Latex Thickening: Interactions between Aqueous Polymeric Dispersions and Solutions

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I. INTRODUCTION

Whenever a polymer emulsion—alternatively referred to as a latex or polymer dispersion—is used as such, it is almost sure to be modified by formulation. The control of flow properties is one of the most important objectives of the process of formulation. Because these emulsions are characteristically very fluid, increased viscosity is usually sought by the addition of "latex thickeners." As a result, the entire subject of the control of flow properties is often referred to under the general term "latex thickening," although this conveys a greatly oversimplified impression of the subject. Because of the increasing utilization of polymer emulsions, the problem of latex thickening is of great industrial importance.

Superficially, the enhancement of latex viscosity by addition of a viscous solution of a water soluble polymer would appear to be a simple process. The subject is increasingly interesting from a scientific standpoint as it becomes apparent that the viscosity of the combined latex and thickener is not a simple additive function of the viscosity of the components. An examination of rheological data of the dispersions, the soluble polymers, and combinations leads one to the conclusion that latex thickening is not a simple process of increasing the viscosity of the continuous phase of the dispersion. The data available indicate that several competitive interactions must be postulated to account for the overall rheological behavior of these soluble polymer-dispersion combinations.

With emulsions of small particles which are not observable with a conventional microscope, where the structure to be examined would be destroyed by drying specimens for inspection under an electron microscope, we must depend upon indirect evidence (usually flow properties) to elucidate the mechanism of latex thickening. Evidence of this type and a qualitative interpretation in terms of colloidal structure are presented in this paper.

II. GENERAL DESCRIPTION AND BEHAVIOR OF THICKENED LATEXES

A. The Dispersion-Solution System

The complications which arise in examination of the rheology of thickened latex are less surprising if the system is described in detail. The latex-thickener combination actually consists of the components: water, water-soluble polymer, insoluble, dispersed polymer, emulsifier, and salts (catalyst decomposition product, etc.). These materials are present in an aqueous phase, a surface phase, and a dispersion (water-insoluble polymer) phase.

Among the components, only water is universal. Wide variations may be made in the dispersed polymer, in the emulsifier employed, and in the thickener. Changes in the emulsifier and the thickener would be expected to be particularly important in their influence upon the flow properties of the thickener-dispersion combination.

B. Observed Behavior of Thickened Latex

A number of observations of the behavior of samples of thickened latex provide persuasive evidence that the process involved in latex thickening is not merely that of enhancement of the viscosity of the continuous (water) phase by the water-soluble polymer. Several classes of evidence are presented below.

(1) Latex Creaming

Many water soluble polymers produce sedimentation (creaming) when present in a polymer emulsion within a rather narrow, low concentration range. Their presence in water increases the viscosity, and if this effect were the only one in the emulsion, decreased sedimentation should result, in accordance with Stokes's Law. The fact that the opposite effect is produced necessitates recourse to quite a different mechanism than a simple

alteration of aqueous viscosity. The mechanism which is generally postulated, and appears to account satisfactorily for observed behavior, is that of a limited flocculation or clustering of particles, perhaps as a result of being bound together by the thickener molecules. Microscope examination or large particle size latexes discloses the formation of clusters in the treated latex consisting of particles loosely bound together. The clusters sediment more rapidly than the ultimate particles as a result of the greater equivalent sedimentation radius.

Assuming that this flocculation results from the binding of the particles by chains of the water soluble polymer, it is readily apparent why there is a narrow concentration range of the soluble polymer for optimum sedimentation. Once the binding is accomplished, further additions of this polymer should raise the viscosity of the continuous phase, slowing sedimentation.

(2) Specificity of Thickening

If latex thickening were simply a process of a thickening, or viscosity enhancement, of the aqueous phase, the effectiveness of various thickeners should be predictable from a knowledge of their viscosity behavior in water.

The viscosity of the emulsion, at constant temperature, is a function of the volume concentration of the disperse phase:

$$\eta_e = \eta_w \left(1 + f(\phi)\right) \qquad (1)$$

where η_e is the viscosity of the emulsion, η_w is the viscosity of water, and ϕ is the volume concentration of the disperse phase. The viscosity of the thickener solution is also a function of the concentration, c, of the water soluble polymer.

$$\eta_t = F(c) \qquad (2)$$

If the emulsion and thickener could be combined so that (1) the interactions, if any, among particles present in the emulsion are not disturbed, (2) the interactions, if any, among the soluble polymer molecules are not disturbed, and (3) no new soluble polymer-dispersion particle interactions are introduced, the calculated viscosity of the thickened latex should be given by:

$$\eta_1{}^c = \eta_t \left[1 + f(\phi)\right] = \eta_t \left(\eta_e/\eta_w\right) \qquad (3)$$

Since the viscosities of the water, the dispersion, the thickener solution, and the thickened latex are all observable, the above equation may be tested. In general, it does not hold, and there is very little correlation between the aqueous viscosity of a polymer and its efficiency in thickening various latexes.

The specificity of the action of latex thickeners again leads to the necessity of postulating a mechanism other than that of increasing the viscosity of the continuous phase.

(3) Structural Viscosity

Many thickened latexes exhibit flow curves which are generally attributed to the presence of "structure,'" that is, the shear breakdown found in thixotropy or in pseudoplasticity may be accounted for by the initial existence of bonds of some sort which produce assemblages of the ultimate units present in the dispersion. These bonds are broken during shearing to give lower viscosity and reform when the shearing stress is removed (rapidly in pseudoplastic behavior, more slowly with thixotropy).

(4) Reversal of Thickening

A few cases have been observed in which the addition of thickener beyond a certain point produces a decrease in viscosity. Indeed, in an example reported below in the Experimental Section, a maximum and minimum are found in the curve of viscosity versus concentration of thickener. Since the viscosity of the thickener solution in water is a monotonically increasing function of concentration, it is obvious that a more complicated set of interactions must exist than that of a simple combination of dispersion and solution viscosities.

III. EXPERIMENTAL

A. Rheological Study

Experimental measurements of flow properties of thickened latexes were made for two purposes. First it was desired simply to characterize the flow behavior of a number of combinations of latexes and thickeners in order to obtain information which might be a guide to their usefulness in applications. Secondly, the objective pertinent to this study was to use the rheological behavior to assist in the analysis of the processes involved in latex thickening. Examination of such complex systems is not susceptible to direct methods, such as microscopy or chemical analysis, because the phase subdivisions are of inconvenient size and are not stable under most ordinary analytical techniques. Therefore, the indirect approach of rheological characterization was chosen.

(1) Apparatus and Measurements

The apparatus chosen for making flow measurements was a modified Stormer viscometer as described by Fischer and Lindsley.[1] The dimensions of the bob and cup used in most of this work were for the bob, 1.23 in. radius, 1.39 in. length; for the cup, 1.375 in. radius, 2.55 in. depth.

The procedures for making measurements were as follows. Enough weight was added to cause the bob to rotate at about 300 rpm. If successive determinations indicated constant viscosity, weights were removed and weight vs. time was recorded for 300, 200, 100, 80, 40, and 20 rpm, approximately. At least three readings were taken with each load, and the times were averaged. The smallest load which would produce observable motion was also noted.

