

A Study of Polyurethane Ionomer Dispersant

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ABSTRACT: Anionic polyurethane ionomers as the dispersant in water-soluble acrylic baked paint were successfully synthesized at our lab and these ionomer structures have been proven by infrared spectra. In aqueous solution, the surface tension for polyurethane ionomer molecules with different ionics was found to increase with increasing the concentration of ionics, as a result of the hydrophobics of ionomer molecules adsorbed at the air–water interface becoming even more ordered. It was also found that the viscosity is higher for polyurethane ionomer with L-2,5-diaminovaleric acid hydrochloride than for polyurethane ionomer with sodium 4,4-dihydroxy-*l*-butane sulfonate (DS200) or with dimethylol propionic acid (DMPA) in water. For the

wettability and dispersion of titanium dioxide pigment present in water-soluble acrylic baked paint, the polyurethane ionomer molecules with respective sodium 4,4-dihydroxy-*l*-butane sulfonate, DMPA, DS200 containing 3% 1,3-propane sultone (ES200) and DMPA containing 3% ES200 are considered to be better dispersants. The titanium dioxide pigment was found to become finer, as the agitation time and the ionic concentration of anionic polyurethane ionomer were increased. In addition, the system with DS200 or dimethylol propionic acid will make the dispersion of titanium dioxide pigment stable in water-soluble acrylic paint. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 103–111, 2005

INTRODUCTION

The compatibility for powders^{1,2} dispersed in water highly depends upon the closeness of their polarity. In fact, the addition of surfactant into water may enable the powder to be dispersed in water uniformly, as a result of changing the polarity of powders. In the past two decades, unlike traditional surfactant, polymer-like surfactant has drawn great attention from both industry and academe. A number of researchers developed polymer-like surfactant and found that these surfactants due to their unique property can be applied to various areas, such as dispersants, emulsifiers, etc. Due to environmental protection, we attempted to prepare anionic polyurethane resin as a dispersant for use in water-based paint coatings and to further study the effect of anionic polyurethane resin on the dispersion and stability of TiO₂ present in water-based acrylic baked paint. The possible structure of anionic polyurethane ionomer as a dispersant for use in paint coating is given in Scheme 1.

EXPERIMENTAL PROCEDURES

Materials

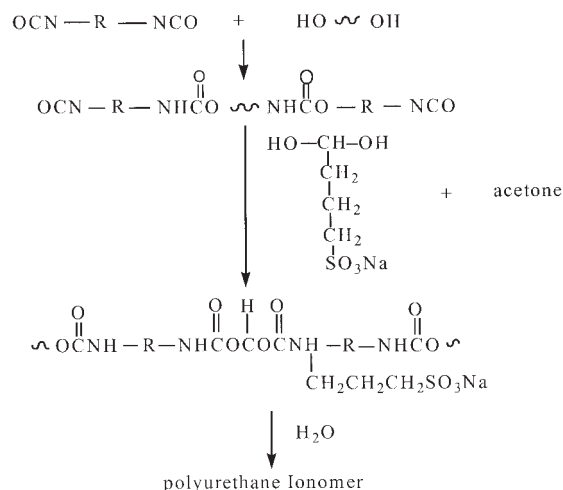
Polyester with molecular weight of 2,800 (OH number ~ 40.1) and polyethylene glycol with molecular

weight of 6,000 were supplied by Tai Chin Chemical Industry Co., Ltd. and Sino-Japan Chemical Co., respectively. Isophorone diisocyanate (IPDI) was purchased from Merck Co. Dimethylol propionic acid (DMPA) and L-2,5-diaminovaleric acid hydrochloride (L-ornithine) were obtained from Alcolac Industrial Chemical (USA) and Sigma Chemical Co. (USA), respectively. *N,N*-dimethyl acetamide and *p*-amino benzoic acid (PABA) were supplied by Jassen Co.(USA) and Ferak Berlin Co.(Germany), respectively. Water-reducible acrylic resin (Eterac 1125–50) and titanium dioxide pigment (R-9000) were received from Eternal Chemical Co., Ltd. (Taiwan) and Dupont Co. (USA), respectively. Zinc sulfide-barium pigment (Lithopone) was obtained from China Metallic Chemical Co., Ltd. Isopropyl alcohol (IPA) and butyl cellosolve (BCS) were received from China Petroleum Oil Co. Melamine formaldehyde resin (Cymel 325) was purchased from American Cyanamid Co. (USA). 1,3-Propane sultone (ES200) and sodium 4,4-dihydroxy-*l*-butane sulfonate (DS200) were received from Taiwan Hopax Chemicals Co. Ltd.

Method

A 0.004 equivalent of polyethylene glycol with a molecular weight of 6,000, 0.026 equivalent of polyester (molecular weight = 2,800; OH number = 40.1), and 0.06 equivalent of DS200 or DMPA, or L-ornithine, or DS200 with 3% by weight ES200 (1,3-propane sultone), or DMPA with 3% ES200, or PABA with 3% ES200, or

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Scheme 1

L-ornithine with 3% ES200 were charged to a 1,000-mL four-necked reaction kettle containing 16 g *N,N*-dimethyl acetamide and equipped with a stirrer, thermometer, and condenser under agitation with a speed of 400 rpm.

Subsequently, 0.108 equivalent of IPDI was added slowly and then reacted in the presence of 0.2% (by weight) dibutyltin dilaurate at around 105 for about 2.5 h in the above flask to form NCO-terminated polyurethane prepolymer. The anionic NCO-terminated PU prepolymer further reacted with approximately 300 g water in the presence of a small amount of diethylene triamine to form anionic polyurethane ionomers. After the acetone was completely removed from the anionic polyurethane ionomer liquids by evaporation, 1.0% by weight of this anionic PU ionomer (approximately 16% solid content) as a dispersant was used in the paint coating and the formulation of water-soluble acrylic baked paint is given in Table I. 19.9% Eterac 1125-50, 6.5% R-900, 3% Lithopone, 1.0% dispersant (anionic PU ionomer), 6.2% IPA, and 12.4% BCS put in an aluminum can with a 2-mm glass bead were sealed and placed in paint conditioners (Red Devil Co., Model 5400, USA) for 15 min, 30 min, 1 h, 1.5 h, and 2 h, respectively, to measure their respective fineness. Subsequently, the glass bead was taken out from the aluminum can, and 8.5% Cymel 325 and 38% water were added to the can under agitation. Triethylamine was used to regulate the pH of these mixtures, and the variation of their fineness³⁻⁶ was measured using a fineness gauge (Byk Germany, Model No. 1512). The formation of water-soluble acrylic baked paint with different types of anionic PU ionomers as a dispersant placed in the aluminum can was sealed at room temperature and stored for 5, 10, 15, 20, 25, and 30 days, respectively, under 60% relative humidity. To study the stability of these samples, the variation of the fineness for these samples versus time

was fully investigated. The experimental accuracy for the above measurements was estimated to be within ± 0.5 .

