

## 라텍스의 레오로지

## Rheology of Latex

金 光 雄

## 1. Introduction

Latex system is a very complex system; multi-phase, multi-component, and multi-interaction system. Almost all constituents have effects on the rheological properties of the latex system. These rheological properties are of both theoretical interest and practical importance in processing and various application areas. Thus, we have to consider all the possible factors to obtain the desired rheological properties and performance for a specific end use.

Of the rheological properties, viscosity is the most important one. Fundamental knowledge of the latex viscosity behavior is key to design and apply a latex system. Factors affecting viscosity of the latex include polymer type, concentration, particle size, particle size distribution, emulsifier, temperature and shear rate.

There are many questions concerning the rheology of latexes, of which very few have complete answers now. Model latexes provide a convenient source of a well defined system for basic studies of flow properties<sup>1</sup>. However, it is extremely difficult to construct a model latex to find one or two isolated effects because in model construction (polymerization) stage several factors vary simultaneously. Consequently, data thus obtained represent many hidden interactions, a combination of several effects of the involved factors.

Application areas of emulsion, a synthetic latex, are too broad to discuss fully here. Naming few, however, they include paint vehicle, adhesive, ink binder, textile binder, leather coatings, paper coatings, caulk and cosmetics. In these areas, the waterbased emulsion occupies a significant portion and its share will increase more with well defined latexes and improved formulation techniques. This trend is further accelerated by the pollution source of the organic solvents in the solvent-based coatings.

A variety of instrument are available for the measurement of rheological properties. Many different types of viscometers can be used to determine viscosity of the latex system. Van Wazer et. al<sup>2</sup> give a useful reference of contemporary viscosity measurements. Basically, there are two types of viscometers; rotational type and capillary type. Depending on the system under study, one has to choose appropriate viscometer and apparatus for the properties interested.

## II. Characteristics of Latex

Fig. 1 shows typical flow curves that one can encounter in polymeric systems. Interestingly, one can observe all the characteristics of Fig. 1 in latex systems. Newtonian behavior can be seen in dilute latex system, typically up to 25% of volume solids. Pseudoplastic (shear-thinning) and dilatant (shear-thickening) flows are opposite properties in nature, and high concentration latexes and pigment slurries are typical examples, respectively. Most of polymeric

한국 과학 기술 연구소 (Kwang-Ung kim, Polymer Processing Lab. Korea Institute of Science and Technology)

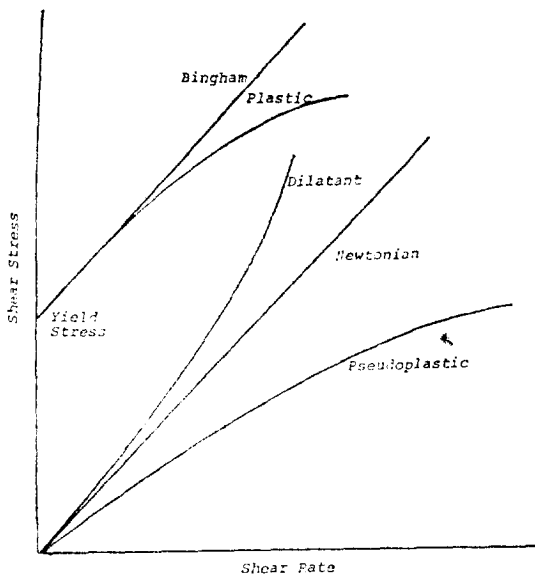


Figure 1. Typical flow curves.

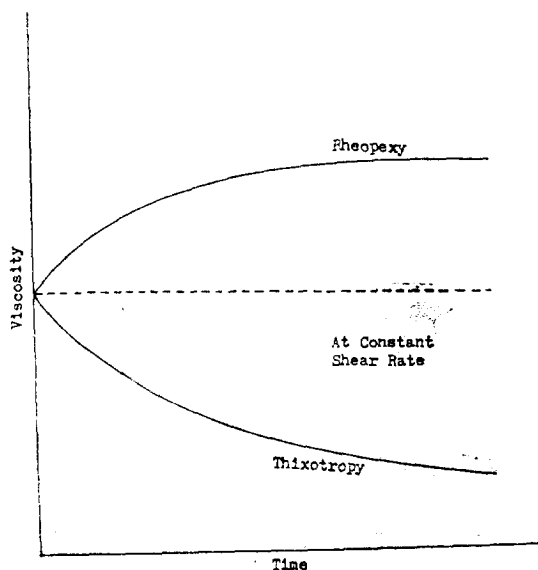


Figure 2. Thixotropy and rheopexy.

materials exhibit pseudoplastic flow. Bauer and Collins<sup>3</sup> reviewed dilatency in dispersed systems along with thixotropy. Yield stress, a chara-

cteristic of plastic flow, may be seen in the formulated paints. The Bingham flow<sup>4</sup>, a Newtonian with yield stress, is included in the plastic flow. The formulated paint requires this yield stress to prevent sagging after application.

Thixotropy is another unique characteristic of the latex system (Fig. 2). At a given shear rate, viscosity may be decreased (thixotropy) or increased (rheopexy) with time. If one use the plot of Fig. 1, a hysteresis loop would be formed by thixotropy or rheopexy. Thixotropy is an extremely important property of the formulated paint to control sagging, paint transfer and brushing. It is often called "structural viscosity", which is easily broken by shearing to give low viscosity but may be reversibly "structured" again on standing. Walton<sup>5</sup> recently gave a quantitative treatment of thixotropy for the formulated paints. Some paint manufacturers add agents for this property; thixotropic agent of chelating agent.