If the elapsed times for successive readings at 300 rpm decreased, a different procedure was followed. The weights required to produce a 300 and a 20 rpm rotation were found, following which the sample was permitted to rest undisturbed for at least one hour. Then, the lesser weight was added and the time for 100 revolutions noted. Five intermediate weights were chosen which increased the load monotonically, and the times corresponding to 100 revolutions with each weight were determined with a minimum of lost time. After determination of the time for the largest weight, the determinations were repeated with the same weights immediately in descending order.

Calculations were made as follows.

Flow Curves. Analyses of the data were made following the methods outlined by Krieger and Elrod.[2]

Yield Stresses. The method used to determine the value of yield stresses as defined herein is not a general one, but is a fortunate accidental consequence in the general shape of the graphs of the shear stress, τ, vs. the shear rate, S. Over the range of shear rates investigated, these were almost without exception accurately parabolic. They could be represented by an equation of the form:

$$S = k(\tau - \tau_0)^2 \qquad (4)$$

Plots of the square root of shear rate vs. shear stress intersect the stress axis at a value which is called the yield stress, τ_0.

(2) Materials and Preparation

The thickeners were prepared and stored as 5% stock solutions. Lower concentrations were prepared as needed by dilution. Methocel (400 cps) and CMC-70H stock solutions were measured by weight because they were too viscous to be handled volumetrically.

Latexes were used as received except in experiments involving latex solids or third components (e.g., ions, pH, etc.). Thickener and latex were mixed slowly with gentle stirring in the order recommended for each thickener.

In most experiments, volume ratios of 100:20 or 100:40 latex to thickener were employed. In latex solids studies, 100 parts of diluted latex were added to 20 parts of thickener so that the total volume and amount of thickener remained constant.

(3) Results of Rheological Measurements

Flow Curves. A number of examples of graphs of square root of shear rate vs. shear stress are illustrated in Figures 1, 2, and 3. The volume ratios of latex to thickener solution are indicated in the legends. The generality with which an approximate straight line was thus obtained through-
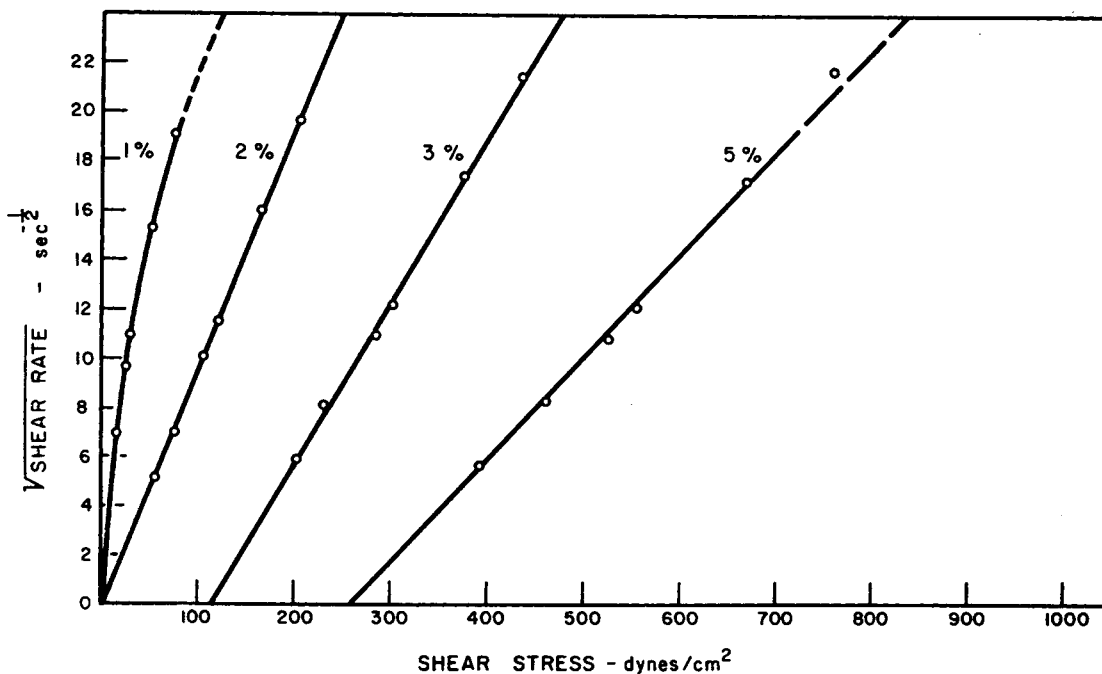
TABLE I
Polymer Emulsions: Properties

Emulsion	Polymer type	Emulsifier	Solids, wt.-%
Rhoplex B-60	Acrylic copolymer	Nonionic	47.5
Rhoplex WN-80	" "	Anionic	39.2
Rhoplex FRN	" "	Nonionic	40.2
Rhoplex ER	" "	Anionic	50.5
Rhoplex SR	" "	Anionic	26.2
GRS, Type IV	Styrene-butadiene copolymer	Anionic	41.0

TABLE II
Thickeners: Properties

	Form	Description	Supplier
Acrysol GS	12.5% aq. soln.	Sodium polyacrylate	Rohm & Haas Co.
Acrysol G-110	23% aq. soln.	Ammonium salt of acid-acrylic copolymer	"
Methocel (15 cps)	Powder	Cellulose-dimethyl ether	Dow Chemical Co.
Methocel (400 cps)	Powder	Cellulose-dimethyl ether	"
CMC-70H	Powder	Sodium carboxymethylcellulose	Hercules Powder Co.

Fig. 1. Shear stress vs. (shear rate)$^{1/2}$.   GR-S IV:Acrysol GS (numbers indicate thickener solution concentration), 100:20.
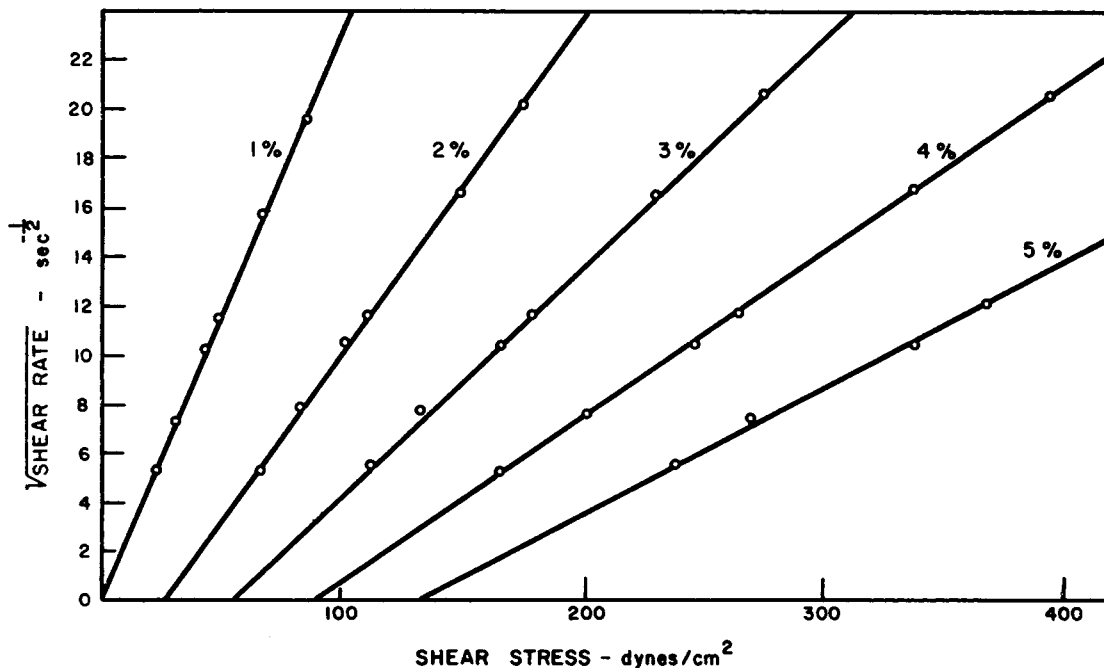