RESULTS AND DISCUSSION

The NCO functional group for IPDI will rapidly react with DS200 (or PABA or L-ornithine/ES200 or DS200/ES200), polyester, and polyethylene glycol in the presence of other additives to form NCO-terminated PU prepolymer. The formation of anionic NCO-terminated PU prepolymer is illustrated by the formation of the absorbance peaks at around 1250 cm^{-1} (C-O-), 1540 cm^{-1} (NHCO), 1620 cm^{-1} (NH), 1720 cm^{-1} (C=O), 3400 cm^{-1} (NH), and by substantially decreased absorbance peaks at approximately 2275 cm^{-1} (NCO) and 3500 cm^{-1} (OH), given in Figure 1. These results demonstrate that the reaction of IPDI with DMPA or DS200, polyester, polyethylene glycol, and other additives to form anionic PU ionomer^{7,8} is possible. Du Noty ring tensiometer was calibrated using water and ethanol and used to measure the surface tension at room temperature as a function of respective ionic content used to prepare anionic PU ionomer. In aqueous solution, the surface tension for anionic polyurethane ionomer appears to increase with increasing the ionic content, given in Figure 2. The electrostatic interaction between charged ionomer molecules may become stronger, as the amount of ionics attached to the backbone of anionic PU ionomer molecules increases. This interaction is likely to make the hydrophobics adsorbed at the air-water interface become even more ordered. Therefore, the surface tension increases, as the ionic content of anionic PU ionomer molecules increases. Viscosity measurements for the DS200 or DMPA type of anionic PU ionomer aqueous solution were carried out at $25 \pm 0.05^\circ\text{C}$ with a Brookfield viscometer. The viscosity data given in Figure 3 appears to be larger for the L-ornithine type than for the DS200 or DMPA type of anionic PU ionomer molecules, as a result of large phase volume formed

TABLE I
Formulation of Water Soluble Acrylic Baked Paint

Base	Parts by weight
Eterac 1125-50 (acrylic latex)	19.9
Cymel 325 (melamine-formaldehyde resin)	8.5
TiO ₂ (R900)	6.5
Lithopone (Zinc sulfide barium pigment)	3.0
Dispersant (anionic PU ionomer)	1.0
IPA (isopropanol)	6.2
BCS (butyl cellosolve)	12.4
TEA ^a (triethylamine)	----
Water	38.0

^a As required to adjust and maintain pH at 8 to 9.

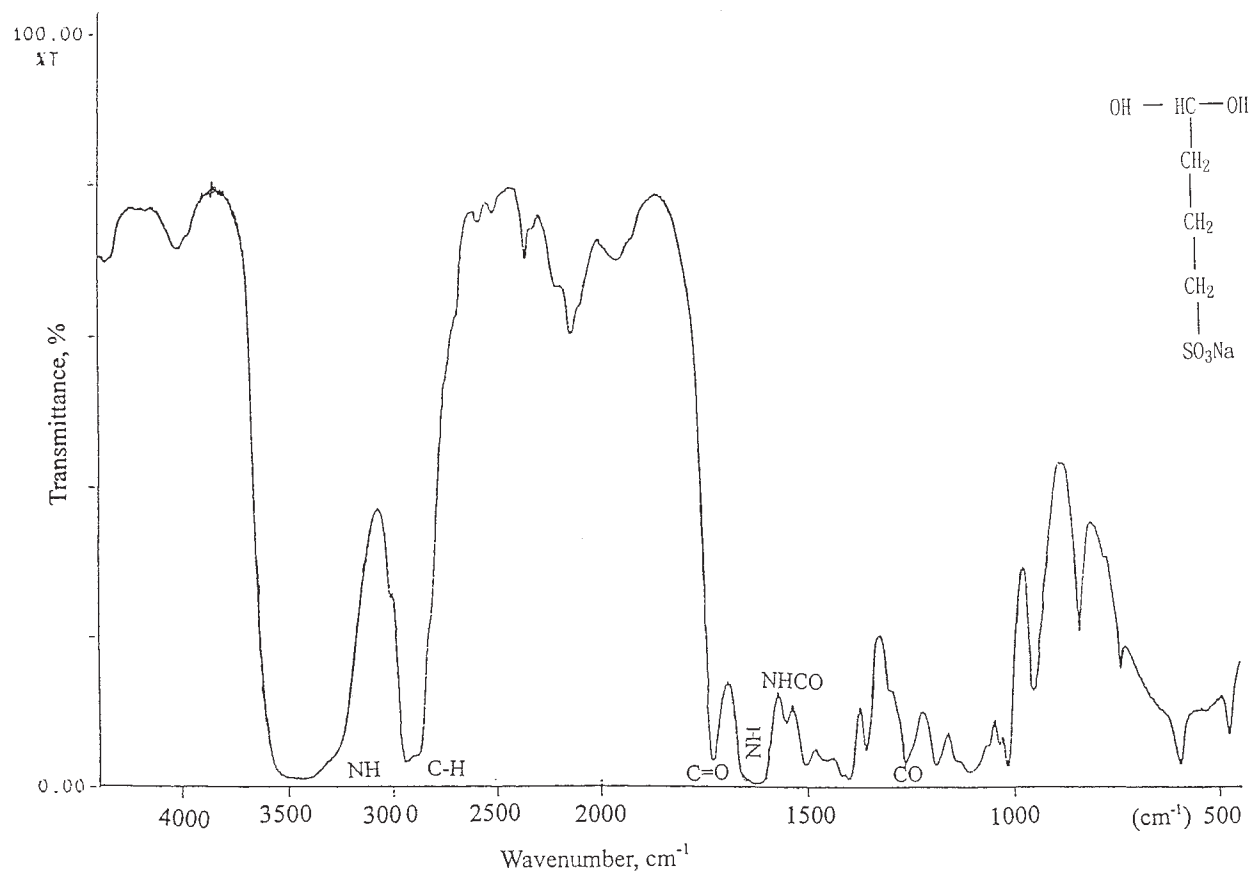


Figure 1 Anionic NCO-terminated PU prepolymer formed after 2-h reaction, $25 \pm 0.05^\circ\text{C}$.