If one constructs viscosity curve with shear rate, Fig. 3 may represent "universal" flow curve. Three distinctive regions in Fig. 3 are first Newtonian region ( $\eta_0$ ), non-Newtonian region ( $\eta$ ), and second Newtonian ( $\eta_\infty$ ). Lenk<sup>6</sup> suggested two more regions beyond the second

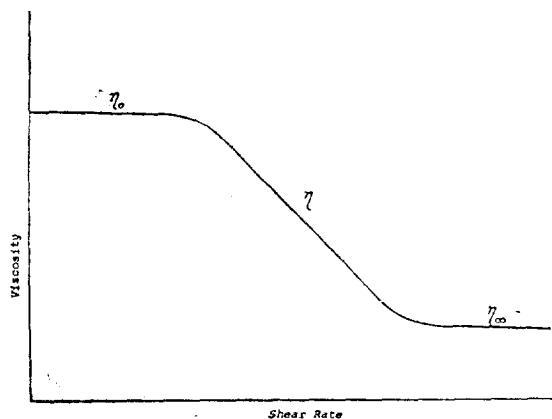


Figure 3. General viscosity curve.

Newtonian region; dilatant and turbulence (or melt fracture). These two regions, however, need more experimental evidences to be included in the flow curve.

### III. Viscosity of Latex

A latex system consists of dispersed phase and continuous phase. Other additives are also present and play significant role to the rheological properties. Table I summarizes factors influencing the rheological properties of latex system<sup>7</sup>.

**Table I.** Factors Influencing the Rheological Properties of Latex Systems

1. Dispersed Phase
* Volume Concentration
* Viscosity
* Particle Size, Distribution, and Shape
* Chemical Constitution
2. Continuous Phase
* Viscosity
* Chemical Constitution
* Polarity, PH
* Electrolyte Concentration (if polar)
3. Surface Active Agents
* Chemical Constitution
* Concentration
* Adsorbed Film at Interface
* Electroviscous Effects
4. Other Additives
* Pigments
* Colorants
* Thickeners

#### III-1. Volume Concentration

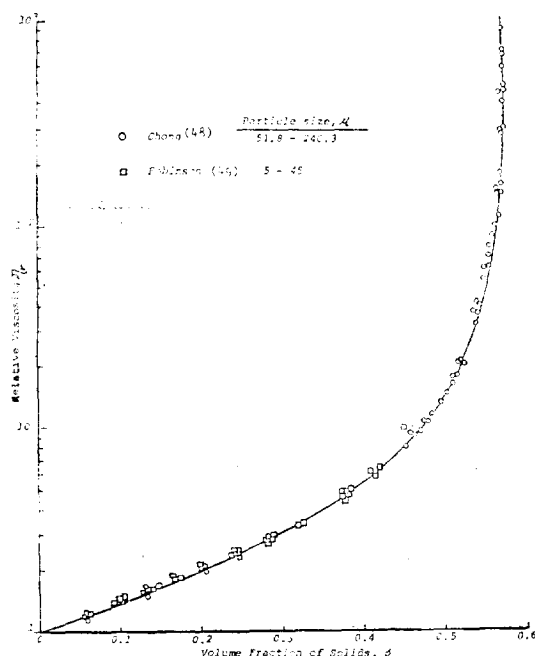
Depending on concentration of the dispersed phase, viscosity of latex may be distinguished into three regions in terms of volume solids( $\phi$ ). At extremely low concentration region ( $<0.02$ ), individual particle is not influenced by its neighbors (no particle interaction). Thus, particle contribution to viscosity is purely

additive and it shows Newtonian behavior. The relative viscosity for the system is given by

$$\eta_r = \frac{\eta}{\eta_s} = 1 + k\phi \quad \dots\dots\dots (1)$$

where  $\eta$  and  $\eta_s$  are viscosities for the system and continuous medium respectively. Einstein<sup>8~10</sup> derived  $k=2.5$  for rigid spherical particles. In an intermediate range (typically up to  $\phi=0.25$ ), particle contribution to viscosity is not additive. Therefore, eq. (1) is not applicable. However, flow is still Newtonian.

At high concentration range ( $\phi > 0.25$ ) to which most practical latex systems belong, particle interactions dominate rheology and flow is non-Newtonian. Thus, viscosity is a function of both concentration and shear rate. Fig. 4 shows the typical viscosity curve of concentrated latex. Two noticeable features from Fig. 4 are; viscosity changes exponentially with volume fraction  $\phi$ , and viscosity at high volume concentration increases asymptotically to infinity.



**Figure 4.** Relative viscosity of monodispersed systems.

For uniform (monodisperse), spherical, tetrahedral packing latexes, the maximum volume fraction  $\phi_{\max}$  is 0.74 theoretically<sup>11</sup>. In practice, however,  $\phi_{\max}$  is lower than 0.74 because of polydispersed particle sizes and inefficient packing.