Fig. 2. Shear stress vs. (shear rate)$^{1/2}$.   Rhoplex ER:Acrysol G-110 (numbers indicate thickener solution concentration), 100:20.

out this work suggested that a single hydrodynamic model will suffice to explain most thickened latex systems. At solids contents below about 15%, the parabolic relationship failed, approaching the Bingham or Newtonian cases with increasing dilution. In a few instances, notably with GR-S, time dependence was observed. However, most flow curves obtained were completely reversible,
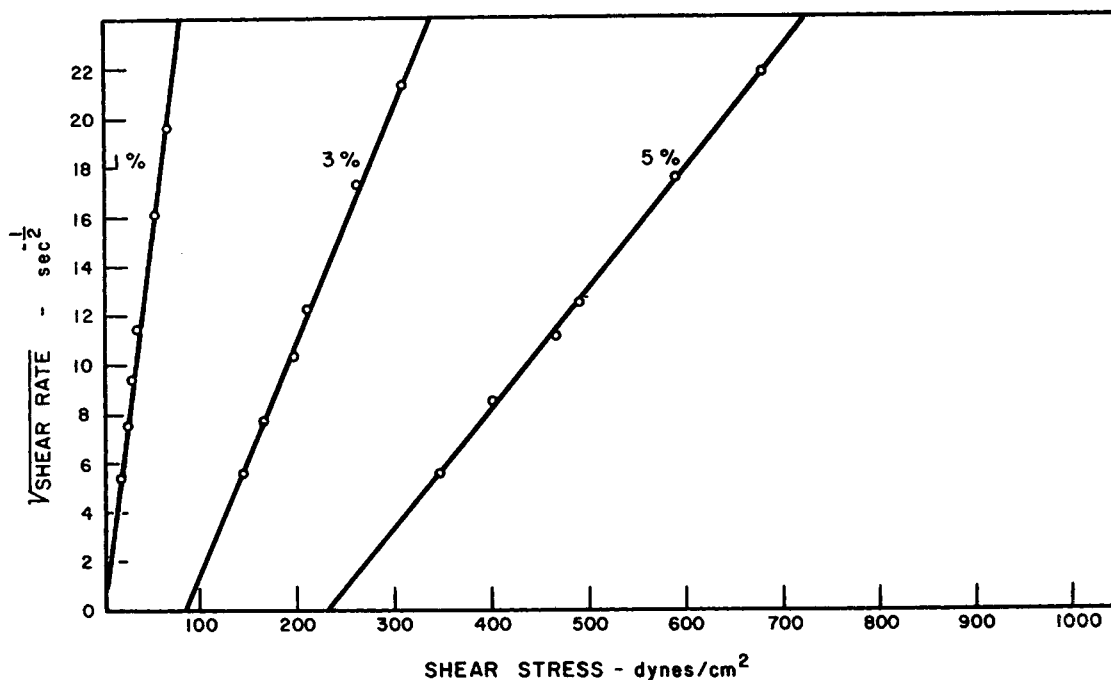
Fig. 3. Shear stress vs. (shear rate)$^{1/2}$. Rhoplex B-60:Methocel (15 cps.) (numbers indicate thickener solution concentration), 100:20.

indicating no thixotropy, false body, rheopexy, or other hysteresis.

This type of flow curve, a rigid region followed by an exponential (parabola) has not been discussed previously. The importance of the discovery, from a pragmatic point of view, is that only two parameters are required to determine a curve

TABLE III
Flow Parameters for Thickened Latices
100:20 Emulsion/Thickener (5% Thickener Solution)

Emulsion	Thickener	k	τ_0
Rhoplex B-60	Acrysol GS	0.0014	160
	Acrysol G-110	0.0019	35
	Methocel (15 cps)	0.0017	73
	Methocel (400 cps)	0.0123	210
	CMC-70H	0.00019	590
Rhoplex ER	Acrysol GS	0.0078	255
	Acrysol G-110	0.0030	135
	Methocel (15 cps)	0.0011	37
	Methocel (400 cps)	0.00011	940
	CMC-70H	0.0026	510
Rhoplex FRN	Acrysol GS	0.0028	70
	Methocel (15 cps)	0.019	61
Rhoplex WN-80	Acrysol GS	0.0028	40
	Methocel (15 cps)	0.357	33
GR-S Type IV	Acrysol GS	0.0019	260
	Acrysol G-110*	0.0028	150
	Methocel (15 cps)	0.013	22
	CMC-70H	0.0010	835

* 2% concentration of Acrysol G-110.

completely. These are k and τ_0, respectively, a width and an intercept (see Table III), where shear rate, S, equals $k(\tau - \tau_0)^2$.

The temptation is to interpret the yield stress, τ_0, as being an indication of weak, reversible structure and k as a measure of the deformability of the flow units. This is not a unique interpretation, however.