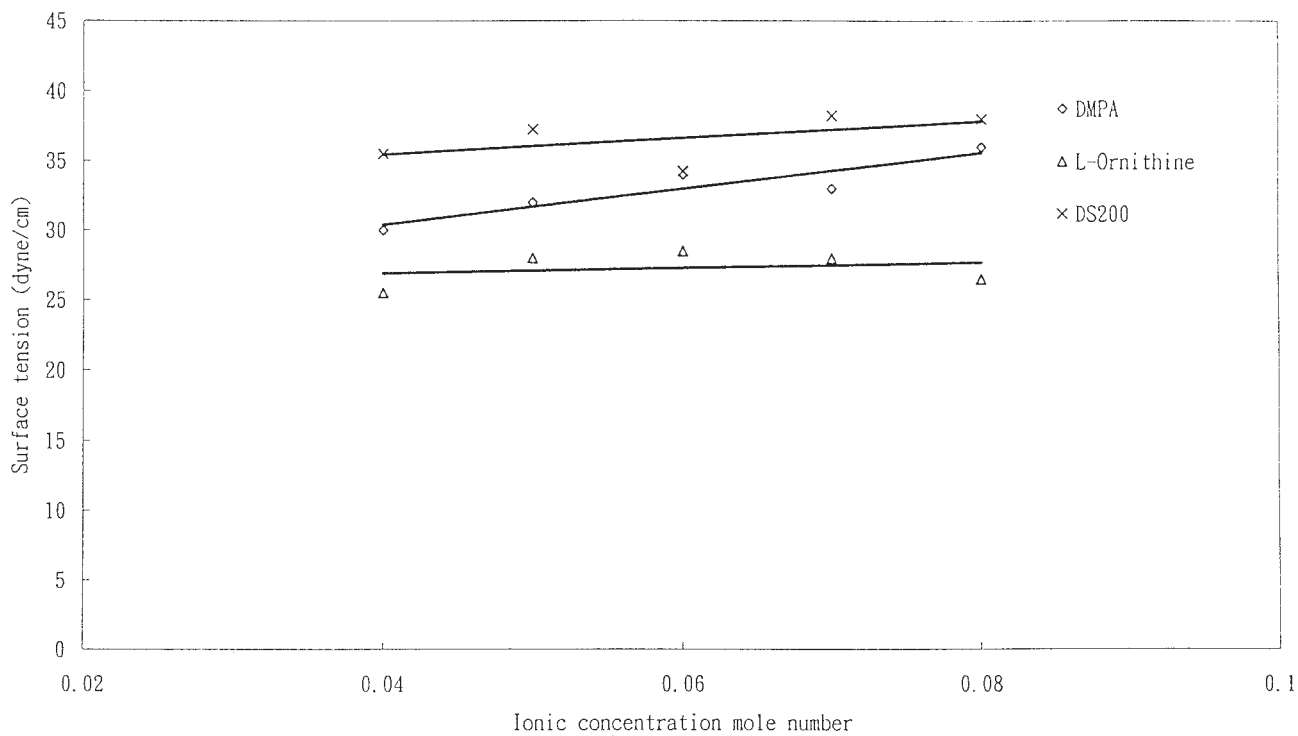


Figure 2 Plot of the surface tension versus the ionic concentration used to prepare anionic PU ionomer at $25 \pm 0.05^\circ\text{C}$.

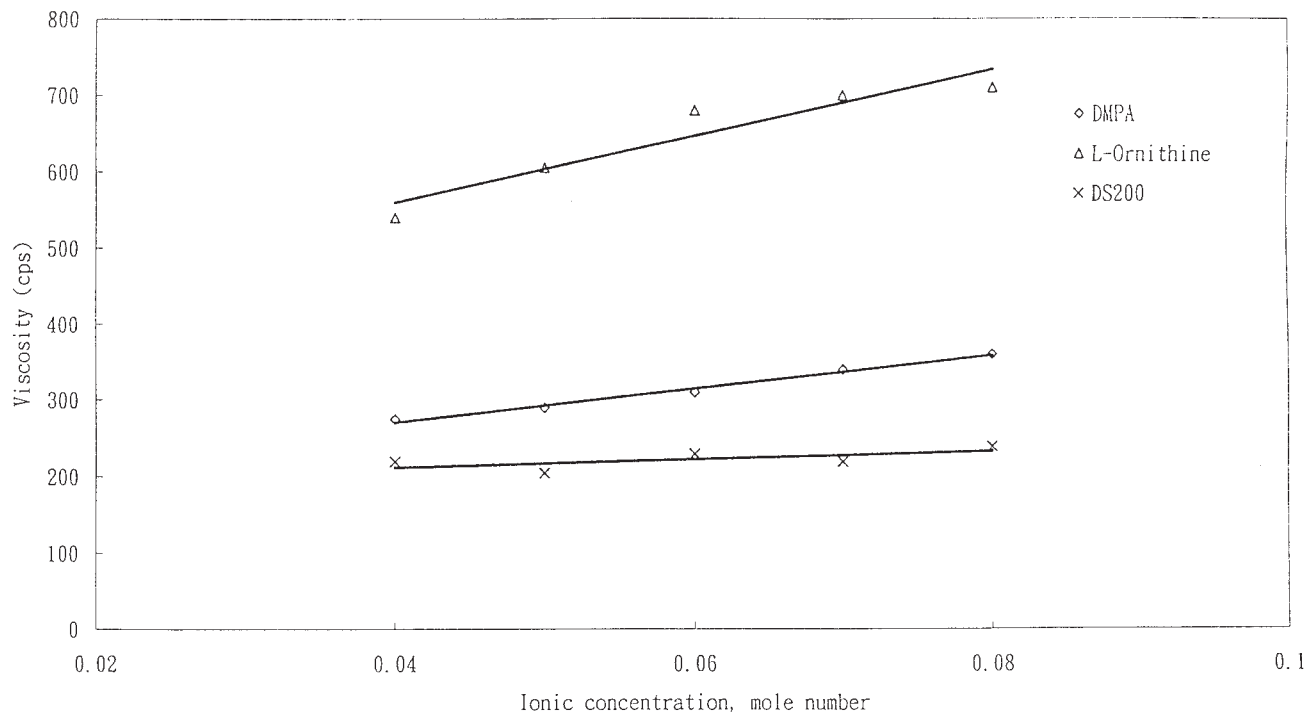


Figure 3 Plot of the viscosity versus the ionic concentration used to prepare anionic PU ionomer at $25 \pm 0.05^\circ\text{C}$.

resulting from the intermolecular interaction between ionomer-ionomer molecules and between ionomer-water molecules.

The fineness of TiO_2 in the presence of anionic PU ionomer with 0.04–0.08 equivalent of ionics as a dis-

persant in water-soluble paint versus agitation time was fully investigated and the results are given in Figures 4–6. Figures 4–6 illustrate that the fineness of TiO_2 appears to decrease rapidly with increasing agitation time and with increasing ionic content as well.

