amount of dye that had dissolved from the coating at various intervals of time. The dissolution of the coating was determined in distilled water, simulated gastric fluid without pepsin, and simulated intestinal fluid without pancreatin (Tables V and VI). In all dissolution media, two-thirds of the dye and, presumably, the coating was dissolved within 7 min. Thus, the film coating would not hinder disintegration and dissolution.

Visual examination of the tablets coated with shellac and polyvinylpyrrolidone revealed that the coat was completely removed from the tablet in all dissolution media. All coated tablets dissolved within 25 min. Examination of tablets coated with ethylcellulose and polyvinylpyrrolidone showed that the coating was ruptured and that small fragments of the coating were attached to the tablet. This did not interfere with the release of the drug because all tablets coated with ethylcellulose and polyvinylpyrrolidone dissolved within 50 min. in all dissolution media. In addition, the dissolution of the ingredients of a tablet and subsequent dialysis through a membranelike sac were reported from intact ethylcellulose films (6).

SUMMARY

Two formulations containing polyvinylpyrrolidone were developed for the film coating of tablets by the pan-coating method.

The addition of ethylcellulose and shellac in the film coating modified the hygroscopicity of polyvinylpyrrolidone so that a nontacky coating was obtained.

The physical characteristics of the coatings were evaluated.

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Physical Properties of Coarse Suspensions

EVERETT N. HIESTAND

Abstract □ The probable mechanism of the control of floc structure by polymeric materials is developed from theory of polymer stabilization of disperse systems. Techniques that provide some insight into the nature of the floc are described. In predicting shelf-life, these concepts shift the emphasis away from the evaluation of sedimentation and caking to a study of potential structural changes of the floc.

Keyphrases □ Suspensions, coarse—stability, physical properties, structure-controlling factors □ Flocculated systems—use in coarse suspensions, structure

Coarse suspensions must be distinguished from colloidal dispersions because peptized particles of the former sediment during the usually desired shelflife of commercial products while the latter do not. With larger particles, settling produced by the gravitational field dominates the very mild mixing produced by ambient thermal fluctuations. Sedimented, peptized particles form hard cakes in the bottom of the container. Consequently, flocculated systems are used with coarse particles to prevent caking. Numerous reports provide a broader understanding of suspensions (1-6) than is given here. This discussion is limited to a few selected topics in an attempt to explain the structure-controlling factors in a flocculated suspension.

Pourable vehicles with sufficient structure to hold particles trapped in a three-dimensional, vehicular assembly are rarely encountered and are not discussed. Because the common viscosity builders and vehicle-structuring agents nearly always adsorb onto solid particles, they seldom act independently of the solid. The adsorbed material participates in the structure of the suspension by affecting the particle–particle interactions in a manner that may determine the floc structure. If the structure of a flocculated suspension is controlled adequately, inelegance and caking are not problems.

PROCESS OF FLOCCULATION

Among colloid chemists there is no generally accepted distinction between flocculation and coagulation; in this discussion, they are considered equivalent. Flocculation (and/or coagulation) occurs when two or more particles come together under conditions such that the net interaction force is attractive and is large compared to the usual thermal energy fluctuations. Thus, the particles stay together (in the absence of external forces) for long time intervals.

The objective in formulating a suspension is to produce the largest possible sedimentation volume while retaining adequate flowability. This requires control of the structure of the flocculated system. If small quantities of solids are present, a large porosity is desired. Ideally, there should be but one floc, and it should extend throughout the entire vehicle. This will be called the "single-floc" condition. This single-floc condition may be considered a weak gel. However, at the particulate level, the particles are not as uniformly distributed as is sometimes implied by the term gel, e.g., the large sediment-volume flocs described previously by the author (6). Specifically, the single-floc condition excludes two extremes: (a) the peptized condition, and (b) the formation of dense, discrete aggregates (flocs) that move as individual particles in flow and/or sedimentation. Thus, there is a continuous structure held together by particle interactions that are sufficiently weak to retain flowability. An exact description for the general case is not easily formulated because of the variations required by the broad range of solid contents encountered in pharmaceutical suspensions. Obviously, a denser floc system is required for large solid contents than for small.

To expedite the discussion, precise language to describe the structure of a specific flocculated suspension would be useful. This is nearly as elusive as a good procedure for the experimental evaluation of a suspension. Obviously, in the "single floc" one must consider both the number and strength of individual particle interactions. The number may be discussed in terms of differences in the average coordination number of the individual particles and should be observed as changes in the sedimentation volume of solids. Viscoelastic properties also may indicate their range of magnitudes.

