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The Flow Properties of Hydrophilic Latexes Thickened with Alkali

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This paper has aimed at the revelation of the thickening mechanism of a latex on the addition of alkali. Experiments have been made on two kinds of latexes dialyzed thoroughly, *i.e.*, the butadiene-methyl methacrylate copolymer latex and the butadiene-methyl methacrylate-methacrylic acid copolymer latex. The degree of the swelling of the latex particles on the addition of alkali has been correctly obtained and has been connected with the thickenability of the latex. The results provide a more rigorous description than Wesslau's suggestion that the thickening of a latex on the addition of alkali is ascribed to the swelling of the latex particles alone. The reason why NH_4OH is a proper thickener is presented, and the most suitable amount of alkali for the thickening of a latex is discussed.

A hydrophillic polymer latex can be thickened by the addition of alkali. Wesslau[1] has suggested that the increase in the particle size in a latex thickened with NH_3 is responsible for the increase in the viscosity of the latex; however, this suggestion is correct only qualitatively. Therefore, influences of other factors on the viscosity of a latex should be examined, as has been pointed out by several investigators.[2-6]

The present investigation has aimed at the revelation of the flow properties of latexes thickened with alkali.

Experimental and Results

Latexes. A butadiene–methyl methacrylate (B–M) copolymer latex and a butadiene–methyl methacrylate–methacrylic acid (B–M–A) copolymer latex were obtained from the Nihon Gas Chemical Co., Ltd.

Table 1. Compositions of copolymers of latexes[a]

Latex designation	Mol% of monomers		
	Butadiene	Methyl methacrylate	Methacrylic acid
B-M	55	45	0
B-M-A	50	46.5	3.5

a) The values listed were determined on the basis of the IR-spectral data of Fig. 1.[7]

Both the latexes used were thoroughly dialyzed with deionized water until their surface tensions were equal or almost equal to that of water. Figure 1 shows the infrared spectra of the copolymer films made from the dialyzed latexes (full line), and from those adjusted to pH 11 with carbonate free sodium hydroxide (dotted line). Table 1 lists the designations of the latexes and the compositions of the copolymers as mol% of the monomers. The particle-size distributions of the latexes used were determined by the measurement of the sizes of about 2000 particles by means

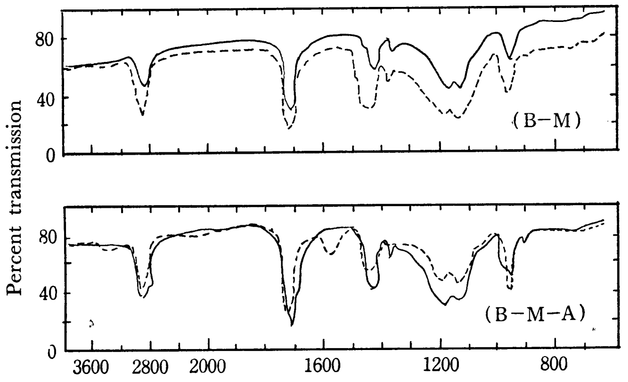

Fig. 1. Infrared spectra of copolymer films. Designations, B-M and B-M-A, are described in Table 1. The full lines and the dotted lines represent the spectra of the films to be made from the dialyzed latexes and those ionized with sodium, respectively.

