Negative Thixotropy in Flocculated Clay Suspensions

By JOSEPH C. SAMYN and WAN YIN JUNG

The flocculated clay system is shown to possess negative thixotropic flow properties. Low and high shear measurements are performed to demonstrate this phenomenon. The variations in floccule sizes and interfloccule contacts are accepted as the cause of this effect. Sediment volume and filtration rate measurements are presented to demonstrate the floccule size-agitation intensity relationship. These reversible changes in apparent viscosity are also shown to occur more readily with low-intensity agitation than with standing. Several commercial suspensions containing this system did not display appreciable negative thixotropy. However, the influence of negative thixotropy in the control of concentrated clay slurries is still considered important.

THIS PAPER reports the negative thixotropic behavior of the flocculated system: clay[1] plus added salts. Flocculated systems displaying negative thixotropy are characterized by a reversible transformation from a more viscous state achieved by high shear to a less viscous state obtained by low shear. The only previous report of negative thixotropy in a pharmaceutical system was that of Chong *et al.* (1) for milk of magnesia.

The differences between negative thixotropy and dilatancy should be emphasized since these two types of flow can be confused. The negative thixotropic systems are necessarily flocculated as reported by Medalia and Hagopian (2). In addition, they are of relatively low concentrations. The flocculated clay systems cited in this report are in the 1–3% range while the milk of magnesia is a 7–8.5% suspension. The dilatant systems are deflocculated and of extremely high solid content, usually 40–50% (3). Chong *et al.* (1) also point out that the negative thixotropic systems are dependent on duration and rate of shear, while the dilatant systems are dependent on rate of shear only.

It will be shown that the negative thixotropic behavior of these clay slurries is observable with either high or low shear viscometers. Selected sediment volume and filtration rate measurements will be presented to further substantiate the flocculation theory for negative thixotropy. A phenomenon analogous to rheopexy, therefore termed negative rheopexy, has also been observed with the clay systems as well as with milk of magnesia. Finally, the practical significance of negative thixotropy will be considered.

EXPERIMENTAL

Apparatus.—The Brookfield viscometer model LVT (Brookfield Engineering Laboratories, Staughton, Mass.) was used for the single-point viscosity measurements. The spindle, speed, and time of measurement were kept constant for each system and are listed in each table of data. The suggested conversion factors were used to express the apparent viscosities in Brookfield units.

A Hercules Hi-Shear viscometer (Martinson Machine Co., Kalamazoo, Mich.) was used for the multipoint measurements. The unit was modified to permit the use of a single cup-bob combination for all measurements. A variable lever arm was coupled to a Statham 1-oz. GI-1-350 strain gauge (Statham Instruments, Inc., Puerto Rico). An Ellis Bridge amplifier (Ellis Associates, Pelham, N. Y.) model BAM-1, provided the power, and data were read from the scale of this unit. Speed changes were manual and performed in a procedure as standard as possible. Although provision for thermostating was available, it was not employed since its effectiveness was largely unknown and the temperature effect, if any, would probably be small and opposite to the negative thixotropic effect.

The sedimentation and filtration measurements were made in standard laboratory glassware. S & S (Schleicher and Schuell) No. 588 fluted filter papers were used for the filtration according to the procedure of LaMer (4). The time of filtration of the second 10 ml. of filtrate for each sample was measured.

Materials.—The clay, sodium benzoate, and polysorbate 40[2] were used as received from the suppliers. The milk of magnesia U.S.P. (Parke, Davis & Co., Detroit, Mich.) was a commercial sample.

Sample Preparation.—The clay slurries were hydrated overnight at RT in distilled water using an Equipoise shaker (Fisher Scientific Co.). Rotation of samples was accomplished by end-over-end tumbling at 14 r.p.m. for the prescribed times. A model GT21 mixer (Gerald K. Heller Co., Las Vegas, Nev.) at 1500 r.p.m. was used for the high speed mixing.

RESULTS AND DISCUSSION

The viscosity measurements with the high shear viscometer were only performed on rotated samples. Since the actual process of measurement resulted in viscosity increase due to the high shear, it was unnecessary to measure additional sheared samples. The low shear measurements, on the other hand,

Received April 28, 1966, from the Product Development Department, Parke, Davis and Co., Detroit, Mich.
Accepted for publication September 19, 1966.
Presented to the Basic Pharmaceutics Section, A.PH.A. Academy of Pharmaceutical Sciences, Dallas meeting, April 1966.