To describe viscosity of the dispersed system, numerous theoretical and empirical equations have been suggested. Recently, Rutgers<sup>12</sup> reviewed about 100 equations and reduced to 5 representatives. Of these, the Mooney's equation<sup>11</sup> has been widely used.

$$l_n \eta_r = \frac{k_1 \phi}{1 - s \phi} \dots\dots\dots (2)$$

where  $S=1/\phi_{\max}$ , "self-crowding factor". Krie-

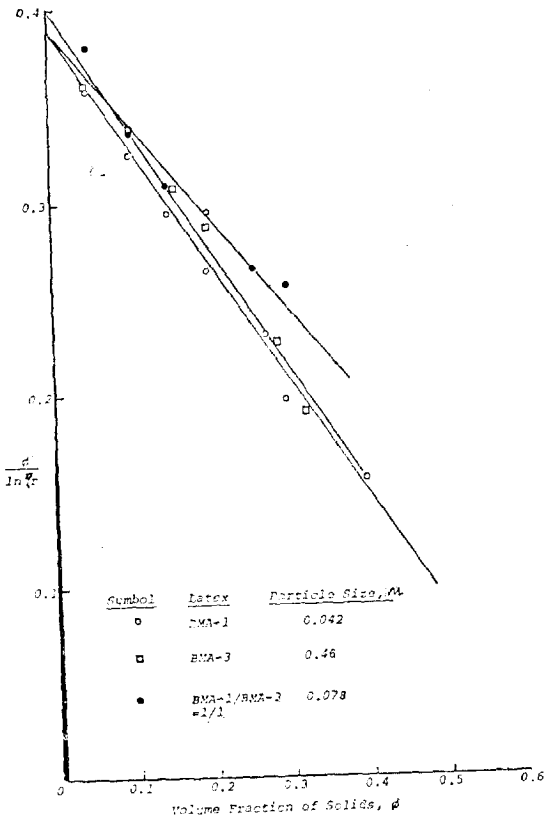


Figure 5. Plots of  $\frac{\phi}{l_n \eta_r}$  vs.  $\phi$  for several latexes.

ger and Dougherty<sup>13</sup> derived a similar equation. Rearranging eq. (2), one has

$$\frac{\phi}{l_n \eta_r} = \frac{1}{k_1} - \frac{s}{k_1} \phi \dots\dots\dots (3)$$

A straight line would be expected by plotting  $\phi/l_n \eta_r$  against  $\phi$  as shown in Fig. 5. Fig. 5 is for two acrylic emulsions and their blend<sup>14</sup>. Table II summarizes parameters obtained from Fig. 5 by the least-square fit.

Depending on the latex tested, values of  $k_1$  and  $S$  are varied. The differences for  $k_1$  may be explained in terms of an adsorbed layer. Fig. 6 gives plot of  $k_1$  versus  $1/D$  from Table II. Extrapolation to zero in abscissa gives  $k_1$  value of 2.5, Einstein's constant. Thus, value of  $k_1$  could be affected by such factors as electrolyte level, emulsifier, stabilizer, and thickener.

Note that value of  $\phi_{\max}$  for unimodal emulsions is about 0.65 in Table II, which is close to

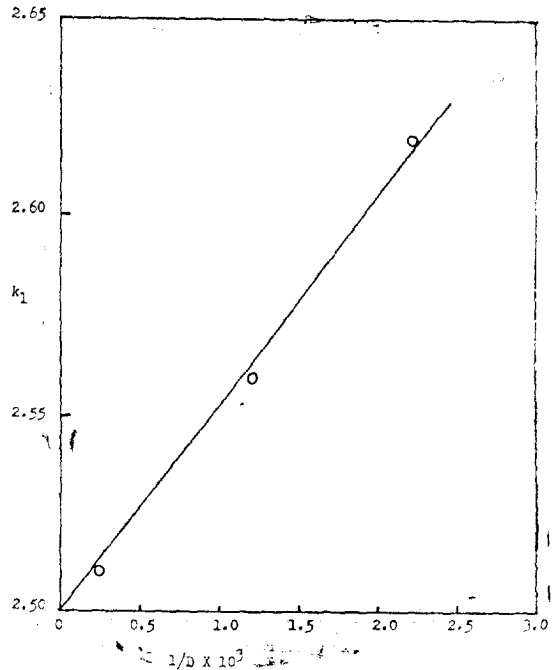


Figure 6. Variation of the einstein constant with latex particle size.

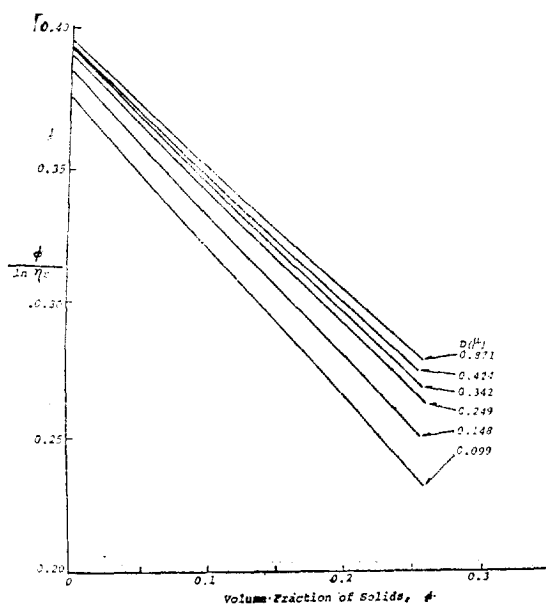
**Table II.** Constants of The Mooney Equation for Latexes in Figure 5.