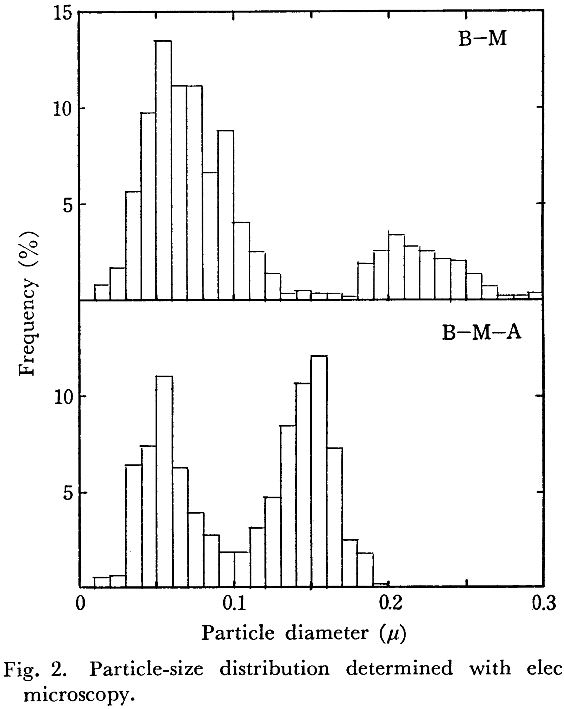

Fig. 2. Particle-size distribution determined with electron microscopy.
The particle frequency is described as a function of diameters.

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[1] H. Wesslau, *Makromol. Chem.*, **69**, 213 (1963).

[2] S. Muroi and K. Hosoi, *Chem. High Polymers*, **26**, 416, 426 (1969).

[3] S. Muroi, *J. Appl. Polym. Sci.*, **10**, 715 (1966).

[4] S. Muroi and K. Hosoi, *Kogyo Kagaku Zassi*, **69**, 1551 (1966).

[5] K. Tyuzyo, Y. Harada, and H. Morita, *Kolloid Z.*, **301**, 155 (1965).

[6] S. Muroi, K. Hosoi, and T. Ishikawa, *J. Appl. Polym. Sci.*, **11**, 1963 (1967).

of the electron microscopy[7,8]; they are shown in Fig. 2.

Viscosity. A colloidal suspension such as a latex is generally a non-Newtonian fluid.[9-12] However, when the concentrations of the latexes used were less than 35 wt% on solids, the flow behavior was Newtonian at rates of shear below 8×10^2 sec^{-1}. Consequently, the concentrations in this investigation were limited to 35 wt% on solids as an initial step toward revealing the intricate flow behavior of latexes.

The viscosities were measured with a Ubbelohde-type viscometer for the latexes dialyzed and for those thickened with NH_4OH and NaOH. Figure 3 shows the relations between the specific viscosity (η_{sp}) and the dried-polymer content (wt%) of the latexes. The B–M latex was hardly thickened by the addition of NH_4OH; on the other hand, the B–M–A latex was remarkably thickened with aqueous solutions of NH_4OH and dilute aqueous solutions of NaOH, but hardly thickened with concentrated aqueous solutions of NaOH.

Swelling and Volume Fraction of Latex Particles. The flow properties of suspensions are generally discussed on the basis of the relation between η_{sp} and vol%(ϕ) on solids. However, when the particles of a latex are swollen, the discussion[1] is based on the data of the wt% on the dried polymer because of the difficulty of determining the volume fraction exactly. In this investigation, the difficulty was overcome with the determination of the degree of swelling for the latex-film instead of that for the latex-particles.

Making of Latex-films. When a polymer latex is evaporated above the glass temperature of the polymer, it becomes a non-porous film.[13,14] Latex-films of about 0.5 mm in thickness were made by means of the evaporation of the latexes on mercury at 60°C.

Swelling of Latex-films. The degree of swelling may be defined as the ratio of the swollen volume of a polymer film to its volume dried.

The films of the latexes used could be swollen in deionized water or in aqueous solutions of alkali, and then again contracted by drying. It was confirmed that the degrees of swelling were reproducible within ±1% by repetition of the swelling and the contraction; this held for different samples too. From these facts, it was presumed that the degree of swelling of a latex-film is equal to that of the latex particles.

In this investigation, the volume of the film was measured with a Beckman-Toshiba air comparison pycnometer, model 930.

Figure 4 shows the dependence of the degrees of swelling of the latex-films immersed in aqueous solutions of alkali on the alkali content of the solution.