Polymer flocculation, i.e., polymer molecule links between particles, may produce stable flocs even though the individual functional groups may have interaction energies with the solid of only a few kT[1]. The multiple-site adsorption of a single macromolecule leads to excellent thermal stability, but it is not clear that multiple-site adsorption should produce equivalent resistance to mechanical stress since tearing action would be applied stepwise to each individual site. Thus, polymer flocculation might be ideal for suspensions since thermally stable flocs might retain reasonable pourability. Furthermore, adsorbed polyfunctional macromolecular substances also may produce protection against flocculation[2]. Therefore, polymers may contribute in two ways to control the average coordination number of the particles and, thereby, the structure of the single floc.

Electrolyte-Induced Flocculation—The Derjaguin–Landau–Verwey–Overbeek theory clarified the role of electrolytes in flocculation, and the subject has been reviewed frequently (1–6). The use of electrolyte flocculation as a method of flocculation control evolved from these concepts. However, theoretical considerations suggest that electrolytes that do not adsorb onto the solid affect only the rate of flocculation. Smoluchowski's equation for rapid flocculation is based on simple diffusional, collision kinetics. Fuchs introduced a stability factor, W, that is a ratio of the Smoluchowski rate to the rate when a potential energy barrier, V, prevents all collisions from being effective in producing flocculation (7). Fuchs' equation is:

$$W = 2a \int_{2a}^{\infty} \exp \frac{V}{kT} \frac{dr}{r^2} \qquad \text{(Eq. 1)}$$

where a is the particle radius, r is the distance between particles, k is the Boltzmann constant, and T is the absolute temperature. V is a function of the concentration of electrolyte; therefore, the rate of flocculation is influenced by the electrolyte. The author is unaware of any other type of equation that relates electrolyte concentration to flocculation. Of course, the rate decreases as flocculation pro-
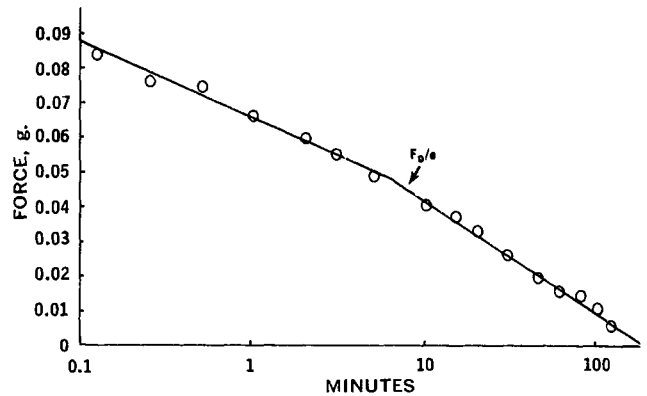
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[1] k is the Boltzmann constant, and T is the absolute temperature.
[2] As discussed later, steric factors prevent flocculation if enough polymer is adsorbed onto particles to eliminate bare areas at which polymer links or direct contact between particles may occur.

Figure 1—*Plot of the relaxation of stress versus log time after a small displacement of a sphere in a suspension containing methylcellulose. The suspension contains 5% solid medicament.* F_0/e *indicates zero-time force divided by 2.718.*

ceeds because of the decreasing number of particles. However, this says little about the resulting floc structure.

Before proceeding with the discussion, some important questions should be posed. What forces act to determine floc structure? Does slow or fast flocculation result in a small average coordination number? If a small average coordination number is formed, is it stable, or will vibration and thermal fluctuations result in rearrangement? The answers to these questions are not clearly established. Yet answers are needed if one is to determine the quality of a suspension formulation.

To produce and maintain a low coordination number, a limited number of interactions must occur, and rearrangement must be inhibited. With spherical, isotropic particles (homogeneous surface energies), there is nothing inherent in flocculation produced by electrolytes that limits the average coordination number; i.e., there are no forces introducing barriers that limit the coordination number below close packing order. Statistically, close-packed structures would not have a high probability of forming spontaneously, but mild stirring and/or settling could result in large average coordination numbers. It is well known that highly anisometric particles often flocculate to form stiff gels. Once flocculated, rear-
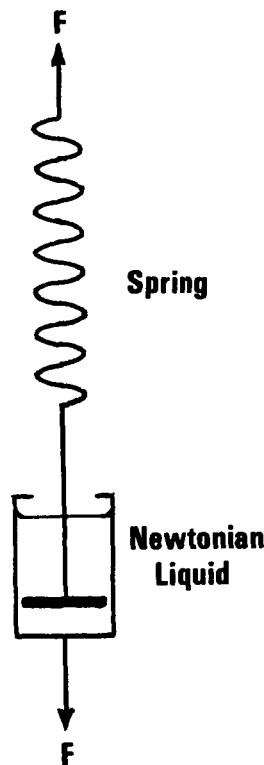