[1] Marketed as Veegum HV by R. T. Vanderbilt Co., New York, N. Y.

[2] Marketed as Tween 40 by Atlas Chemical Co., Wilmington, Del.

were performed on samples prepared by rotation and by high shear since the measurements did not alter the samples in the above manner.

Milk of Magnesia and Dispersed Clays.—The data in Table I on milk of magnesia were obtained with a Brookfield viscometer after low speed rotation and high speed mixing. These data clearly show that the negative thixotropy of this system is measurable with this procedure. The reproducibility of the measurements as well as the reversible nature of the effect can also be noted.

Table II reports the viscosity values for three dispersed clay slurries after low and high shear mixing. The thixotropic effect, rather than the negative phenomena, is to be noted in these data. The high speed mixing gives the reduced viscosity values for these dispersed systems. These data on disperse systems are presented in order that the contrast in behavior between it and the data on the flocculated systems may be completely obvious.

Clay–Salt Systems.—Figure 1 was prepared from data on clay slurries at two concentrations, each at several salt levels. Each sample was rotated overnight, apparent viscosity measured, stirred at 1500 r.p.m. for 5 min., and then remeasured. At the lower salt levels, the usual thixotropic behavior is evident. In this region, the high shear destroys the particle-to-particle contact and results in reduced apparent viscosity. At the higher salt concentrations, the negative thixotropic effect is noticed. In this region, slow rotation of the samples has facilitated the build-up of relatively large compact floccules. This leads to a lower apparent viscosity because of the increase in free fluid between the floccules and a decrease in contacts between these larger floccules. The application of high shear to these systems disperses these floccules and increases interparticle contact and the apparent viscosity.

In many of the samples prepared by rotation, it was noticeable that some coagulation of the clay particles had occurred on the inner surface of the glass bottle or the cap liner. It seemed possible that this material on redispersion with high shear would explain the apparent viscosity rise with high shear. The data in Table III indicate that this was not the case with these samples. Three flocculated systems were studied by three procedures. In the usual procedure the rotation, measurements, and high shear were performed in a single container for each system. In the second procedure, the clay–salt slurry was transferred to a clean container for measurements and high shear treatment after the rotation step. In this instance, any coagulated clumps of clay adhering to glass and cap surfaces were effectively removed from the system. In the third treatment, the glass containers used were Siliclad[3] treated. No adhering clay was noted in these samples. The data in Table III demonstrate that the negative thixotropy reported for these systems is not affected by the amount of material adhering to the glass and cap surfaces. It should be noted, however, that at much higher clay–salt ratios, slow sample rotation has resulted in almost all the clay adhering to the glass and cap surfaces. In such instances, the viscosity measurements would obviously be affected. It is also worth noting that these coagulated clay particles are sometimes observable as a "gummy

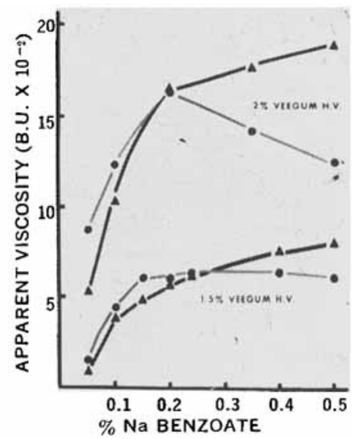

Fig. 1.—Clay–salt slurries. The influence of increasing salt concentrations. Key: ▲, mixed; ●, rotated.

Table III.—Clay–Salt Slurries Influences of Coagulated Clay Particles on the Apparent Viscosity Values

Systems	Procedure	Treatment: Overnight Rotation (Brookfield Units)[d]	Treatment: Mix 5 min. (Brookfield Units)[d]
1% Clay	a	160	430
0.5% Na benzoate	b	180	430
	c	190	430
1% Clay	a	100	400
1% Na benzoate	b	100	410
	c	100	410
1% Clay	a	90	380
1.5% Na benzoate	b	90	390
	c	80	380

[a] All measurements in one container. [b] Material transferred after rotation. [c] Silicone treated container. [d] No. 2 spindle, 30 r.p.m., 3 min., readings × 10.