Sample	$k_1$	S	$\phi_{\max}$
BMA-1	2.62	1.54	0.649
BMA-3	2.51	1.55	0.645
BMA-1/BMA-3=1/1	2.56	1.22	0.820

0.637 value for the random packing of monodisperse spheres<sup>15</sup>. However,  $\phi_{\max}$  for blend systems is much higher than unimodal systems because of the bimodal distribution of particles. Commercially, there are many bimodal emulsions having up to 65% solids.

### III-2. Particle Size

In general, viscosity of a dispersion is decreased as the particle size increases at a constant solid content. The Mooney plots for monodispersed polystyrene latexes are given in Fig. 7<sup>16</sup>. Straight lines and lower viscosity for larger particle are seen from Fig. 7. When the



**Figure 7.** Mooney plots for monodisperse polystyrene latexes.

particle size becomes larger at a constant solid content, interparticle distance becomes larger (see Fig. 10 in next section). Thus, interactions between particles are reduced to give lower viscosity. In practice, however, other factors such as particle size distribution, electrolyte level and shear rate also play significant role to the rheological properties. Considering all of the variables, effects of particle size and particle size distribution can be summarized as follows:

- Larger particle size latexes give lower viscosity.
- Narrow distribution has higher viscosity than broad distribution.
- Bimodal distribution has lower viscosity than narrow distribution.

### III-3. Surface Area and Number of Particles

Interparticle spacing is governed by the diameter of the particles, the type of particle packing, and the volume fraction of the polymer solids in the latex. Latex viscosity, stability and particle interactions are important resultant properties of the interparticle spacing. At a given solid content, therefore, surface area and number of particles are function of particle diameter and interparticle distance.

A face-centered cubic packing arrangement of uniform spheres are assumed for the latex. One layer of such a packing is shown in Fig. 8. Each succeeding layer of particles rests in the depressions of the layer immediately beneath it; thus, each particle has twelve nearest neighbors. This type of packing (tetrahedral arrangement) is the most efficient way of packing uniform spheres. Then, the volume of a latex particle  $v_p$  is

$$v_p = \frac{\pi}{6} d_p^3 \dots \dots \dots (4)$$

and total volume  $v_t$  for  $n$  number of particles

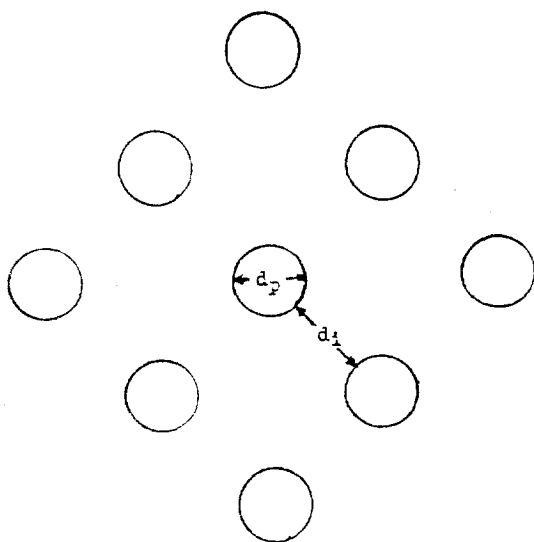


Figure 8. Particle packing.

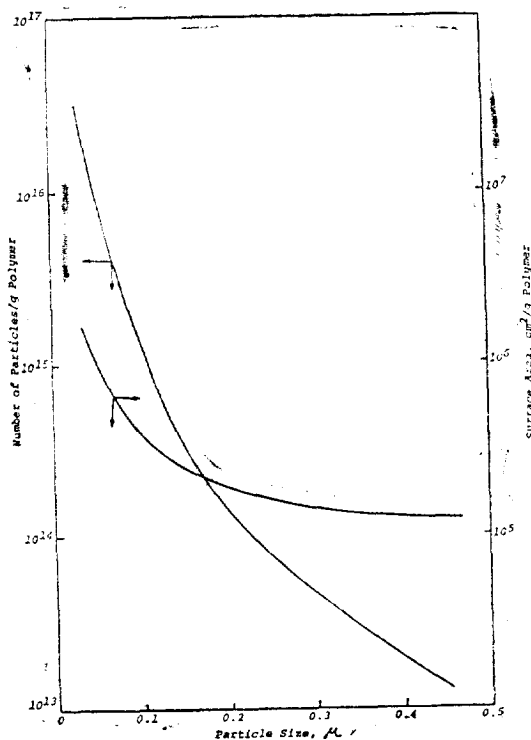


Figure 9. Relationship of particle diameter with number of particles and surface area.

$$\text{is, } v_t = \frac{\pi}{6} n d_p^3, \quad n = \frac{6v_t}{\pi d_p^3} \dots\dots\dots (5)$$

Then, surface area for a latex particle  $s_p$  and whole latex  $s_t$  are

$$S_p = \pi d_p^2 \dots\dots\dots (6)$$

$$S_t = n \pi d_p^2 = \frac{6v_t}{d_p} \dots\dots\dots (7)$$

Thus, latex surface area varies inversely with the particle diameter. Fig. 9 illustrates the relationships of number of particles and surface area with particle diameter.