Figure 2—*Maxwell model for relaxation process described by* F = F₀ *exp* (−t/τ), *where* t *is the time and* τ *is the relaxation time constant.*
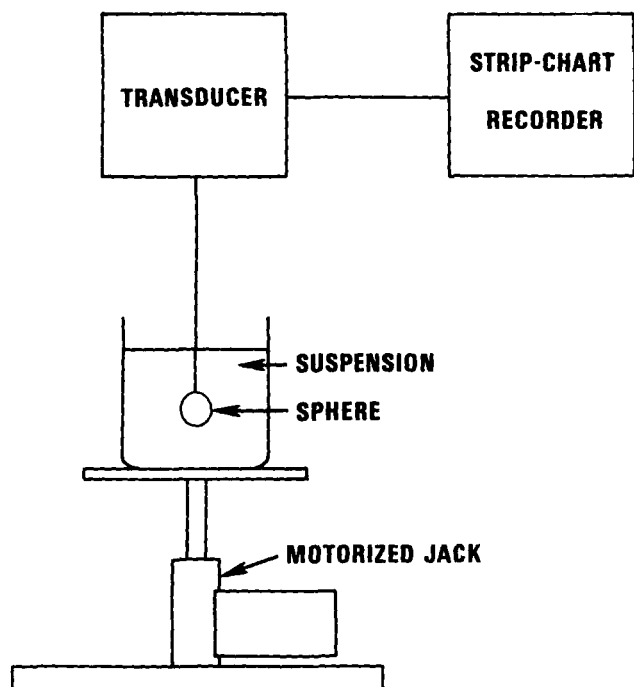
Figure 3—*Diagrammatic representation of the apparatus used to observe stress relaxation in a suspension.*

rangement of anisometric particles may require momentary separations of regions of close contact. The energy required for this operation may arise from a geometric factor resisting change of structure in a manner analogous to the resistance of a cubic box to rolling. When the low average coordination number is dependent on geometric factors alone, mild shearing should alter the structure and cause the average coordination number to increase. This argument applies to flocculation both in the secondary and the primary minimum.

The heterogeneity of the surface energy may introduce directional properties to the particle–particle interactions. Clays are examples in which the particle edge may possess a different charge from the crystal face. This can lead to edge-to-face flocculation, sometimes called the house-of-cards structure. The formulator of pharmaceutical products seldom has a solid material that behaves like a clay. Therefore, electrolyte flocculation alone often is not adequate to produce the desired product characteristics.

Adsorbed Macromolecules—Most suspending agents are polymeric materials, and many are also polysaccharides. Because they dissolve in water to produce pseudoplastic solutions, their role in suspension formulation has often been considered as thickening or viscosity building. However, such polymeric materials adsorb at a
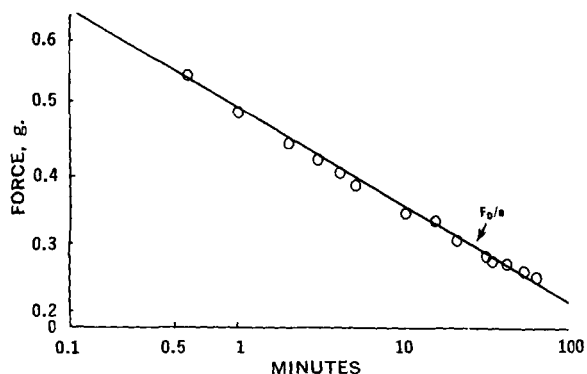

Figure 4—*Plot of the relaxation of stress versus log time after a small displacement of a sphere in a suspension containing a proprietary product containing a complex of magnesium aluminum silicate. The suspension contains 10% solid medicament. F_0/e indicates zero-time force divided by 2.718.*

solid–liquid interface. Moreover, polymeric materials influence the flocculation behavior of disperse systems.