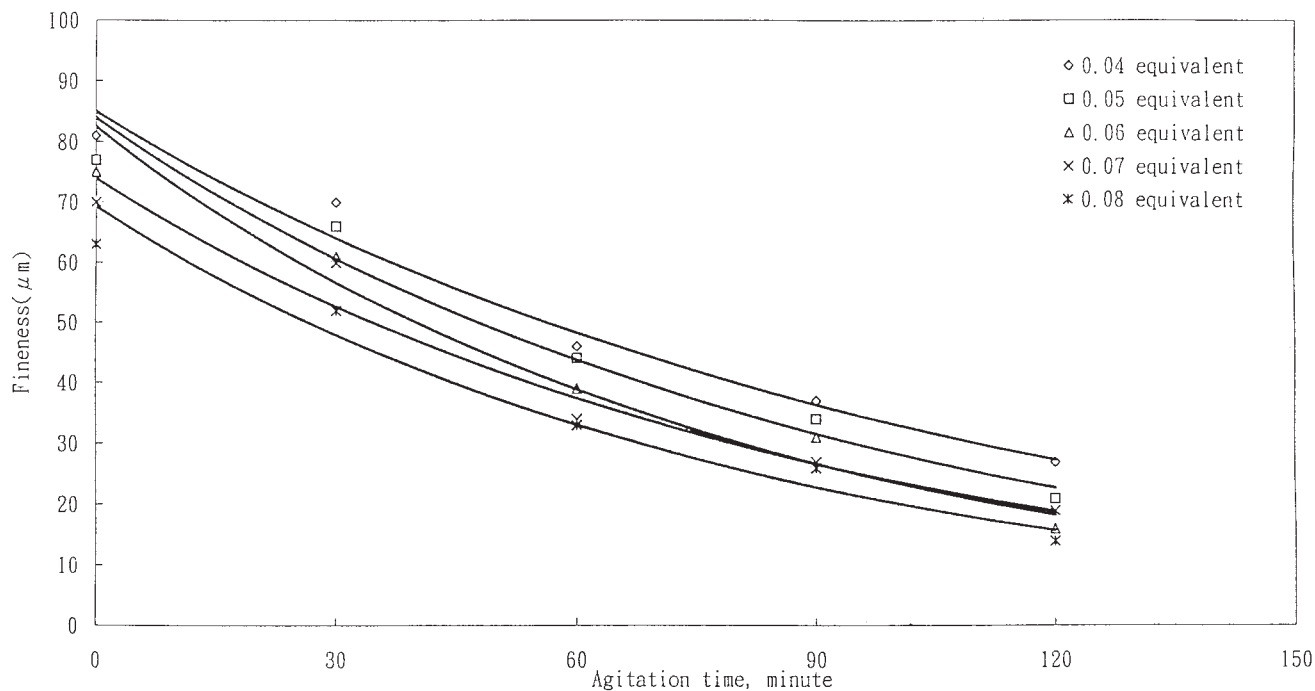


Figure 4 Plot of the fineness of TiO_2 in the presence of anionic PU ionomer with 0.04–0.08 equivalent of DS200 as a dispersant in water-soluble paint versus agitation time at $25 \pm 0.05^\circ\text{C}$.

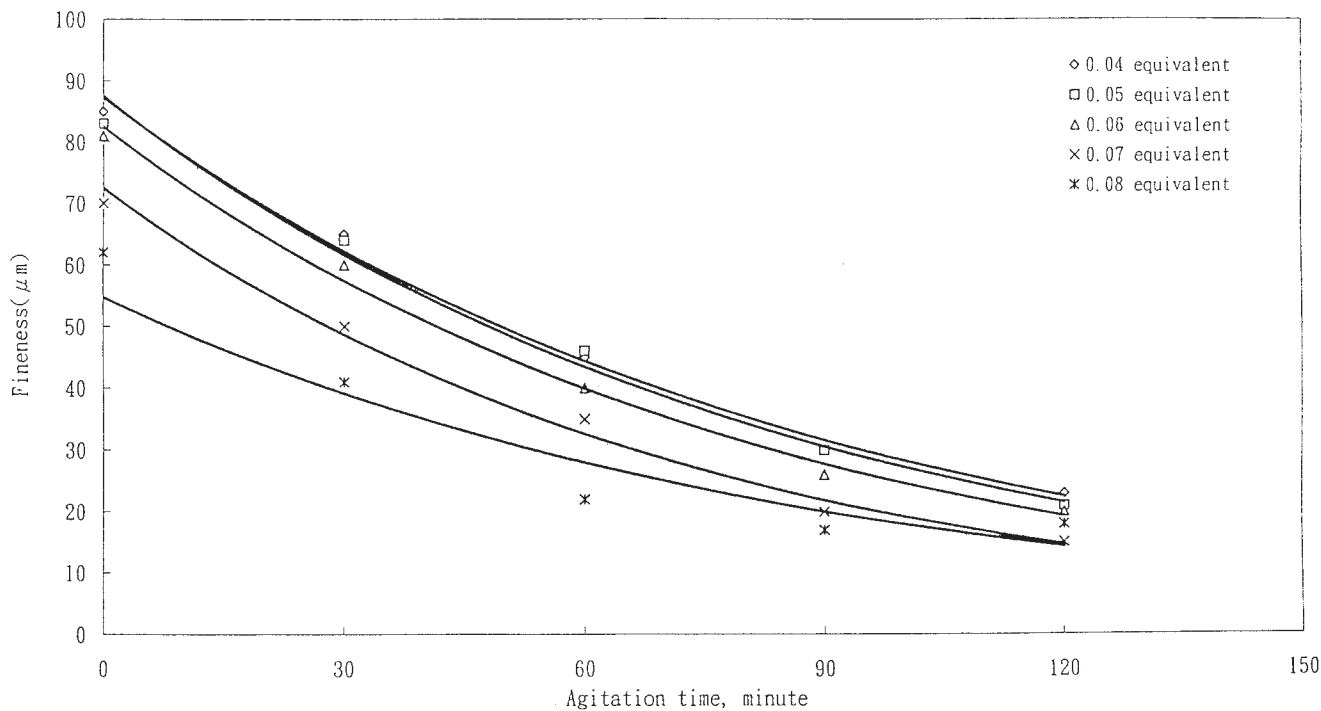


Figure 5 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.04–0.08 equivalent of DMPA as a dispersant in water-soluble paint versus agitation time at $25 \pm 0.05^\circ C$.

In general, the fineness of TiO_2 , due to the collision between glass bead and TiO_2 by using anionic PU ionomer as a dispersant in the aluminum can, will indeed become smaller as the agitation time increases.

Besides, the increased amount of ionics attached to the backbone of PU ionomer as a dispersant in water soluble paint will, in fact, provide good wettability and dispersion for TiO_2 present in water-soluble paint.