The interparticle distance  $d_i$  is described as a function of the particle diameter  $d_p$  and volume percent of particle  $\phi$ .

$$\frac{d_i}{d_p} = \frac{1}{\sqrt{2}} \left( \frac{200\pi}{3\phi} \right)^{\frac{1}{3}} - 1 \dots\dots\dots (8)$$

In terms of the weight percent  $W$  and the polymer density  $\rho_p$ , eq. (8) becomes

$$\frac{d_i}{d_p} = \left( \frac{100\sqrt{2}\pi}{6W} \rho_p \right)^{\frac{1}{3}} - 1 = \left( \frac{74}{W} \rho_p \right)^{\frac{1}{3}} - 1 \dots\dots\dots (9)$$

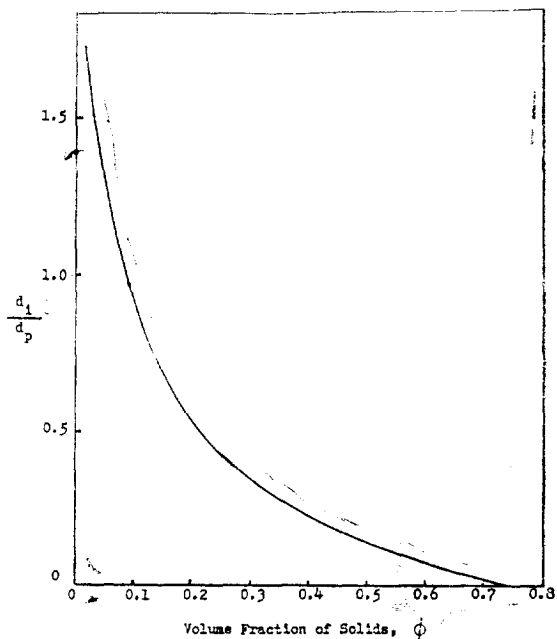


Figure 10. Variation in ratio of interparticle distance to particle diameter with volume fraction.

Fig. 10 shows variation of  $(d_i/d_p)$  with volume percent  $\phi$ , eq. (8). The particles are in contact with each other at the volume fraction of 0.74, and at a volume percent of about 0.093, the interparticle distance is same as the diameter of the particles.

### III-4. Electrolyte Level

In latex system, additives such as surfactants, stabilizers, and thickeners, are incorporated into the system during the process of synthesis and formulation. Unfortunately, these additives have profound effect on the rheological properties even with small amounts through adsorption to the particle surface or formation of electrical double layer<sup>17~22</sup>. Fig. 11 gives effect of three different anionic surfactants on viscosity of a latex system<sup>23</sup>. For a given surfactant, a mini-

mum viscosity is seen, at which the particle surface is saturated with surfactant giving minimum particle interactions. Viscosity increase after the minimum may be due to formation of new micelles with the excess surfactant.

Woods and krieger<sup>18</sup> also observed a minimum in the viscosity  $V_e$  electrolyte level curve in a study of polystyrene latexes. Schaller and Humphrey<sup>24</sup> have investigated particle size and ionic strength showing that eq. (2) can be used to describe ionic strength of polystyrene latexes.

### III-5. Latex Blends.

When two latexes differing in particle sizes are blended, the finer particles in a dispersion behave essentially as a fluid toward the coarser particles. The most illustrative work was by Fidleris and Whitmore<sup>25</sup> who have investigated the settling velocity of large spheres in a 20% suspension of uniform-sized small spheres. The results of their investigation showed that if the size ratio (small to large) was 0.1 or less, then the large spheres encountered the same resistance to motion when passing through a suspension of smaller spheres as when it passed through pure liquid of the same viscosity and density as the suspension. When the size ratio became greater than 0.1, the falling spheres appeared to encounter the same resistance but followed a zig-zag random path instead of a linear path. Later, Farris<sup>26</sup> derived the viscosity-concentration relationship for the blended multimodal dispersion systems from the unimodal components.

$$\eta_r = \prod_{i=1}^N H(\phi_i) \dots \dots \dots (10)$$

where  $H(\phi_i)$  is the relative viscosity of  $i$ -th component. For a blended bimodal system, eq. (10) becomes