Before attempting to put these facts together and suggesting the functional role of macromolecular materials, it is desirable to discuss some experimental observations of flocculated suspensions containing suspending agents. This work was mentioned in a previous review (6), and it is especially pertinent in this discussion. Figure 1 shows the relaxation of stresses on an object after repositioning it in a suspension. It is instructive to develop relaxation concepts from a simple analogy. The relaxation of force of a simple, single dash-pot and spring (Maxwell) model can be characterized by an exponential decay of force having a single relaxation time. Figure 2 shows diagrammatically such a model. The relaxation time is the time it would take for the force in the simple model system to decay to $1/e$ of its initial value. However, note that in Fig. 1 the linear[3] plot is of force *versus* log time, not log force *versus* time. A large number of dash-pot spring elements with a variety of relaxation times may produce a plot like Fig. 1. This special combination of terms is sometimes called the box distribution (8). In the flocculated suspension, the decay of force must result from the breaking rate of stressed interparticle bonds. Equivalent bonds may reform at a new position of reduced stress, which means that the particles may have different neighbors than before.

To obtain the data in Fig. 1, a sphere of 9.5-mm. diameter was suspended in the suspension from an overhead force transducer (balance or strain gauge) connected to a recorder. Figure 3 shows this arrangement diagrammatically. After standing for several hours, the suspension was raised a few millimeters, just sufficient to produce maximum stress on the sphere. The recorder provided a plot of the changes of stress with time following this stress application. This is similar to the apparatus described by McVean and Mattocks (9).

In the example shown in Fig. 1, the maximum force was 0.120 g. The force fell to $1/e$ of its initial value in 9 min. Without a quantitative analysis of these data, the maximum force identified with the long relaxation time forces is unknown. However, it is evident that relatively large forces, necessary to have relaxation times in excess of 9 min., represented a significant portion of the total. Extrapolation of Fig. 1 to zero force indicated that relaxation continued for about 200 min. Figure 4 is another example. The zero-time stress was larger, 0.74, and there was only one apparent slope. In the author's laboratory, the relaxation phenomena of some suspensions were observed for over 24 hr., and these continued the linear force *versus* log time relationship throughout this time interval. Since particles are held in these suspensions with strong enough forces to give long relaxation times, they would not move rapidly in the force field produced by a gravitational acceleration of $1 \times g$. If the suspension is a single floc, the shelflife stability should be good; *i.e.*, very little subsidence should occur.

Equilibrium vehicle from a suspension may be obtained by centrifugation followed by decantation. Relaxation rate studies of the equilibrium vehicle measured in the same apparatus indicate that a much weaker structure exists in the absence of solid particles. In the first case shown, the structure of the equilibrium vehicle was so low it could not be measured with this apparatus. Another interesting comparison can be made—*viz.*, the equilibrium vehicle to the original vehicle to which solids were not added. It was found that the maximum stress was less in the equilibrium vehicle than in the original vehicle. Thus, it appeared that much of the suspending agent was adsorbed onto the solid particles and was missing from the equilibrium vehicle. (Other methods, some more direct, could be used to establish the degree of adsorption of the polymer.) Apparently, the particles with adsorbed suspending agent were primary contributors to the structure in these suspensions.

Healy and LaMer (10) described a simple mechanism to account for polymer flocculation. It was assumed that polymer molecules adsorbed to cover part of the surface of particles. This protected these regions from flocculation with other covered regions. Polymer molecules produce flocculation by adsorbing simultaneously onto two particles; the length of the molecule and the distribution of functional groups along the polymer backbone make this possible. The protective mechanism acting at covered areas limits the particles to developing small average coordination numbers, the very effect one wants to achieve in a suspension.

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[3] Usually only one slope is observed. The explanation of these two regions is not obvious to the author.

Not all investigators have agreed with the details of LaMer's analysis of the polymer flocculation process (11). However, the bridging mechanism is widely accepted, and the protective action of polymers has been known for many years. Clayfield and Lumb (12) considered the entropic repulsion produced by random polymer chains terminally adsorbed onto surfaces. The entropic contribution arises from the compression of the polymer molecule as adsorbed molecules on separate particles approach each other. Thus, fewer configurations of the molecules are possible. However, Napper (13) concluded from studies with polyoxyethylene derivatives in water that the configurational entropy increased with interpenetration of the chains, thus promoting flocculation. He explained this by assuming that water molecules previously "bound" by the polyoxyethylene were released and gained new degrees of freedom. This effect was larger than that due to the loss of configuration by the macromolecule. In addition to the entropic term, the interaction energy of the polymer with the solvent may contribute to the free energy of the chain interpenetration process. This would occur as the interactions change from polymer–solvent to polymer–polymer as penetration proceeded. When the free energy increased with interpenetration, stabilization would be promoted. Napper (13) called this enthalpic stabilization; the combined entropic–enthalpic stabilization was designated as steric stabilization. Napper confirmed the previous observations that when the surface coverage was incomplete, flocculation occurred. This was true even when the vehicle was a considerably better solvent than a θ-solvent[4]. Poorer than θ-solvency would be required for the enthalpy of interpenetration to be positive and to promote flocculation. Water is a better than θ-solvent for polyoxyethylene chains. However, in nonaqueous suspensions, solvent quality might be less than θ-solvency for the polyoxyethylene group and the enthalpy term could promote flocculation.