Effect of Thickener Concentration. In Figures 4 and 5, the viscosity at 100 sec.$^{-1}$ is plotted as a function of the concentration of thickener solution added to various polymer emulsions. The volume ratios of emulsion to thickener and the emulsion types are indicated. For Acrysol GS, both at 100:20 and 100:40 volume ratios, the increase in viscosity was linear with thickener concentration. For Methocel (15 and 400 cps) and for CMC-70H, the viscosity increased faster than thickener concentration, perhaps indicating a competitive adsorption which removed thickener from solution until the adsorbing surface was satisfied. No such simple picture was evident in the case of Acrysol G-110. Here, the viscosity varied both faster or slower than thickener concentration, depending on the emulsion, indicating a marked specificity in its interaction power. This is not an unusual phenomenon and has been reported for other thickeners in other systems. Actually, Acrysol GS probably constitutes the exception
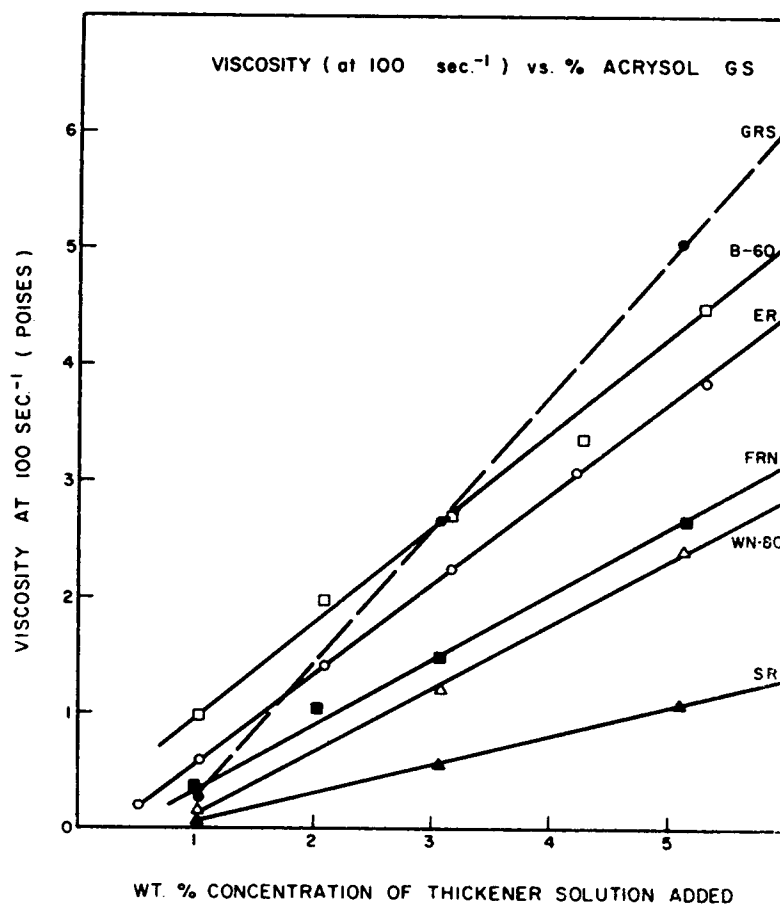
Fig. 4. Viscosity at 100 sec. $^{-1}$ vs. thickener concentration. 100 volumes latex: 20 volumes thickener solution, various latexes plus Acrysol GS.

in exhibiting such apparently simple dependence on thickener level.

Effect of Latex Solids Concentration. Several series of experiments were run in which latex solids content was varied at constant total volume and thickener level. In Figures 6 and 7, viscosity at 100 sec. $^{-1}$ is plotted versus parts of undiluted latex. The calculated curves were obtained by assuming the relationship

$$\eta_{TLC} = (\eta_{TL\text{-}100} - \eta_{TL\text{-}0})C^N$$

where η_{TLC} is the viscosity of the thickened latex at an arbitrary intermediate concentration, C, η_{TL-100} is the viscosity of the thickened full-strength latex, $z_{TL\text{-}0}$ is the viscosity of the thickener with the latex replaced by water, and N is a positive number. These assumptions are open to some criticism, but do serve to illustrate the very strong dependence of viscosity on latex solids. The exponent N varied from 2 to about 4. With Rhoplexes B-60 and ER, Methocel (15 and 400 cps)

showed the steepest dependence on latex solids, Acrysol GS the least. With thickeners such as Methocel, absolute viscosity control is extremely difficult to achieve because of the apparent fourth power dependence on solids content.

Yield Stress. Yield stresses referred to herein were obtained by methods described above, i.e., by extrapolation of a flow curve. They are not comparable to data obtained in creep experiments because of the different time scales involved. They are true yield values, however, in the sense that no detectable motion was observed within the duration of an experiment when lesser stresses were applied. Somewhat lower values were found when a larger gap between cup and bob was used.

In Table III, the values of the yield stresses obtained with 100:20 latex/thickener at 5% thickener level are shown for all the systems investigated (GR-S Type IV was thickened with 2% Acrysol G-110). If it is possible to generalize on the basis of these limited data, Methocel (15 cps) showed
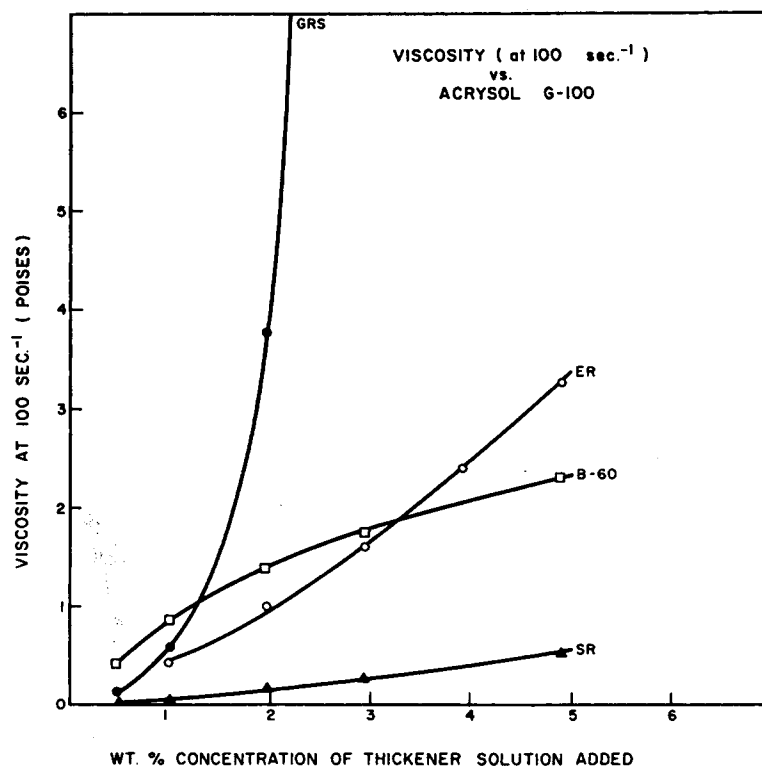
Fig. 5. Viscosity at 100 sec.$^{-1}$ vs. thickener concentration.   100 volumes latex:
20 volumes thickener solution, various latexes plus Acrysol G-110.

consistently low yield stresses, CMC-70H showed consistently high yield stresses; Acrysol GS to some extent and Acrysol G-110 to a great extent showed variability, while with GR-S Type IV the latex was too thick to measure at the 5% thickener level.

In Figure 8, yield stress as a function of thickener level is plotted for a few systems.   Yield stress is seen to increase rapidly as thickener level increases above a minimum value.   This minimum concentration of thickener may be thought of as analogous to the minimum number of crosslinks to cause gelation (three-dimensional structure) in a polymer network.   The low value of the minimum effective concentration indicated in the B-60/GS system is consistent with the observation of flocculation and creaming in this system at low thickener levels. Acrysol GS seems to be quite effective in tying Rhoplex B-60 particles together in aggregates. Such creaming was much slower in the B-60/G-110 system, in which a lower yield stress was observed.

Effect of Added Electrolytes.   Various concentrations of NaCl and HCl were added to thickened latices in order to determine their effects on the flow curves.   These data are too limited to permit quantitative interpretations.   Some generalizations can be made, however.   The polyelectrolytes (Acrysol GS, Acrysol G-100) were more sensitive than the nonionic Methocel (15 cps), both to salt and to acid.   The effect of acid on viscosity was variable, leading to agglomeration in some cases, to thinning in others.   The most striking single observation was the relative invariance of the yield stress in all cases.   This suggests a certain amount of independence between the physical interpretation of the parameters k and τ_0, which may be used to characterize the flow of thickener latices.

