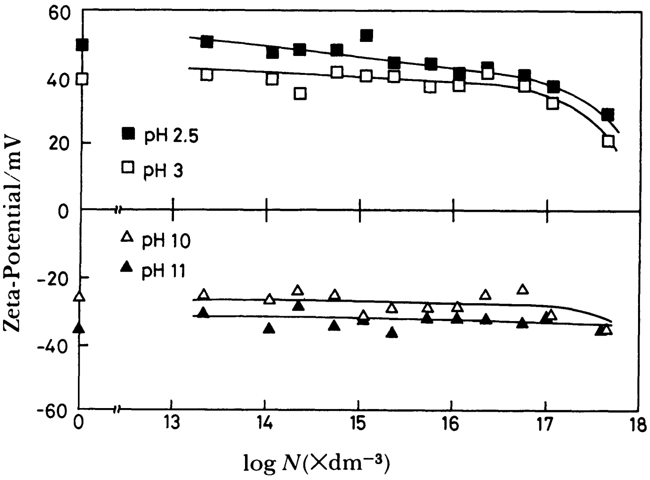

Fig. 3 The change in zeta-potentials of mixed suspension with number of latex particles added at pH 2.5, 3.0, 10.0, 11.0.

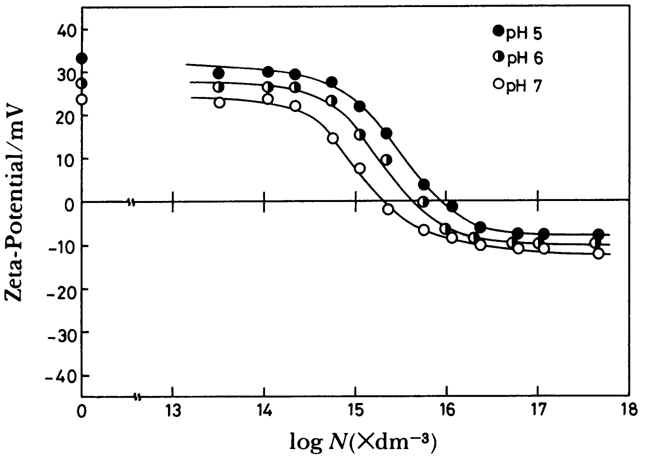

Fig. 4. The change in zeta-potentials of mixed suspensions with number of latex particles added at pH 5.0, 6.0, 7.0.

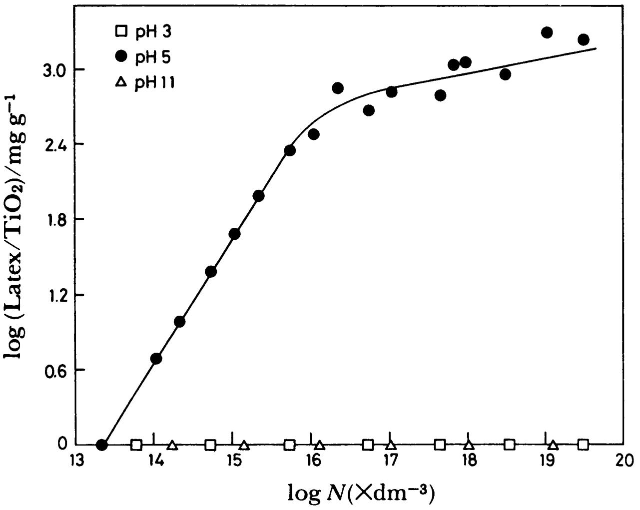

Fig. 5. The amount of latices adsorbed on surface of TiO$_2$ particles at various pH of suspended solution at 25 °C.

Figure 5 shows the amount of latices adsorbed onto the surface of TiO$_2$ particles. At pH 3 and 11 of the mixed suspended solutions, hardly any latex particles adsorbed onto TiO$_2$. This was because of the electric repulsion between the latex particles and the TiO$_2$ particles. On the other hand, at pH 5 the amounts of latices adsorbed increased in proportion to the number of latex particles added until they were approximately constant. These results indicate that the latex particles surely adsorb onto the surface of TiO$_2$ particles in the range of the opposite charge between these particles.

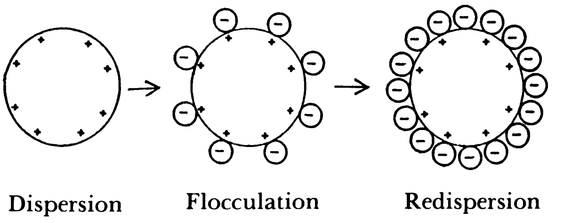

Fig. 6. A model for mechanism of flocculation and redispersion.

Accordingly, the flocculation and the redispersion phenomena in the mixed suspension can be explained by the adsorption of the latex particles onto the TiO$_2$ particles. A model for the mechanism of these phenomena is shown in Fig. 6:

(a) At the initial state, without the addition of any latex, TiO$_2$ particles disperse in the aqueous solution because of the electric repulsion of their own surface's negative charge.

(b) With an increase in the number of the latex particles which have a negative charge, the latex particles are adsorbing on the TiO$_2$ particles which have a positive charge, and the zeta-potential of the TiO$_2$ particles covered with latex particles alters from positive to zero. As a result, the flocculation of the mixed suspension occurs at a point of zero charge of the mixed suspension, a result mainly of the electric force of attraction. The results are also supported by the good agreement between the number of latex particles (N) at flocculation (shown in Fig. 2) and that at the point of zero charge of the mixed suspension (shown in Fig. 4).

(c) At a high concentration of the latex particles, as more of the latex particles adsorb on TiO$_2$, the mixed suspension redisperses, a result of the electric repulsion among latices which have a negative charge. As a result, the TiO$_2$ particles have a negative charge in the redispersed state. These results are supported by the agreement between the values of the zeta-potential of the single latex and that of the zeta-potential of TiO$_2$ in the redispersed state (pH 5.0, 6.0, and 7.0).

Furthermore, with an increase in the pH from 5 to 7, since the negative charge of the latex particles increases and the positive charge of TiO$_2$ particles decreases, the particle number of the latex (N) required for the flocculation of the TiO$_2$ particles is shifted to a low concentration with the pH.

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