The B–M latex-film was hardly swollen with an increase in the NH_4OH concentrations; the degree of swelling of the B–M–A latex-film was suddenly increased at a moderate concentration of NH_4OH and then slightly decreased with a further increase in the concentration. In the case of the swelling in solu-

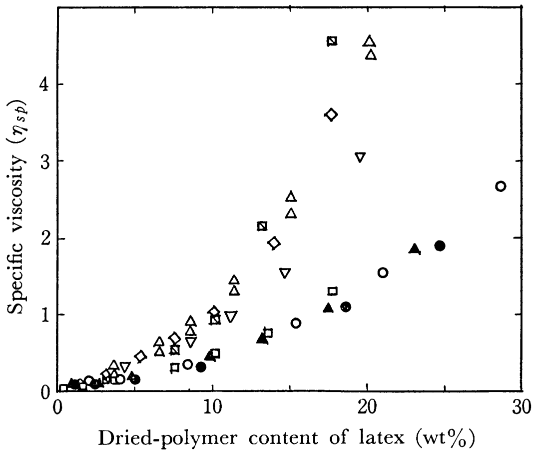

Fig. 3. Influence of thickening with NH_4OH and NaOH on η_{sp}—wt% relationship.
B-M ●: H_2O, ▲: NH_4OH 0.1N
B-M-A ○: H_2O, △: NH_4OH 0.1N, ▽: NH_4OH 1N, □: NaOH 1N, ⊠: NaOH 0.1N, ◇: NaOH 0.01N
Above concentrations (N) of NH_4OH and NaOH indicate those in the serum of the latexes. All viscosities were measured at 35.00±0.01°C.

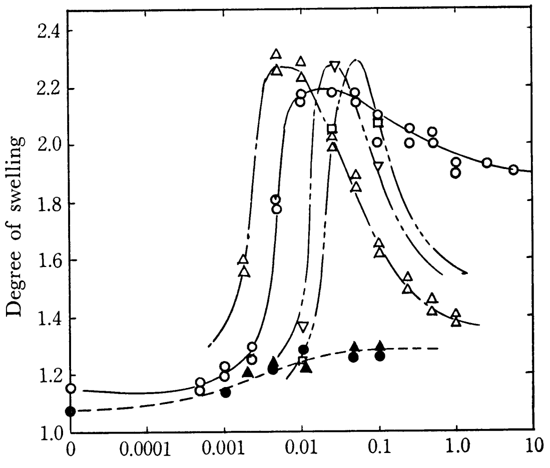

Fig. 4. Degrees of swelling of latex-films immersed in aq. solutions of various alkali concentrations.

Alkali in soln.	Copolymer-film	Wt% of film in soln. of alkali
NH_4OH	------ ●: B-M	1.0
	——— ○: B-M-A	1.0
NaOH	——— ▲: B-M	1.0
	——— △: B-M-A	1.0
	——— ▽: B-M-A	10.0
	——— □: B-M-A	20.1

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[7] S. Shishido and S. Suzuki, *Chem. High Polymers*, **26**, 451 (1969).

[8] K. Kato, *J. Electron Microscopy*, **14**, 219 (1965).

[9] M. Moony, *J. Colloid Sci.*, **1**, 195 (1946).

[10] S. H. Maron, B. P. Madow, and J. M. Krieger, *ibid.*, **6**, 584(1951); S. H. Maron and B. P. Madow, *ibid.*, **8**, 130 (1953).

[11] J. M. Brodnyan and E. L. Kelley, *ibid.*, **20**, 7 (1965).

[12] Y. L. Wang, *J. Colloid Interfac. Sci.*, **32**, 633 (1970).

[13] T. F. Protzman and G. L. Brown, *J. Appl. Polym. Sci.*, **4**, 81(1960).

[14] J. G. Brodnyan and T. Konen, *ibid.*, **8**, 687 (1964).

tions of NaOH, the swelling behavior of the B–M film was similar to that in the case of NH_4OH; the degree of swelling of the B–M–A film was suddenly increased at a moderate concentration and then remarkably decreased with a further increase in the concentration.

It is worth noting that the carboxyl groups in the B–M–A film immersed were equivalent to the alkali content in the solution at the maximum point of swelling.