B. Interactions in Latex Thickening

Other than the general similarity of the forms of the flow curves found in the rheological study, the effects of combining various latexes and thickeners were very specific to the pairs involved.   In an attempt to clarify the various specific interactions, a number of additional experiments was performed. The first set of experiments consisted of the thickening of six dispersions with each of three water-soluble polymers.   The six dispersions were prepared by emulsion polymerization of styrene or methyl methacrylate with three different surfactants.
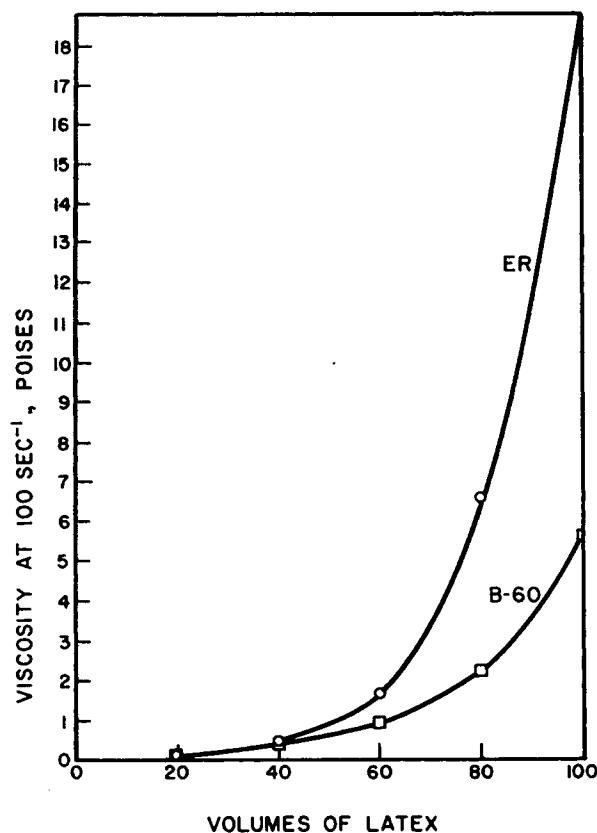
Fig. 6. Viscosity at 100 sec.$^{-1}$ vs. latex solids. 100 volumes latex plus water: 20 volumes thickener solution (5% Methocel 400).

Fig. 7. Viscosity at 100 sec.$^{-1}$ vs. latex solids. 100 volumes latex plus water: 20 volumes thickener solution (5% Acrysol GS).

A number of other experimental observations were either made or collected from other sources in an attempt to reduce the dispersion-thickener combinations to simpler combinations which should allow somewhat more intelligible interpretation.

(1) Methyl Methacrylate and Styrene Emulsions with Various Emulsifiers

Six polymer emulsions were prepared for us by Dr. William Conn, Rohm & Haas Co. Research Laboratories, consisting of styrene or methyl methacrylate, each polymerized in the presence of sodium stearate, a nonionic surfactant of the octylphenoxy polyoxyethylene type, and a commercial anionic surfactant. Three water-soluble polymers were employed as thickeners: sodium polyacrylate (Acrysol GS), a sodium salt of a low molecular weight styrene-maleic copolymer, and hydroxyethyl cellulose.

The water-soluble polymers were diluted to 0.5, 1.0, 2.5, and 5.0% solids with water. Thirteen grams of such a solution was added to 117 grams of 40% latex, giving final compositions of 36% latex
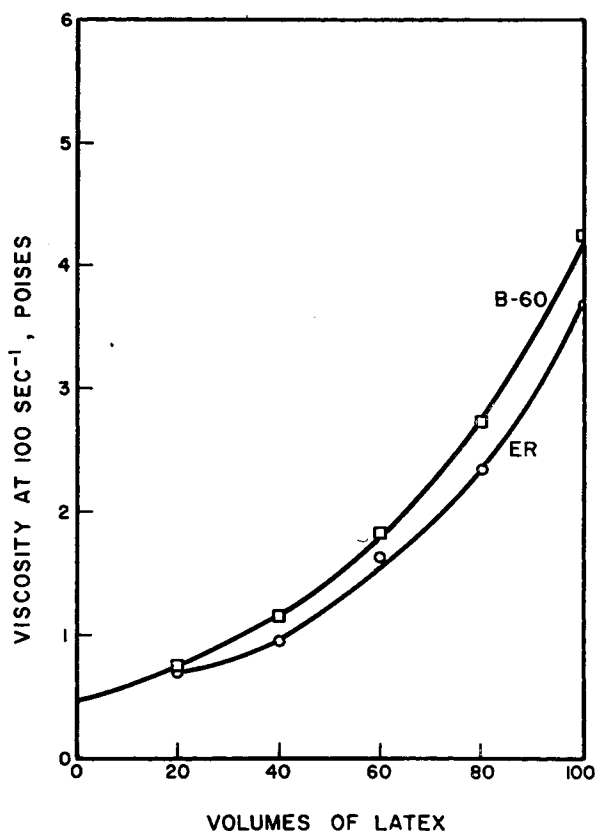
solids with 0.05, 0.10, 0.25, and 0.5% thickener. Dispersion-thickener mixtures were equilibrated at 25°C. and viscosities determined with a Brookfield LUF viscometer at all four speeds, using the appropriate spindle. Values at 12 rpm are reported.

The viscosity measurements are presented in Figures 9, 10, and 11. Two features of the data should be especially noted. The first is the curve of the viscosity of the anionic-methyl methacrylate emulsion thickened with styrene-maleic copolymer, which first increases and passes through a maximum, decreases and passes through a minimum, and then again increases, as thickener concentration is increased. The same curve would obviously be present for the sodium stearate-methyl methacrylate emulsion had lower concentrations been examined, since the viscosity must somewhere decrease with decreasing thickener. These complex effects obviously cannot be accounted for by a simple thickening of the aqueous phase. The second feature to be noted is in cross-comparisons with variation of either polymer or
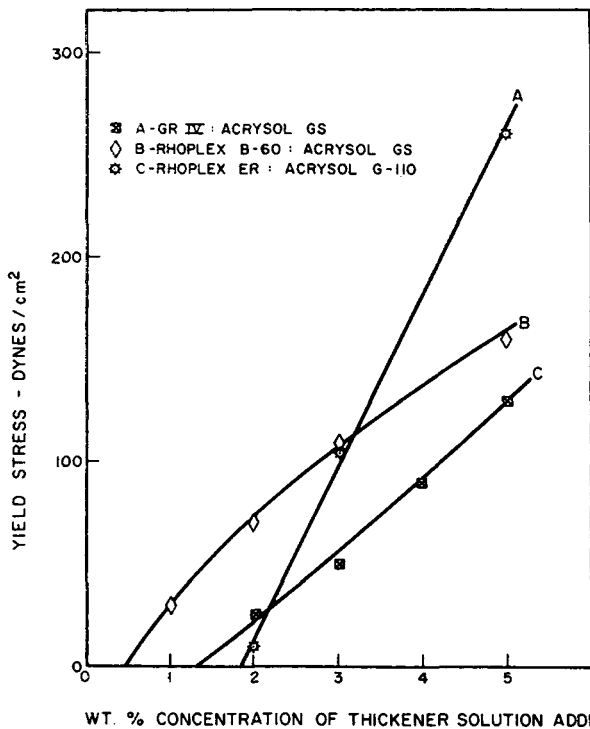
Fig. 8. Yield stress vs. thickener concentration. 100 volumes latex: 20 volumes thickener solution.

comparisons, again demonstrating the specificity interactions.