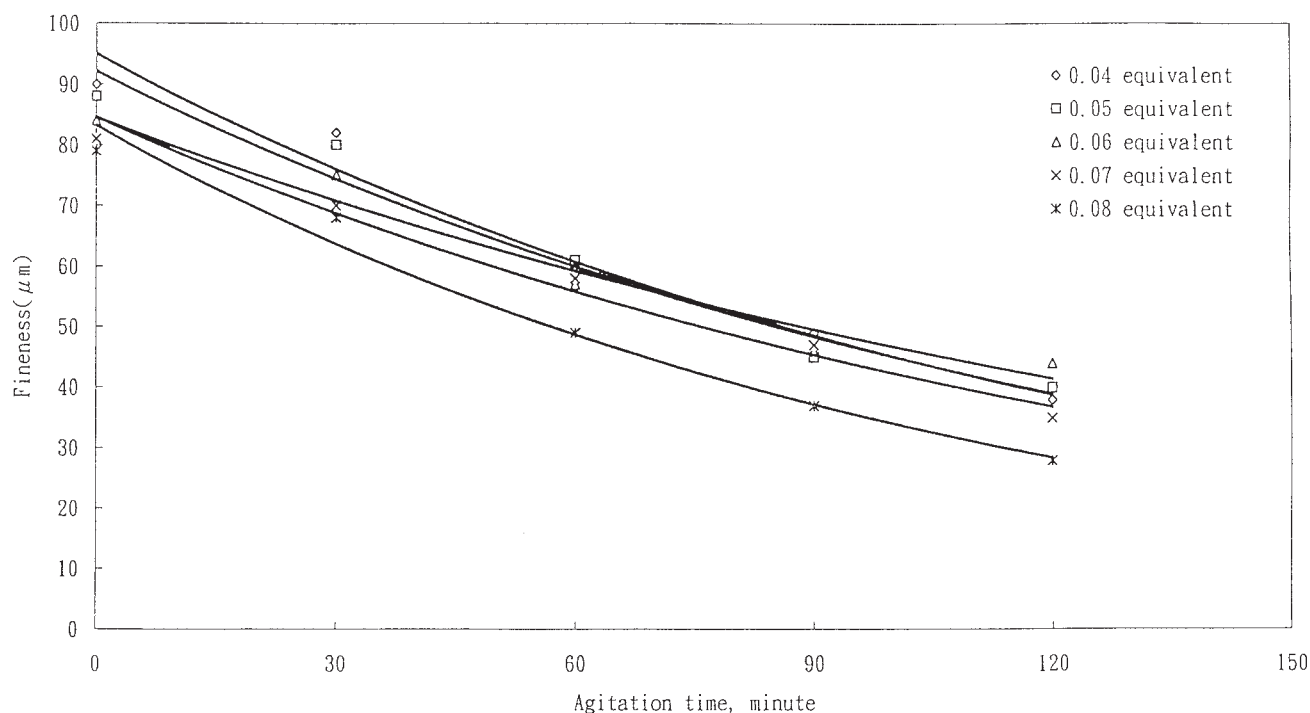


Figure 6 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.04–0.08 equivalent of L-ornithine as a dispersant in water-soluble paint versus agitation time at $25 \pm 0.05^\circ C$.

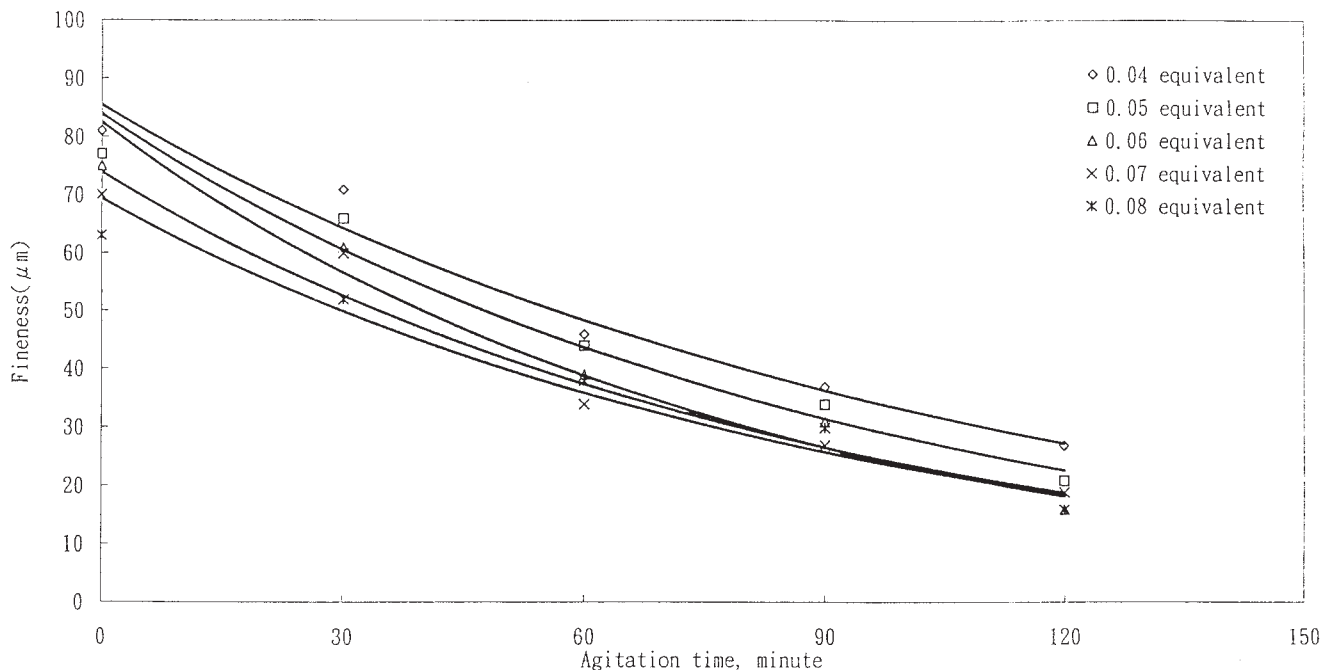


Figure 7 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.04–0.08 equivalent of DS200 containing 3% ES200 as a dispersant in water-soluble paint versus agitation time at $25 \pm 0.05^\circ\text{C}$.

Therefore, the fineness of TiO_2 becomes small. In comparison of Figures 4–6, it clearly indicates that the fineness of TiO_2 is seen to be greater for the PU ionomer with L-ornithine than for the PU ionomer with DS200 or DMPA. Owing to the hydrogen bonding

formed between the L-ornithine molecule and the water molecule, increased phase volume of the L-ornithine molecule may not provide good wettability and dispersion for TiO_2 . This is the reason why the PU ionomer with L-ornithine as a dispersant present in