Discussion

Although the B–M–A latex is more similar to the samples used by Muroi *et al.*[2–4] than to those used by Wesslau[1] in view of the presence of carboxyl groups in the copolymer, this latex, which is unsoluble even in a concentrated NaOH solution, is a suitable sample for an investigation of the flow behavior of a thickened latex, as was proposed by Wesslau.

Equation of Viscosity. The wt% in Fig. 3 may be rewritten as in Fig. 5 in terms of the vol% on the basis of the presumption that when a film and latex-particles of an equal content on solids are thickened with an alkali solution of an identical concentration, the degrees of swelling of both samples are equal.

In Fig. 5, the plots for the B–M latex and the B–M–A latex at 50°C are added.

All the plots were on a curve represented by a full line in this figure and expressed in terms of an empirical formula (1):

$$\eta_{\rm sp} = (\eta/\eta_0) - 1 = 2.5\phi + 9.6\phi^2 + 31.6\phi^3, \qquad (1)$$

where η and η_0 are the viscosities of the latex and its serum, *i.e.*, the dispersing medium, respectively. The broken line represents Einstein's theoretical equation[15] (2), the chain line is Hermans' theoretical equation[16] (3), and the dotted line is Einstein's equation (4) at a very high dilution:

$$\begin{aligned}\eta/\eta_0 &= (1+\tfrac{1}{2}\phi)/(1-2\phi)\\ &= 1 + 2.5\phi + 5\phi^2 + 10\phi^3 + 20\phi^4 + \cdots, \qquad (2)\end{aligned}$$

$$\begin{aligned}\eta/\eta_0 &= 1/(1-2.5\phi)\\ &= 1+2.5\phi+6.3\phi^2+15.6\phi^3+39.0\phi^4+\cdots, \qquad (3)\end{aligned}$$

$$\eta/\eta_0 = 1 + 2.5\phi. \qquad (4)$$

The (1) empirical formula resembled both the theoretical equations, (2) and (3), and was half-way between Guth-Simha's[17] (5) and Vand's empirical formulae[18] (6), which have often been used:

$$\eta/\eta_0 = 1 + 2.5\phi + 14.1\phi^2 + \cdots, \qquad (5)$$

$$\eta/\eta_0 = 1 + 2.5\phi + 7.35\phi^2 + \cdots. \qquad (6)$$

The activation energies of flow for both latexes were independent of the concentration and were the same as that for water.

These results suggest that the viscosity of the latex is dependent on that of its dispersing medium and the volume fraction of its particles, and is independent of other factors for the first approximation.

Thickening of Latex with Alkali. As a comparison between the thickenability of the B–M–A latex with alkali in Fig. 3 and the degree of swelling in Fig. 4 shows, the results of the experiment support Wesslau's suggestion.[1] The fact that Eq. (1) was applicable to all the series in Fig. 5 provides a more rigorous description than Wesslau's, though; that is, an increase in the viscosity of a latex on the addition of alkali can be ascribed only to the swelling of the latex-particles.

This conclusion needs to be compared with Muroi's suggestion[2–4] that the dissolution of the surface layers of latex particles containing carboxyl groups and swelling of their cores on the addition of alkali cause the thickening of the latex. The dissolution of the surface layers in his investigation was ascribed to the larger number of carboxyl groups concentrated in the particle surface layers than in the present investigation. Accordingly, the conclusion in the present report does not contradict Muroi's suggestion.

Selection of Alkali for Thickening. It is usually said that the best alkaline thickener is one giving a thickening curve such as B in Fig. 6, and that NH_4OH is the best reagent. These facts can easily be illustrated by a comparison between the curve of the swelling of the B–M–A film with NH_4OH in Fig. 4 and the B-curve in Fig. 6. On the other hand, a