(2) Latex Creaming

The phenomenon of latex creaming is frequently observed in the experimental evaluation of thickeners. For many latexes, a narrow range of concentration of added thickener produces creaming. Two examples of this behavior are presented in Figure 12. A 10% solution of the ammonium salt of styrene maleic copolymer or of sodium polyacrylate was added to 40% GR-S Type 4 latex in amounts up to 1.5% soluble polymer solids on latex solids. The treated latex was allowed to stand at 25°C. until equilibrium was reached in sedimentation, and the amount of clear (serum) layer and dispersion layer observed.

Within a range of thickener concentration, sedimentation is pronounced. At lower concentrations, the latex is present in the form of dispersed ultimate particles. Above a critical value, creaming decreases as the result of an increased viscosity of the continuous phase and/or a change in the structure of the aggregates formed.

(3) Flocculation and Deflocculation

The deflocculation of dispersions by various types of surfactants is a well known phenomenon.

emulsifier, the other being held constant. There is no constancy in the order of the thickening efficiency of the water-soluble polymers in these
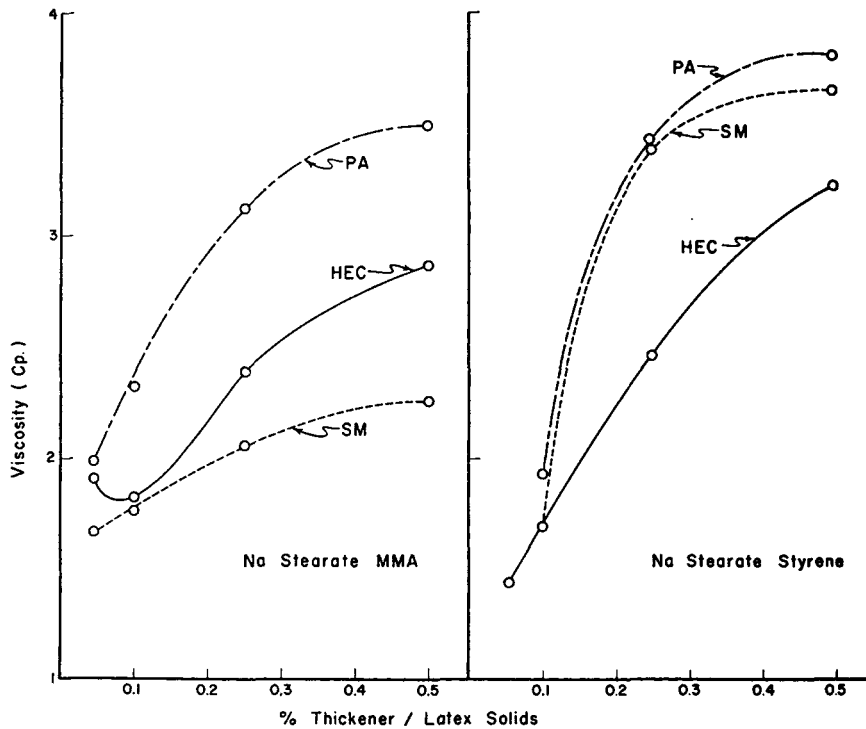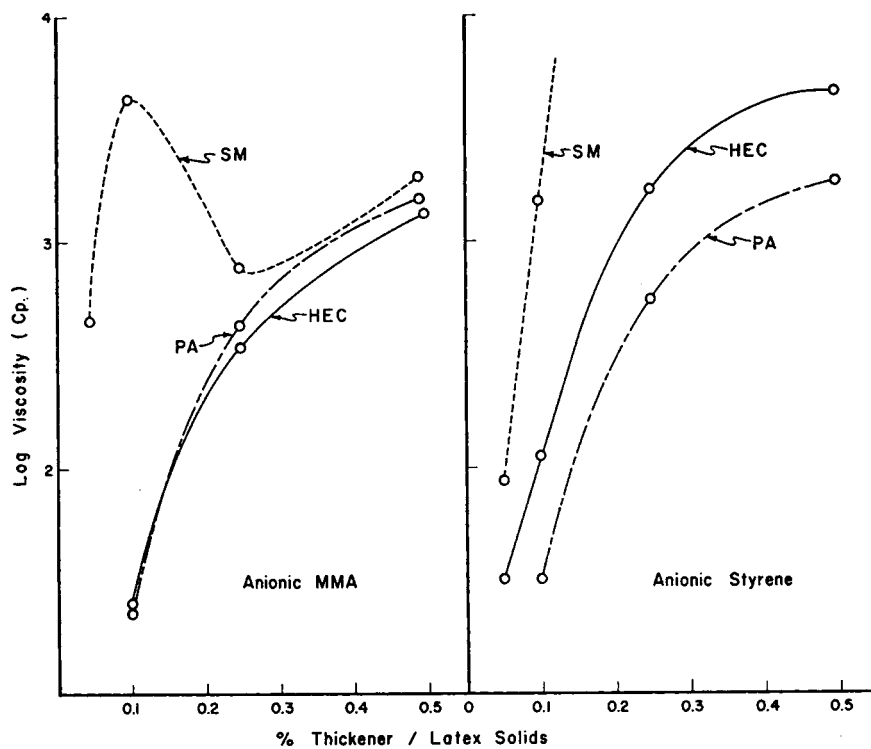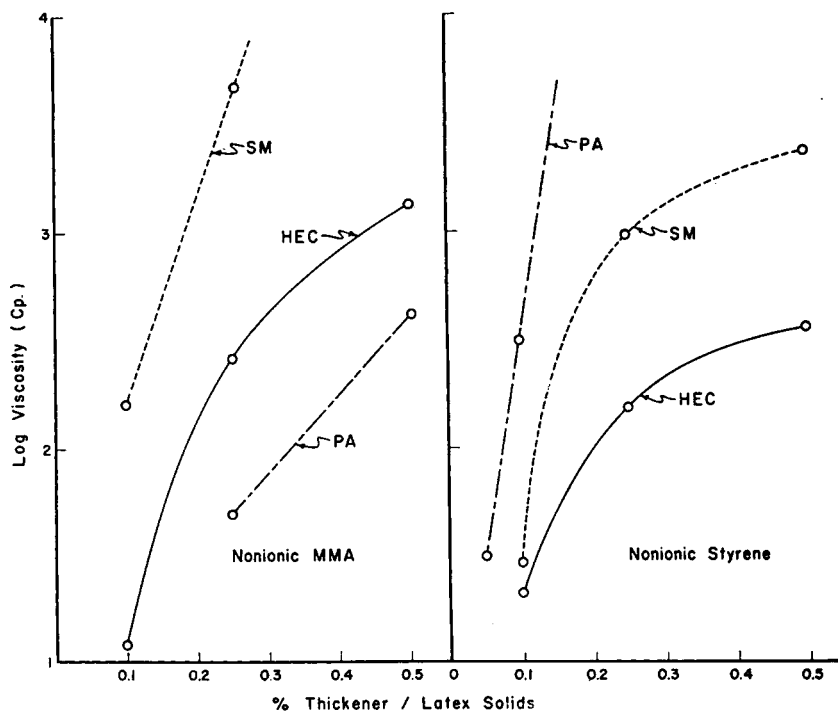

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

gether two or more particles, which adds stability to the aggregate.