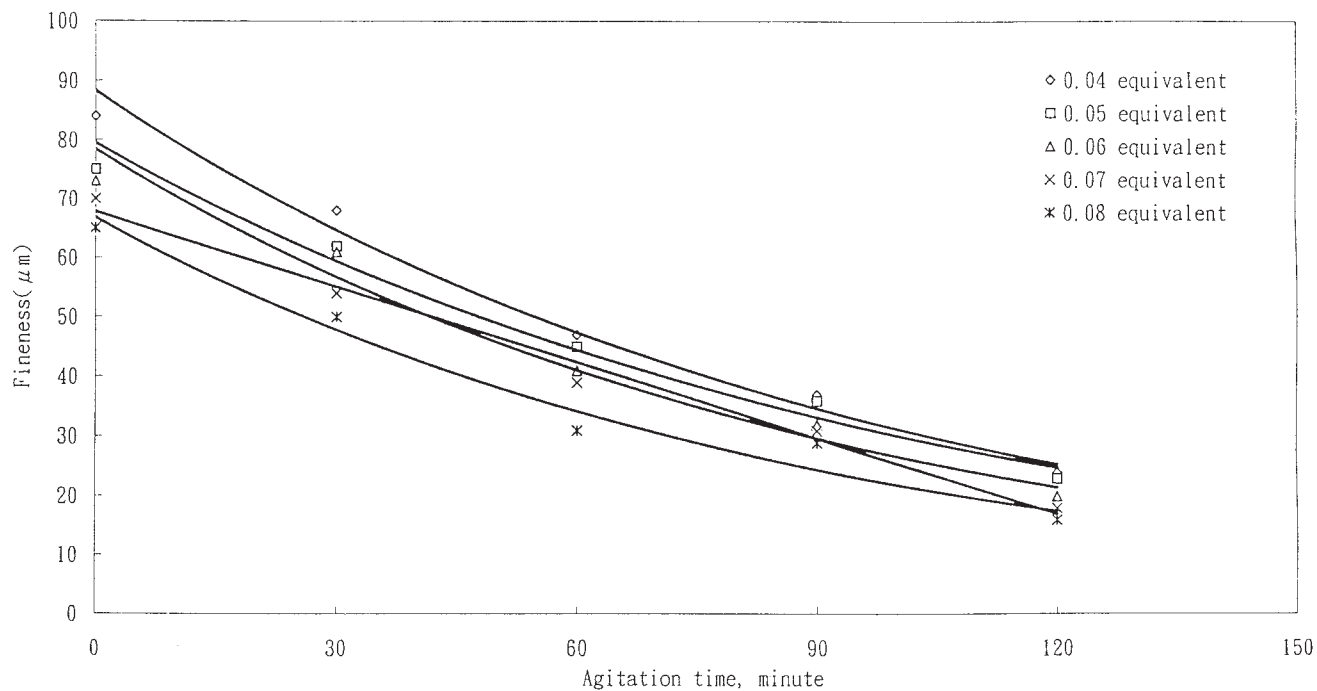


Figure 8 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.04–0.08 equivalent of DMPA containing 3% ES200 as a dispersant in water-soluble paint versus agitation time at $25 \pm 0.05^\circ\text{C}$.

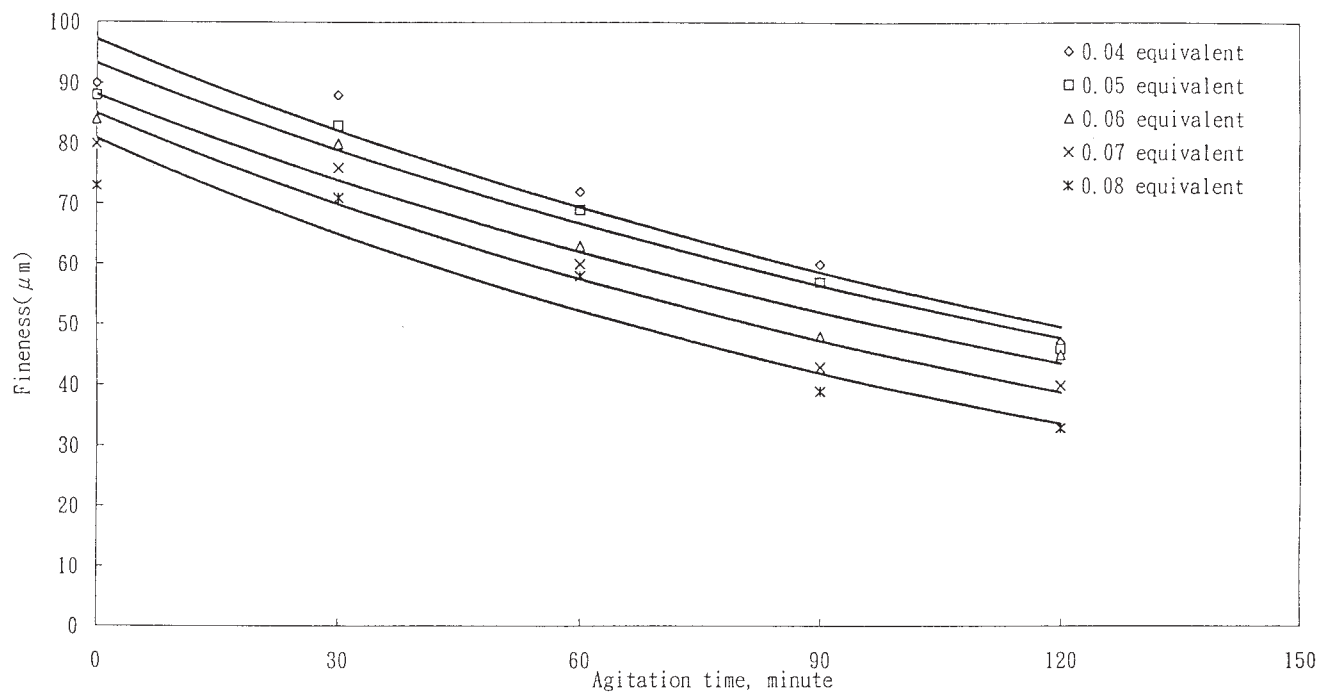


Figure 9 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.04–0.08 equivalent of L-ornithine containing 3% ES200 as a dispersant in water-soluble paint versus agitation time at $25 \pm 0.05^\circ\text{C}$.

water-soluble paint will not increase the fineness of TiO_2 in comparison to that of PU ionomer with DMPA or DS200. The effect of anionic PU ionomer molecules with a fixed 3% ES200 on the fineness of TiO_2 , under the same experimental condition, is given in Figures

7–10. Figures 7–10 show that the fineness of TiO_2 decreases drastically with increasing agitation time and with increasing the ionic content of the PU ionomer molecule. The explanation for this is almost the same as described in Figures 4–6. However, besides