$$\eta_r = H(\phi_f)H(\phi_c) \dots \dots \dots (11)$$

in which  $H(\phi_f)$  and  $H(\phi_c)$  denote relative

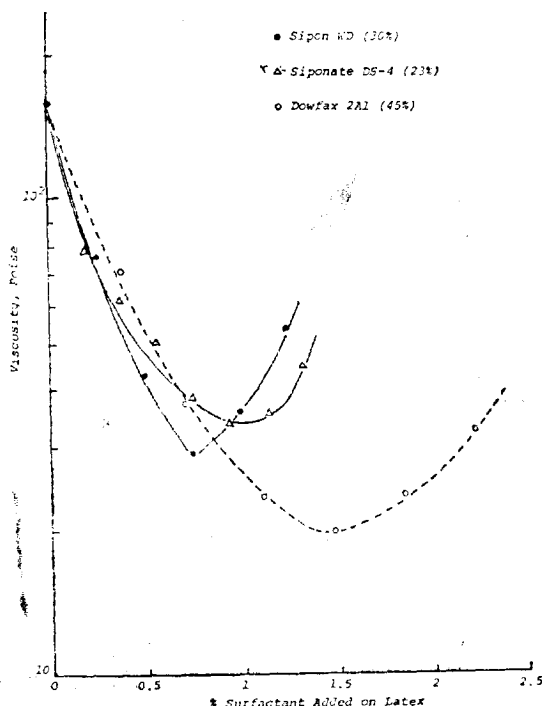
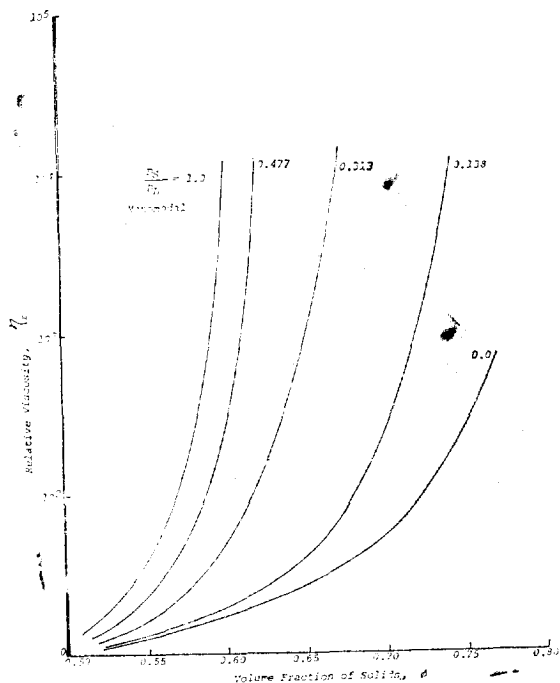


Figure 11. Viscosity of A thickened latex with surfactant level.

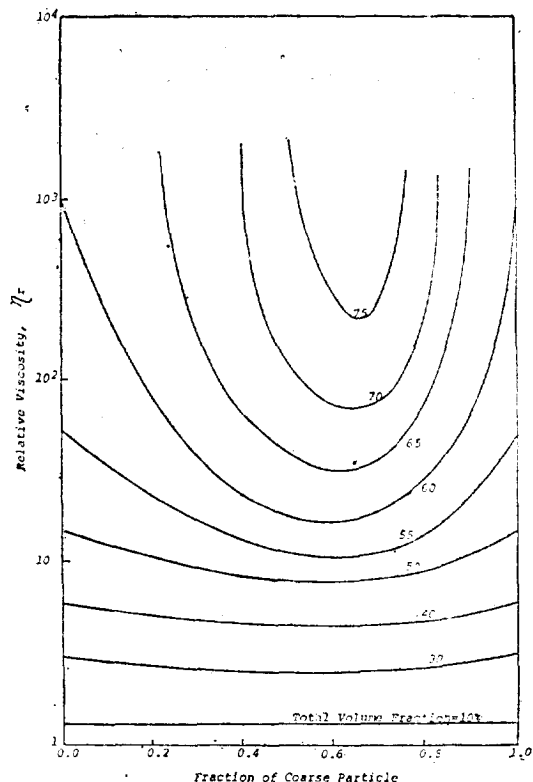


**Figure 12.** Relative viscosity of monomodal and bimodal suspensions for various particle size ratios (Volume fraction of small spheres = 25% of total volume fraction).

viscosities of fine and coarse particles, respectively. Fig. 12 shows relative viscosity curves of several bimodal blends with a fixed fraction of fine spheres (based on total volume fraction, not the same  $\phi$ ). Fig. 13 illustrates the relative viscosities for bimodal systems versus blend ratio for a number of concentrations. A few noticeable points from Figs. 12 and 13 are:

(a) The volume fraction for the bimodal suspension can go much higher than the unimodal case. This is very important point for the practical use where high solid dispersion is much desirable. In fact, there are many commercial bimodal dispersions with more than 60% solids whereas the unimodal system is limited to below 50% due to high viscosity.

(b) As the size ratio decreases, the relative



**Figure 13.** Relative viscosity of bimodal suspension for various blend ratios and volume fractions.

viscosity of the bimodal dispersion is decreased at a given volume fraction. In other words, manipulation of fine and coarse particle sizes enables us to design the bimodal system with relatively high concentration.

(c) A minimum viscosity can be obtained with proper blends of fine and coarse particles at high concentrations. At low concentrations, however, viscosity is practically independent of the blend ratio. Earlier, Johnson and Kelsey<sup>27</sup> also observed minimum viscosity in the bimodal blend systems.

Although the blending technique indicates that the high concentration is possible as seen in Figs. 12 and 13, the blending technique offers no advantage in practice. It is because individual

dispersion should be made before blending, which is limited to low concentration. However, if one can prepare the bimodal latex by polymerization, not by blending, the high solid latex can be obtained as commercially proven.

#### IV. Latex Thickening

The latex system usually consists of latex binder, pigments, fillers, thickener, and other additives. As mentioned earlier, since these ingredients produce very complex interactions, it is difficult to study effect of only one or two ingredients on the rheological properties of latex system. Nevertheless, general macroscopic phenomena of these components are fairly well studied in terms of overall performance of the coating, and the rheological properties are often controlled by formulation techniques.

##### IV-1. Polymer Adsorption.

A common phenomenon of the water soluble polymer in the latex system is adsorption to the particle surface. The adsorption behavior of polymer or surfactant can change the rheological properties of the latex system. Also, displacement from the particle surface of one polymer by another polymer or a surfactant can produce some significant changes. Therefore, a knowledge of the adsorption characteristics of these materials in latex system is helpful to understand stability and rheological properties, and to guide formulation studies.