Table I.—Milk of Magnesia U.S.P.—Apparent Viscosity Readings after High and Low Shear Treatments

Treatment	Brookfield Units[a]
Mix (1500 r.p.m.), 5 min.	720
Mix (1500 r.p.m.), 5 min. more	720
Rotation, 3 days	450
Mix (1500 r.p.m.), 5 min.	610
Mix (1500 r.p.m.), 5 min. more	690

[a] No. 2 spindle, 30 r.p.m., 3 min., readings × 10.

Table II.—Clay Slurries—Apparent Viscosity Readings After High and Low Shear Treatment

System	Treatment: Rotate Overnight (Brookfield Units)[a]	Treatment: Mix 5 min. (Brookfield Units)[a]
3% Clay	260	40
4% Clay	1500	560
5% Clay	3070	2410

[a] No. 3 spindle, 30 r.p.m., 3 min., readings × 40.

[3] Clay-Adams, Inc., New York, N. Y.

ring" in suspensions containing flocculated clay particles.

Table IV illustrates negative thixotropy of a clay–salt system as measured with the high shear viscometer. Curve *1* was obtained beginning at the lowest shear rate, increasing to a maximum, and then at progressively decreasing rates. Curve *2* was repeated in the same manner immediately after the completion of curve *1* on the same sample. The negative thixotropic effect is clearly seen in curve *1* by the increase in shearing stress values at comparable shear rates. Curve *2* indicates little additional change.

Clay–Salt–Surfactant Systems.—The addition of a surfactant to the clay–salt system results in a degree of redispersion. This is seen in the high shear data of Table V for increasing concentrations of polysorbate 40. The two lower concentrations exhibit the negative thixotropy associated with flocculation, while thixotropy is noted in the 0.2% polysorbate sample. Additives such as surfactants or protective colloids tend to reduce the flocculation and explain to some extent why negative thixotropy is not observed in the complete formulations containing these ingredients.

Negative Rheopexy.—The phenomenon of rheopexy is often associated with thixotropy. The term itself derives from the Greek *pectos*, meaning "curdled" or "solidified" (5). It is generally applied to thixotropic systems which set more rapidly by gently rolling or tapping than by standing. It is reasoned that the orientation of particles is facilitated by the gentle motion induced by these treatments.

For the negative thixotropic systems described in this paper, an analogous effect was noted. Here, too, the gentle rolling resulted in a more rapid change of the system than did the standing. However, since the system "thinned" rather than jelled, the term negative rheopexy was used to describe this effect in a manner analogous to the use of the term rheopexy for the thixotropic systems. The data in Fig. 2 illustrate the negative rheopexy of milk of magnesia and a clay–salt system. For the milk of magnesia samples, it was necessary to rotate the standing samples once by hand prior to measurement because of some internal settling. A single rotation of this nature had no effect on the other rotated or stirred samples.

Floccule Size.—Sediment volume and filtration rate measurements on selected systems were performed to further substantiate that the phenomenon of negative thixotropy was related to floccule size. Although only systems in a limited concentration range could be measured by sediment volume and filtration rate techniques, the data gathered support

TABLE IV.—NEGATIVE THIXOTROPY IN SYSTEM OF 3% CLAY AND 3% SODIUM BENZOATE—HIGH SHEAR DATA[a]

Shear Rate, sec.$^{-1}$	Shearing Stress, dyne cm.$^{-2}$ Curve *1*		Curve *2*	
	Begin ↓			
140	130	290	Repeat ↓	280
250	210	310	310	300
360	230	320	330	320
470	260	340	340	. . .
590	280	350	360	340
1200	360	410	430	400
1760	430	460	470	460
2340	500		510	

[a] See text for general procedure of obtaining the data.