Electrolyte Flocculation in the Presence of Macromolecules— It is difficult to assess the effect of electrolyte flocculation in the presence of a polymer because very few data are available. Lyklema (14) suggested that numerous types of curves may be constructed, describing the potential energy of interaction as a function of the separation between particles. These result from the combination of the double layer and the steric protection factors. The maximum in the potential energy for the double-layer repulsion may occur at greater separations than the maximum for the steric term. Thus, the combination may yield a shallow minimum between the two. Within limits this minimum can be designed into the system by the proper selection of a macromolecular, steric-protecting agent and the careful adjustment of the height of the double-layer energy barrier. With enough additional information, ζ-potential measurements might be useful in this case.

Some of the differences in observations reported in the literature may result from a failure to recognize these possibilities. Blackadder *et al.* (15) stated that: "When polymer flocculant was used to flocculate an electrolytically stable suspension . . ., compact sediments of lower porosity (0.69–0.76) invariably formed." They argued that: "The flexible polymer chains tie the particles together but still permit geometrical rearrangements due to the mobility of the macromolecules." They were discussing the density after sedimentation. Using different materials, Slater and Kitchener (11) concluded that: "Highly-charged particles are not flocculated by polymer until their zeta-potential has been reduced to a low value, either by use of polyelectrolyte of opposite sign or by the addition of suitable supplementary electrolyte." They also concluded that: "Polymers produce large, 'tougher' flocs than do simple electrolyte coagulants." None of these investigators was attempting to produce the single-floc state; instead, they were seeking efficient filtration, *i.e.*, porous filter cakes. However, their observations are not inconsistent with the concepts suggested herein. Thus, the author has concluded that after enough surface has been protected with adsorbed polymeric materials so that a large coordination number is not probable, electrolyte flocculation may be advantageous. Glazman (16) reported extensive studies with various alkyl ethers of polyethylene glycols [with general formula $C_mH_{(2m+1)}O(CH_2CH_2O)_nH$] adsorbed onto silver iodide and/or arsenic sulfide. Both sensitization and protection were observed. Electrolyte flocculation values were determined as a function of polymer concentration for various chain length polymers and for various ratios of n to m in the molecule.
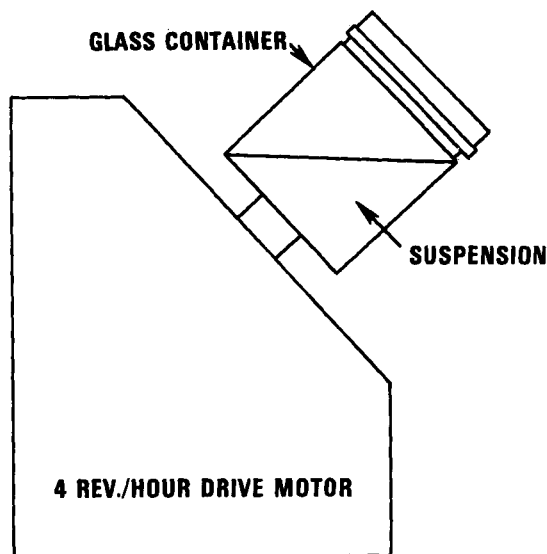

Figure 5—*Diagrammatic representation of an apparatus for evaluating very, very low shear rate effects.*

The results are consistent with the steric protection theory and demonstrate the marked influence of long chains extending into the vehicle from the solid surface.

Slater and Kitchener (11) compared, for a single system, five parameters used by various investigators as criteria for flocculation. The criteria were: settling rate, height of settled bed, height of consolidated filter bed, refiltration rate, and clarification. They did not discuss their observations in terms of the control of the average coordination number. However, based on the previous discussion in this article, one would expect the minimum average coordination number and the concomitant maximum sedimentation height to occur at relatively low polymer dosage. Their observations showed the maximum sediment height occurred at a lower polymer dosage than the maximum of any of the other four criteria.