We have seen surface coverage behavior of three surfactants in terms of viscosity of a latex system (Fig. 11). Fig. 14 gives adsorption behavior of methylcellulose onto monodisperse latexes with different surface coverages of sodium lauryl sulfate<sup>28</sup>. Brodnyan and Kelly<sup>29</sup> reported adsorption of polyacrylic acid and hydroxyethylcellulose on synthetic acrylic latexes. They also studied adsorption of sodium lauryl sulfate and

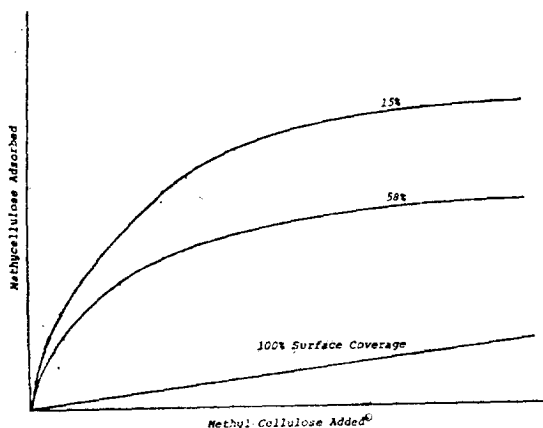


Figure 14. Adsorption of methylcellulose on latex particle surface covered with sodium lauryl sulfate.

determined the molecular adsorption area. Many other researchers<sup>30-36</sup> reported similar adsorption studies in connection with stability, flocculation, and thickening mechanism. These studies indicate that the adsorption characteristics of the water soluble polymer or surfactant are largely dependent on the surface characteristics of particles. Fig. 14 dramatically demonstrates effect of free surface available on the adsorption behavior of methylcellulose. The surface characteristics include chemical compositions of particles, particle size, emulsifier level, electrolyte level and other additive levels.

##### IV-2. Mechanism of Latex Thickening

Brown and Garrett<sup>31</sup> postulated mechanism of thickening in terms of adsorbing effects resulting in flocculation or deflocculation of the dispersed phase. Latex thickening is not simply an enhancement of the viscosity of the aqueous phase. Fig. 15 shows schematic of latex thickening and Fig. 16 describes schematic of multicomponent interactions of a pigmented latex system. The evidence for these figures is circumstantial at best but they are the widely acce-

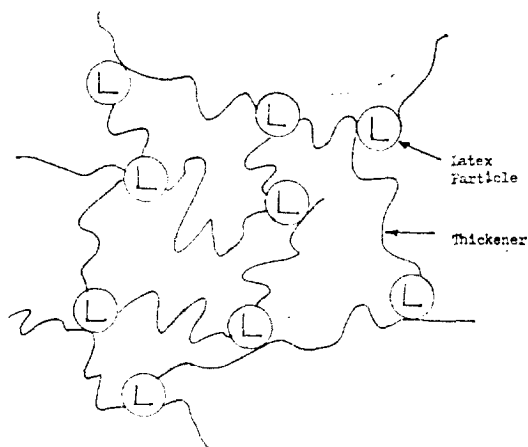


Figure 15. Structure produced by thickener and latex particles.

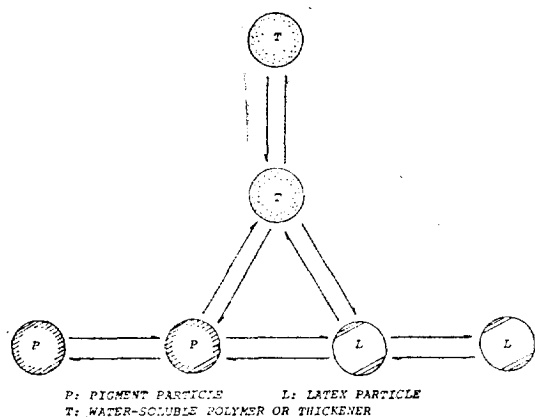


Figure 16. Multicomponent interacting system.

pted hypothesis in the coating field.

Rheology of the thickened latex systems is also studied by other workers<sup>32, 37, 38</sup>. They studied the thickened latex systems in terms of flow behavior, yield stress, thixotropy, temperature and aggregate formation. In particular, interactions between pigments, latex particles and thickeners (see Fig. 16) form "pseudo-structure" which seems to give the yield stress and thixotropy; highly desired properties of the latex system.

### W-3. Association and Swelling of Particles

Two relatively new concepts in latex thickening are particle "association" with hydrophobic-polymers and particle "swelling" with alkali sensitive polymers. Essentially, both techniques have been known for a while but only recently they received attention as thickening agents in coatings. Schematic presentations are given in Fig. 17.

There are a few commercial "associative" thickeners<sup>39-41</sup>. Main advantages of this thickener class are:

(a) They have relatively low molecular weight so that relatively high concentration solutions can be made. Conventional thickeners such as hydroxyethyl cellulose and carboxymethyl cellulose should use low concentrations due to high solution viscosity.

(b) Thickening efficiency, however, is comparable with the conventional thickeners. In other words, the unique nature of hydrophilic-hydrophobic segments produces very complicated interactions in the pigmented or unpigmented latex systems. Although no exact mechanism is known, associations between particles and polymer segments seem to be main thickening mechanism (see Fig. 17)

(c) Perhaps, the most striking feature of associative thickeners would be ability to manipulate the rheological properties of the latex system<sup>42</sup>. For example, these thickeners can improve flow and leveling of the latex paint significantly.