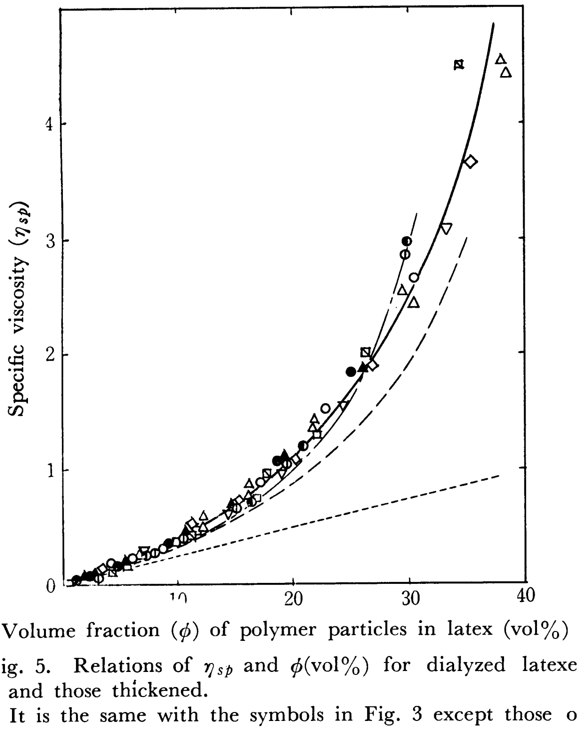

Fig. 5. Relations of η_{sp} and ϕ(vol%) for dialyzed latexes and those thickened.

It is the same with the symbols in Fig. 3 except those of the dialyzed latexes at 50°C, B-M ◐: H_2O and B-M-A ◑: H_2O.

—— Einstein's theoretical equation (2)

– – – Hermans' theoretical equation (3)

------ Einstein's equation at very high dilution (4)

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[15] T. Katsurai, "Koroido no Riron," Kawaide Shoboo, Tokyo, (1947) p. 46; A. Einstein, *Ann. Physik*, (4) **19**, 289(1906), **34**, 591 (1911).

[16] J. J. Hermans, "Flow Properties of Disperse Systems," North-Holland, Amsterdam (1953) p.167.

[17] E. Guth and R. Simha, *Kolloid-Z.*, **74**, 266 (1936).

[18] V. Vand, *J. Phys. Col. Chem.*, **52**, 277 (1949).

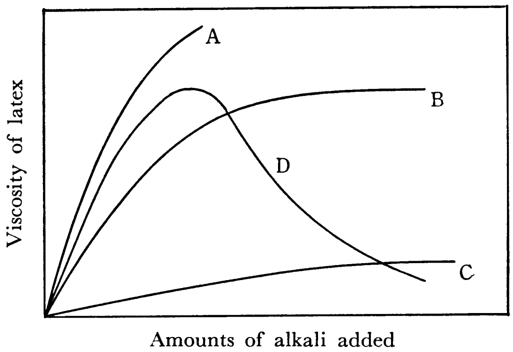

Fig. 6. Thickening of latex on addition of alkaline thickener.

concentrated aqueous solution of NaOH can not be regarded as a good thickener, as is shown in Fig. 3; the D-curve in Fig. 6 is a schematic illustration of this, and it can also be expected from Fig. 4.

The alkali concentration at the maximum value of the degree of swelling, as is shown in Fig. 4, provides information about the most suitable amount of alkali for the thickening of a latex because of the equivalence in the amounts of the carboxyl groups and the alkali ions, as has been described previously.

Particle Size and Its Distribution. Although both the latexes used differed considerably in their particle-size distributions, as is shown in Fig. 2, the $\eta_{sp}\sim\phi$ relations, Eq. (1), were nearly akin to Einstein's relation, Eq. (2), for suspensions of spheres of uniform size. These results suggest that a latex possessing such a size distribution may be regarded as a mono-dispersed system in view of fluid mechanics.

The viscosity of a latex containing a surface-active agent is dependent on the particle size and its distribution.19) When such latexes are thickened, their flow properties become complex, as has been reported by several investigators.5,6)

The simpler results obtained in the present investigation may be supposed to be caused by the complete dialysis of the latex.

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19) C. Parkinson, S. Matsumoto, and P. Sherman, *J. Colloid Interfac. Sci.*, **33**, 150 (1970).