An effect which has received even less attention is that of the reversal of flocculation—that is, initial flocculation by a polymer followed by deflocculation with further addition of the polymer. A demonstration of this is given in Figure 13. Polyacrylamide (Dow Separan) or a quaternary ammonium polymer (polydimethylaminoethyl methacrylate), both of high molecular weight, was added to a suspension of 10 grams Kaolin per 100 ml. of water and the settling rate observed. Sedimentation increased dramatically with small additions of polyacrylamide, passes through a sharp peak and decreases rapidly. Qualitatively similar effects are observed with the poly cation, although it is quantitatively much less effective in this case. The viscosity of the continuous phase is not altered significantly in the region examined, so the reversal cannot be explained on this basis.

IV. DISCUSSION AND CONCLUSIONS

With the complexity of the foregoing experimental observations in mind, we shall attempt to draw a general, qualitative description of the nature of latex thickening. The various effects encountered are believed to be a result of the describable interactions of the various components present. The net result in any one latex-thickener system is the cumulative of all of these effects, with one interaction predominating in one case and another interaction in a different case; these interactions often change radically with minor alterations in concentration or composition.

The various interactions are outlined below:

I. Adsorption effects: adsorption of water-soluble components on the surface of the disperse polymer phase.

   A. Flocculation.

      1. Adsorption of soluble polymers or surfactants which neutralize the normal protective charge and give partial or complete coagulation.

      2. Adsorption of high molecular weight polymers on two or more particles to give interparticle bonding resulting in aggregation.

   B. Deflocculation.

      1. Adsorption of low molecular weight polymer or surfactant to serve as protective colloid.

      2. Adsorption of sufficient high molecular weight polymer, which is normally a floc-
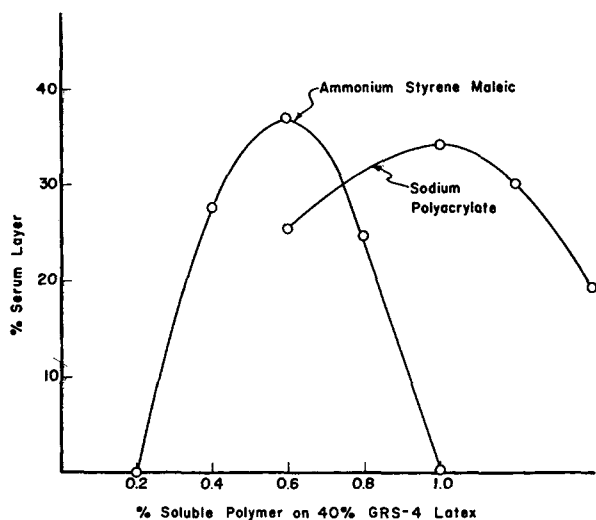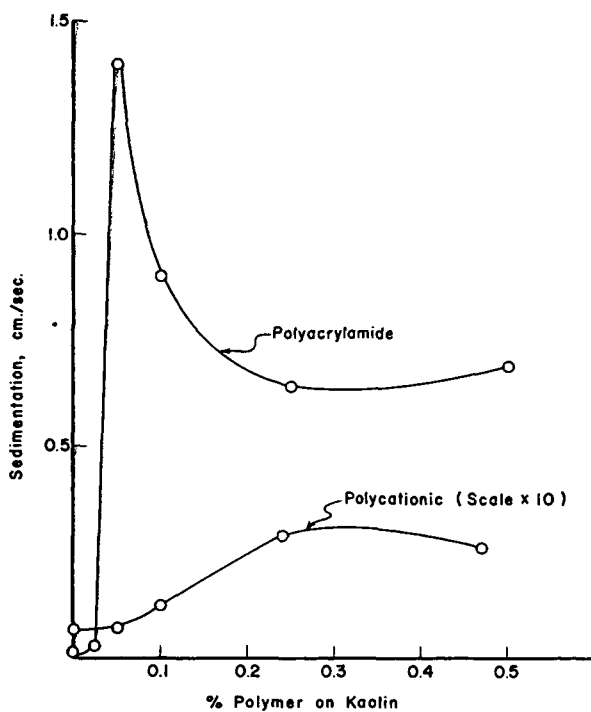
Flocculation and floc stabilization of dispersions by ionic or neutral polymers of high molecular weight has in recent years become increasingly studied. These phenomena have in common the adsorption of a material at a liquid-solid interface, but the rather gross difference is the result of the disparity in size of the materials effective in the two cases. Flocculation may be accomplished by small molecules through charge neutralization. Although the soluble high polymers may act in this manner, in addition, they sorb on and bond to-

culant at lower concentrations, to reverse flocculation and give a deflocculated system.

II. Bulk phase effects.

A. Contribution of dispersion to viscosity. Viscosity contribution is a product of this contribution and that of the continuous medium, that is, the viscosity increase due to the presence of the particles is proportional to the viscosity of the continuous phase, and, if the latter is high, the presence of the disperse phase may result in appreciable viscosity enhancement.

B. Viscosity increase of continuous phase. The normal aqueous viscosity of the thickener used may be modified because its concentration is effectively decreased if adsorption occurs. Viscosity will also be altered in the presence of salts (the electroviscous effect, etc.) and in the presence of surfactants (the result of some type of complex formation, etc., not understood at present).

It is proposed that the viscosity enhancement in the thickened latex is the result of the viscosity contributions by the disperse phase, by the thickener present in the continuous phase, and by the interaction of the thickener and dispersion to produce a specific type of "flocculation," "agglomeration" or "structure." The contribution which results from the flocculation is postulated to be of great importance where highly effective thickening is found, that is, where a water soluble polymer of relatively low solution viscosity acts as an extremely effective agent in imparting latex viscosity.

Although an extensive product and patent literature is available on latex thickeners, very little has been published concerning the mechanism involved. Baseden[3] has studied the thickening of polyvinyl acetate paints, and states that the structure induced by the presence of a cellulose ether in an emulsion paint is truly reversible, irrespective of the way in which it is sheared and is clearly not of the brush-heap type. It seems most probable that it is caused by an interaction between cellulose ether chains, the titania flocs, and, probably, the p.v.a. particles, so as to produce a three-dimensional network of cellulose ether chains with the flocs contained in the reticulum.