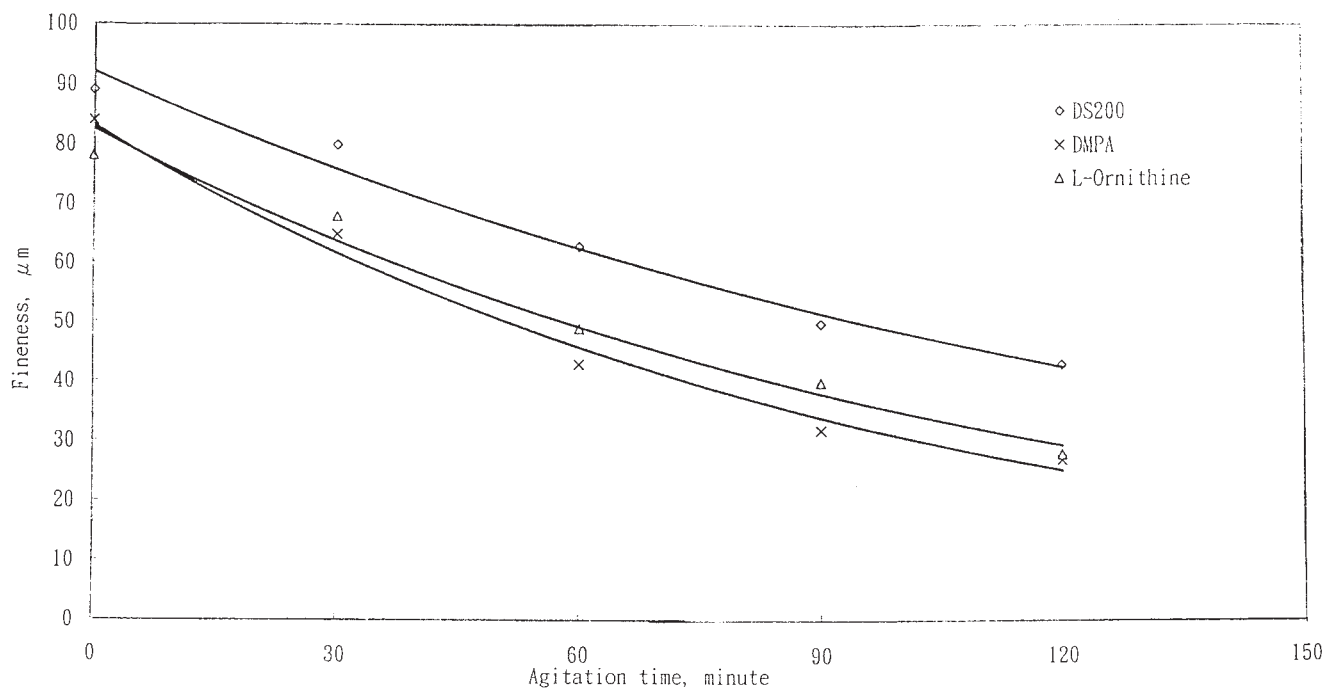


Figure 10 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.05 equivalent of ionic component as a dispersant in water-soluble paint versus agitation time at $25 \pm 0.05^\circ\text{C}$.

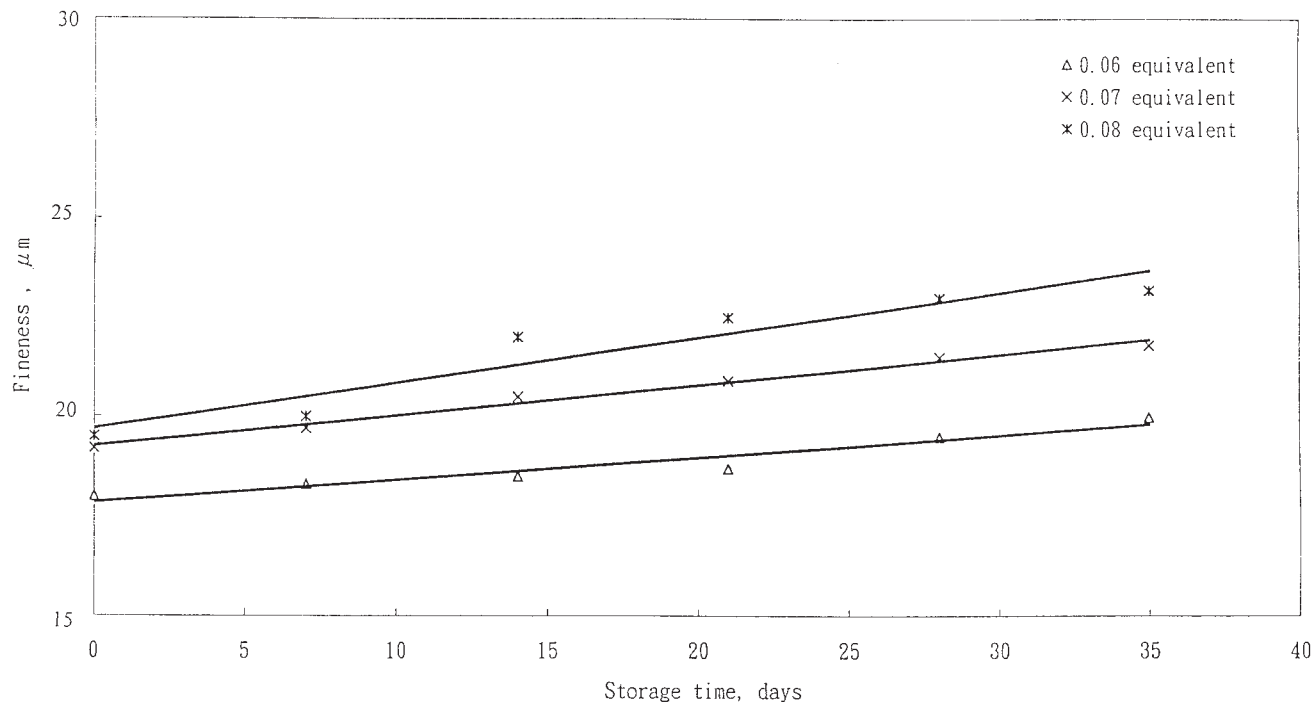


Figure 11 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.06–0.08 equivalent of DS200 as a dispersant in water-soluble paint versus storage time at $25 \pm 0.05^\circ\text{C}$.

the explanation given in Figures 4–6, the conformation of anionic PU ionomer molecule itself, as a dispersant, also plays an important role in water-soluble acrylic paint, but, at the present time, we are not able to provide this information. The stabilities of the fine-

ness of TiO_2 versus the storage time for PU ionomer molecules with respective ionics alone and with respective ionics containing 3% (by weight) ES200 are given in Figures 11–13. Figures 11–13 clearly indicate that the fineness of TiO_2 slightly increases with increas-