For the general case, only one method of flocculation appears intrinsically to provide control of the average coordination number. This arises when part of the surface of the particles is covered with a steric protection agent and part is not. The unprotected part of the particle may participate in polymer link formation (polymer flocculation) or, if the double-layer potential is small, in flocculation by contacting the unprotected part of another particle. By proper selection of the flocculant and its concentration and by adjustment

Table I—Helipath Readings[a]—Relative Values
(6 r.p.m. with d-Size T-Bar)

	Suspension A			Suspension B	
	1 Day	1 Month	12 Month	1 Day	1 Month
From Top	4	58	58	<5	120
	4	58.5	62	<5	150
	4	59	70	<5	205
	4	60	75	<5	300
	4	60	80	<5	332
	4	60	82	<5	359
	4	62	82	<5	440
To					
	4	62	83	<5	>Scale
	4	62	83	<5	>Scale
	4	63	83	<5	>Scale
	4	63	83	<5	>Scale
	4	63	83	<5	>Scale
	4	64	84	<5	>Scale
	4	64	84	<5	>Scale
	4	66	84	<5	>Scale
Bottom	4	66	84	<5	>Scale

[a] Data supplied by E. L. Rowe. Suspension A was acceptable, and Suspension B was unsatisfactory.

[4] A simplified definition of θ-solvent is: a solvent in which the polymer–solvent interaction is equal to the polymer–polymer interaction.

of the double-layer potential, an elegant suspension formulation should be possible.

SUSPENSION EVALUATION

The single-floc concept and knowledge of the role of macromolecules in promoting stability have led to a reassessment of the various evaluation procedures helpful to the formulator. The following discussion is limited to methods other than the relaxation studies already reported here.

One commonly used method is to subject the suspension to centrifugation. What does this reveal about floc structure? A study of subsidence rate in a given field of force might be interpreted in terms of the porosity and the strength of interaction between particles. However, the author knows of no reports of this kind of analysis. If a large centrifugal force field is used, it becomes somewhat analogous to trying to determine how long a house will stand by crushing it with a bulldozer. One thing of real importance that is learned from mild centrifugation studies is whether a sediment, if it should form, is going to close pack and thereby produce a caked sediment. However, not much is revealed about the structure of the flocculated system before it was sedimented by brute force.

A way of gently stressing the system is shown diagrammatically in Fig. 5. This device rotates the bottle at 4 *revolutions per hour*. By such gentle action, significant stirring is avoided. However, the rolling action gently breaks the bonds of the floc structure and new ones form. If the particles have not attained their maximum coordination number previously, they tend to do so under these conditions. The appearance of the suspension may change to a coarse aggregate. This "curdled" look results from a serious change in floc structure. Such a suspension may not withstand the vibration and gentle rocking of shipping. A discussion by Reich and Vold (17) of the analogy between temperature in a chemical reaction study and agitation in a flocculation study provides additional insight into the conceptual basis of this device.

Rheological methods also have limitations. Pseudoplastic rheological characteristics are difficult to interpret in terms of floc structure. Apparent yield values depend on the apparatus and on the procedure used in the measurement. Furthermore, one must disturb the system to make the measurement. Under ideal conditions, particle particle interaction forces were evaluated (18); with real products, this cannot be done.

The helipath attachment with the Brookfield viscometer provides a different kind of data but perhaps it is more significant. Table I shows a series of values as the T-bar spindle moves downward (in a helical path) through the previously undisturbed suspension. Comparative values between fresh and aged suspensions are useful and will detect changes in structure and sedimentation. The ability to evaluate an undisturbed suspension is a most important capabilty of this device.

Temperature cycling or storage at various temperatures provide useful data. In most cases, these tests are not accelerated aging studies. Instead, they usually provide only assurance that the suspension will remain stable when exposed to possible storage conditions. However, cycling may accelerate crystal growth. In this regard, another important benefit may result from polymeric adsorption- -*viz.*, inhibition of nucleation (19).

Relaxation curves such as those shown earlier provide relative data that are useful. Obviously, more information is needed before meaningful limits on the strength of the floc structure can be established. However, it is a technique worthy of further evaluation.

CONCLUSION

All of the above concepts are useful in guiding the formulator. Seldom will the first formulation be satisfactory. The curdled look after flocculation suggests that inadequate polymeric material is present because the average coordination number is too high. Settling to produce a very thick, noncaking sediment may be due to excessive protection by the suspending agents. Quantitative predications are much more difficult to make.

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