Workers at Dow Chemical Co. have studied the agglomeration and electrolyte stability of latex systems upon addition of water soluble polymers such as methyl cellulose and proteins. Photo-micrographs have been published by Frantz, Sanders, and Saunders[4] of large particle size vinyl toluene latex thickened with methyl cellulose and protein. Small additions of methyl cellulose cause agglomeration of the latex, whereas larger additions result in deagglomeration and stabilization of the latex. Soybean protein produces agglomeration, even at higher concentration; but when sufficient additional emulsifier is present, no agglomeration is observed. Related observations have been made by Saunders and Sanders[5] on the electrolyte stability of dilute synthetic latexes to which methyl cellulose is added. Small concentrations sensitize the latex to electrolyte addition; larger concentrations stabilize the latex.

Since smaller particles cannot be observed microscopically, and since the water-soluble polymer cannot be observed in any event, the nature of latex thickening must be inferred. Our inference as to the mechanism is as follows.

High molecular weight polymers which sorb on the particle surface produce creaming when added in small concentrations to a latex. A small number of particles are bound in a compact aggregate which sediments more rapidly than would the individual particles, in accordance with Stokes' Law. In most latex systems, the unmodified particles would not sediment under normal gravitational acceleration, since they are sufficiently small to be maintained in suspension by Brownian Motion. Further addition of thickener alters the viscosity by one or more of the following four means.

1. The viscosity of the water phase is increased as higher concentrations of the water-soluble polymer are reached.

2. Flocculation proceeds to such an extent that large aggregates are formed. Although each particle in the aggregate touches two or more particles, the entire aggregate is spongy in nature, so as to occlude large quantities of water and/or is of such shape that efficient packing of aggregates is impossible. The entire system does not undergo sedimentation because the sedimentation volume is equal to the entire volume of the system. Viscosity is high because of the difficulty of moving the aggregates past each other.

3. Flocculation proceeds to produce a pervasive network of particles bonded together by thickener molecules. As thickener is added, a portion of it forms interparticle bonds and a portion is absorbed with a single molecule on a single particle. Thus, a three-dimensional network is established in which

the particles are bonded together but do not collapse into a compact structure because of the stabilizing influence of hydrophilic colloid present over the entire particle surface. Latex creaming does not occur because the average interparticle distance remains large, even though the particles are bonded. The viscosity is high as a result of the gel network, which must be destroyed temporarily to allow flow.

4. Flocculation produced at a low concentration of thickener is destroyed as additional polymer is adsorbed, approaching saturation of the particle surface. For some reason, the interparticle bonding achieved at low concentrations is destroyed, each thickener molecule now being attached to a single particle. This can occur if certain adsorption sites of the particle are energetically more favorable and are the first occupied. The bonds responsible for adsorption are undoubtedly in dynamic equilibrium, and, as more soluble polymer is added, these bonds are constantly broken and reformed. The most favorable configuration from the standpoint of entropy would be achieved when one polymer molecule was bonded at several points to a single surface.

On the basis of the foregoing suggestions, the complex behavior of certain systems can be accounted for. The initial rise in viscosity of latex, followed by a viscosity decrease and a subsequent rise as thickener is added incrementally may result, for example from sorption to produce a network structure, deflocculation with additional thickener, and viscosity increase in the aqueous phase as still more thickener is added.

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Synopsis

Latex thickening—the process of increasing the viscosity of a polymer emulsion by addition of a water-soluble polymer—has been studied by rheological measurements and by the examination of other colloidal properties. For the systems studied, which represent a range of polymers in both the dispersion and solution phases, the flow curves were represented over a wide range of shear rate by the equation, $S = K(\tau - \tau_0)^2$, where S is shear stress, τ is shear rate, and K and τ_0 are constants, of which the latter is considered to be a yield stress. Aside from the generality of the mathematical function, the behavior of various latex-thickener pairs is extremely specific to the pair involved. Additional data on latex creaming and on the influence of the thickener and latex concentrations confirms the specificity. The available data indicate that latex thickening is not simply an enhancement of the viscosity of the aqueous phase by the thickener, but that in addition to this the ability of the thickener to flocculate or deflocculate the latex is an important part of the mechanism of thickening. These colloidal interactions change, often precipitously, with minor changes in the polymers, the latex emulsifier, and the *concentrations of the components.*

Résumé

L'épaississement d'un latex—procédé d'augmentation de la viscosité d'une émulsion polymérique par addition d'un polymère soluble dans l'eau—a été étudié par des mesures rhéologiques et par l'examen d'autres propriétés colloïdales. Dans le système étudié comprenant une série de polymères à la fois en phase dispersée et en solution on peut représenter les courbes d'écoulement pour une gamme étendue de tension de cisaillement par l'équation suivante: $S = K(\tau - \tau_0)^2$. Dans cette équation S représente la tension de cisaillement, τ représente la vitesse de cisaillement, K et τ_0 sont des constantes, la dernière étant considérée comme une tension limite. Outre le caractère général de la fonction mathématique, le comportement de couple latex-épaississant est extrêmement spécifique pour le couple impliqué. Des données supplémentaires sur l'épaississement du latex, sur l'influence de l'épaississant et des concentrations en latex en confirment la spécifité. Les données disponibles montrent que l'épaississement du latex n'est pas simplement dû à une augmentation de la viscosité de la phase aqueuse par l'épaississant mais que la capacité de celui-ci de floculer ou de défloculer le latex joue un rôle important dans le mécanisme de l'épaississement. Ces interactions colloïdales changent, souvent rapidement, avec une variation minime du polymère, de l'émulsifiant et de la concentration des composants.

Zusammenfassung

Latexverdickung, nämlich die Erhöhung der Viskosität einer Polymeremulsion durch Zusatz eines wasserlöslichen Polymeren, wurde durch rheologische Messungen sowie durch Überprüfung anderer kolloidaler Eigenschaften untersucht. Für die untersuchten Systeme, die eine Reihe von Polymeren sowohl in der Dispersions- als auch Lösungsphase umfassten, konnten die Fliesskurven über einen weiten Bereich der Schubgeschwindigkeit durch die Gleichung $S = K(\tau - \tau_0)^2$, dargestellt werden, wo S = Schubspannung, τ = Schubgeschwindigkeit und K und τ_0 Konstante sind, von denen die letztere als Fliessgrenze betrachtet wird. Abgesehen von der Allgemeinheit der mathematischen Funktion, hängt das Verhalten verschiedener Latex-Verdickerpaare äusserst spezifisch vom verwendeten Paar ab. Zusätzliche Angaben über das Aufrahmen des Latex und über den Einfluss der Konzentration des Verdickungsmittels und des Latex bestätigen diese Spezifität. Die vorhandenen Daten sprechen dafür, dass Latexverdickung nicht einfach in einer Erhöhung der Viskosität der wässrigen Phase durch das Verdickungsmittel besteht, sondern dass darüber hinaus die Fähigkeit des Verdickungsmittels zur Koagulierung oder Stabilisierung des Latex einen wichtigen Beitrag zum Verdickungsmechanismus liefert. Diese kolloidalen Wechselwirkungen ändern sich, oft sehr plötzlich, bei kleinen Änderungen der Polymeren, des Latexemulgators und der Konzentration der Komponenten.