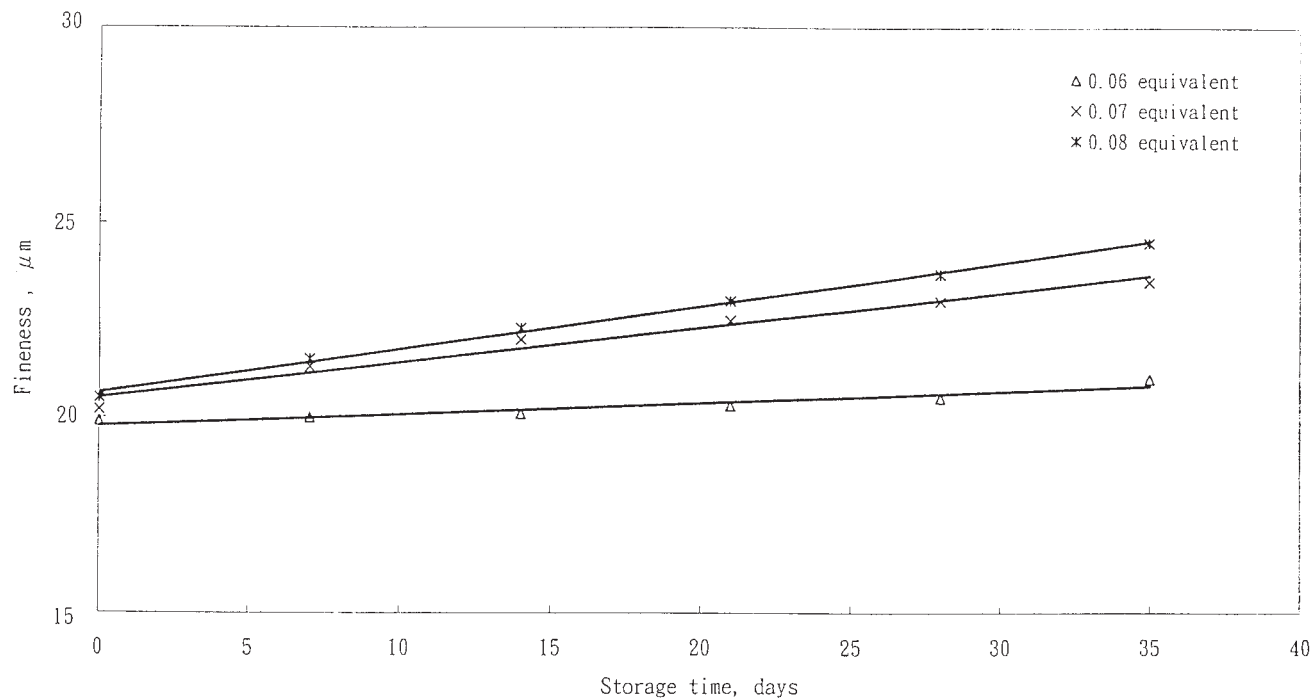


Figure 12 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.06–0.08 equivalent of DMPA as a dispersant in water-soluble paint versus storage time at $25 \pm 0.05^\circ\text{C}$.

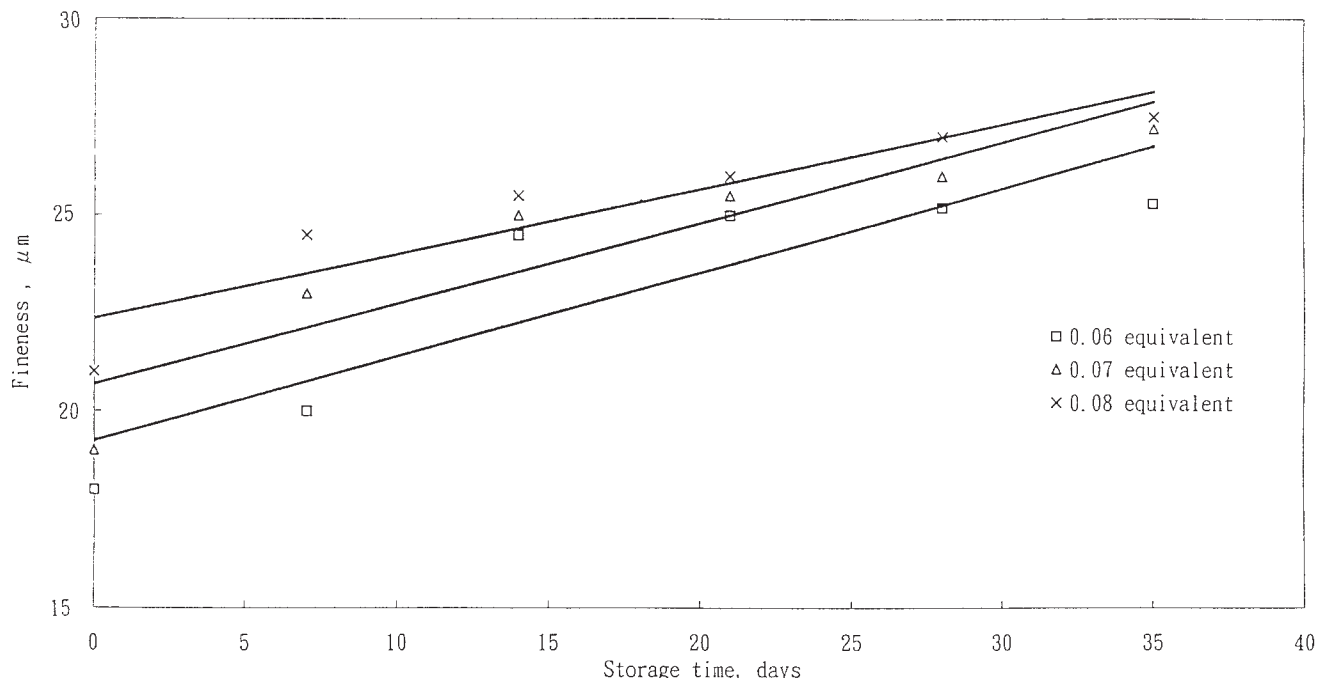


Figure 13 Plot of the fineness of TiO_2 in the presence of PU ionomer with 0.04–0.08 equivalent of L-ornithine as a dispersant in water-soluble paint versus storage time at $25 \pm 0.05^\circ\text{C}$.

ing the storage time for PU ionomer molecules with respective ionics, as a result of the hydrogen bonding formed between charged PU ionomer molecules themselves and between charged PU ionomer–water molecules containing other ingredients. Since the variation of the fineness of TiO_2 is smaller for use of the PU ionomer with DS200 or DMPA ionics than for use of the PU ionomer with L-ornithine ionics as a dispersant in water-soluble acrylic paint, therefore, the PU ionomers with DS200 or DMPA will make the system stable. In this case, the PU ionomer with DS200 or DMPA is considered to be a good dispersant.

CONCLUSION

The reaction of IPDI with polyester, polyethylene glycol, and DS200 or DMPA or L-ornithine in the presence of other ingredients to form the anionic PU ionomer has been proven by infrared spectra. For the anionic PU ionomer molecule in aqueous solution, the surface tension appears to increase with increasing the ionic concentration of the anionic PU ionomer, as a result of hydrophobics of ionomer molecules adsorbed at the air–water interface becoming even more ordered.

It is interesting to note that the viscosity results are seen to be larger for the L-ornithine type than for the DS200 or DMPA type of anionic PU ionomer. This may be the result of large phase volume formed for the anionic PU ionomer with L-ornithine ionics result-

ing from strong intermolecular interaction between ionomer–ionomer molecules and between ionomer–water molecules.

The fineness of TiO_2 , present in water-soluble acrylic paint, becomes smaller as the agitation time and the ionic concentration used to prepare the anionic PU ionomer increase. Our experimental results indicate that PU ionomer molecules with DS200 or DMPA or DS200 with 3% ES200 or DMPA with 3% ES200 are considered to be better dispersants for used in water-soluble acrylic paint. Furthermore, the system with DS200 or DMPA or DS200 with 3% ES200 or DMPA with 3% ES200 ionics will make the dispersion of TiO_2 stable in water-soluble acrylic paint.

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