The other class of thickener is the alkali "swellable" or "soluble" polymers when neutralized with a base resulting in a significant increase in viscosity<sup>43-46</sup>. Fig. 18 shows viscosity and pH curves of a commercial product upon neutralization with two bases<sup>47</sup>. About 4000 times increase in viscosity can be achieved by

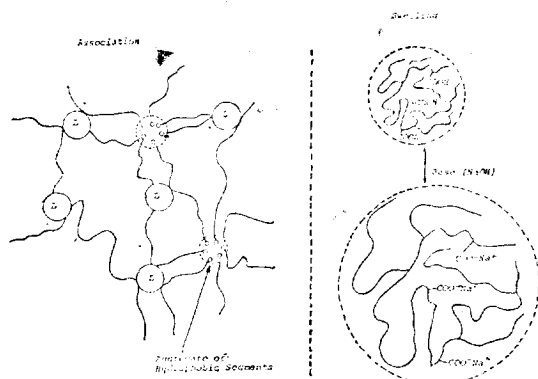


Figure 17. Schematic representation of association and swelling of polymer.

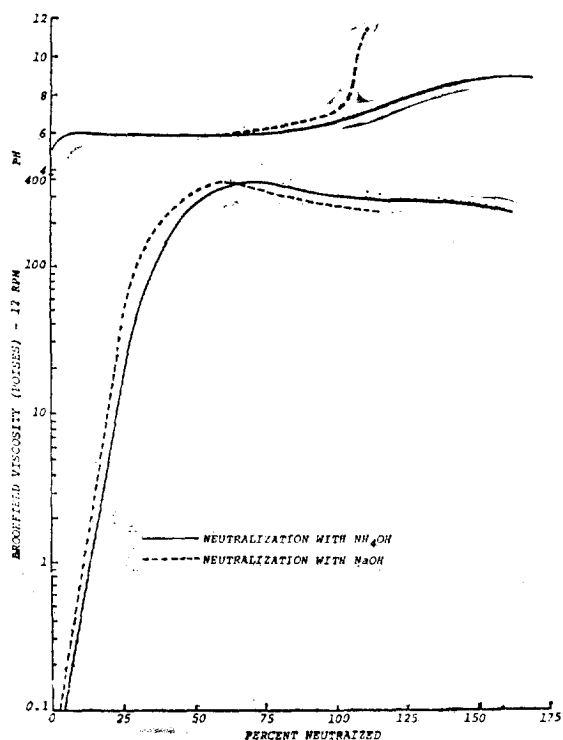


Figure 18. Viscosity and PH change upon neutralization of acrysol ASE-60 with bases at 5% polymer solids.

neutralization. Verbrugge<sup>46</sup> has investigated the mechanism of alkali thickening of a number of

acid containing latexes by viscosity and light microscopy. He reported that the important variables in the swelling and solubilization of acid containing latexes upon neutralization are percent acid, the glass transition temperature of polymer, and hydrophobicity. A distinct feature of this new thickening agent is in its capacity to change solution properties by simple manipulation. As shown in Fig. 18, the latex has very low viscosity at low pH but the desired viscosity can be obtained upon neutralization with the selected base whenever necessary.

## V. Conclusion

It has been shown that rheology of the latex systems depend on many factors arising from the differences in latex preparation and formulation. In a relatively simple latex system, some of those factors may give generally predictable contributions. However, since the majority of latex systems in use possess many important factors originated from very complex interactions and physical changes, it is very difficult to generalize any effect of those factors.

In describing viscosity of the latex systems, the Einstein equation is generally valid with very dilute latex system. The Mooney equation is more widely used to describe the viscosity-concentration relationship. Some latexes are Newtonian at low volume fraction ( $<0.25$ ) but non-Newtonian behavior (shear-thinning) is more general in the most latex systems. Thixotropy is another desirable property in certain latexes, particularly in the pigmented latex systems such as paints and caulks. Particle size and particle size distribution also exhibit significant effect on latex viscosity. Effects of concentration and particle size are more profound at high solid contents where a higher limiting packing fraction is possible with the bimodal emulsion technique.

Emulsifiers and water soluble polymers alter surface characteristics of latex particles and rheology of the system through adsorption, association or swelling. Although mechanisms of these interactions are not well known, the coating industry has begun to look these technologies for controlling the rheological behavior.

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## 牛乳에 의한 重金屬捕捉

이 方法은 이온交換의 原理에 의한 것으로 casein 이 pH 4 以上에서 cation 을 吸着하고, pH 3 以下에서 anion 을 吸着하는 性質을 이용한 것으로 特히 Cr 이 效果의로 500ppm 以上의 Cr 酸鹽을 포함한 溶液이 粒狀의 casein 을 충전한 直列의 4 本의 칼럼층을 통과하고나면 Cr 酸鹽의 濃度는 1ppm 以下가 된다. Casein 은 0.1N 의 ammonia 水로 再生되고, Cr 은 Cr 酸鹽의 ammonium 鹽으로 回收된다. 水溶性인 Casein 은 formaldehyde 로 處理하면 不溶性으로 되기때문에 문제는 없다고 보아진다. 곧 이어 pilot plant 의 단계까지 進행될 豫定으로 되어 있다.