TABLE V.—CLAY–SALT–SURFACTANT SYSTEMS HIGH SHEAR MEASUREMENTS

System	Rate of Shear, sec.$^{-1}$	Shearing Stress, dyne cm.$^{-2}$ Curve *1*		Curve *2*		Curve *3*	
2% Clay	140	140	210		220		240
0.5% Na benzoate	250	150	230	230	240	240	260
0.05% Polysorbate 40	360	170	240	240	250	260	270
	470	190	250	260	260	270	280
	590	200	260	270	280	290	300
	1200	290	320	320	330	340	350
	1760	360	370	380	380	390	400
	2340	420	420	430	430	440	450
	2960	470	470	480	480	490	500
	3550	520		530		540	
2% Clay	140	110	210		240		
0.5% Na Benzoate	250	130	220	230	260		
0.1% Polysorbate 40	360	150	240	250	270		
	470	160	250	260	290		
	590	180	260	280	300		
	1200	200	320	340	350		
	1760	330	380	390	410		
	2340	400	430	450	480		
	2960	460	480	500	520		
	3550	530		560			
2% Clay	140	80	110				
0.5% Na Benzoate	250	120	120	120	120		
0.2% Polysorbate 40	360	140	140	130	130		
	470	160	150	150	140		
	590	180	170	160	150		
	1200	280	240	230	170		
	1760	350	310	300	300		
	2340	410	380	360	360		
	2960	460	450	430	430		
	3550	520		480			

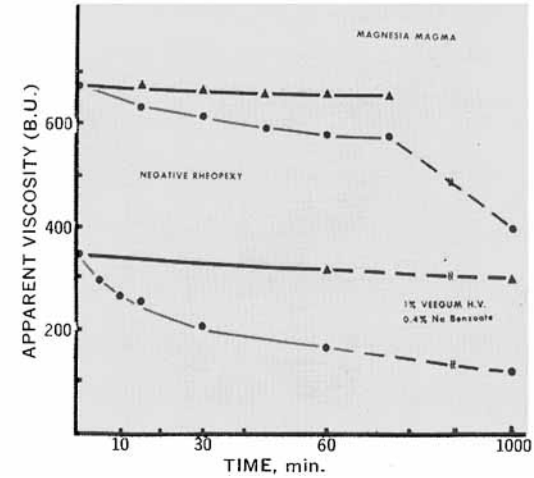

Fig. 2.—Negative rheopexy for milk of magnesia and a clay–salt system. Key: ▲, standing; ●, rotation.

the theory that the floccule size varies with sample treatment.

The process of slow rotation results in the formation of relatively large, compact floccules. This yields more free fluid in the system and reduces floccule-to-floccule contacts. Consequently, these rotated samples filter and sediment more readily. The sheared samples present the reverse situation. The large floccules are destroyed and smaller flocs with greater floccule-to-floccule contacts are produced. These sheared samples settle and filter more slowly, both characteristics of the smaller effective particle size. The sedimentation data are shown in Table VI. Sediment volume is expressed as per cent of total volume, 1 day after the shear treatment.

First attempts to demonstrate floccule size by the vacuum filtration procedures of LaMer (6) were unsuccessful. The pressure differential appeared to destroy the floccule structure. However, gravity filtration procedures as used earlier by LaMer (4) were quite successful and gave additional supporting evidence for the floccule theory of negative thixotropy. The system, 1% clay and 0.4% sodium benzoate, selected earlier as an example of negative rheopexy (Fig. 2), was studied. Filtration rate measurements were performed on this system after stirring and after rotation for different time intervals. The data are shown in Table VII. The gradual decrease in filtration times and the apparent viscosities of these systems with rotation is interpretable as negative thixotropy.

Significance of Negative Thixotropy.—The clay–salt systems described are used as part of the formulas of many suspensions. Since the clay is generally flocculated to induce the viscosity increase, the negative thixotropic properties which have been described might be of importance in the complete suspensions.

The coagulation of clay particles to the inner glass and cap surfaces has already been suggested as being similar to the "gummy ring" encountered in some of these systems. Silicone treatment of the container is suggested from these studies.

In the testing of a series of eight commercial suspensions containing the clay–salt systems, only two samples exhibited higher apparent viscosities under high shear than under low shear. In both cases, the magnitude of the effect was small compared to the negative thixotropy observed in the clay–salt systems. Therefore, other than milk of magnesia, negative thixotropy in these complete formulations would not appear to contribute much confusion to apparent viscosity measurements.

In any attempts to control or correlate complete suspension apparent viscosities with the apparent viscosities of the concentrated clay slurries, negative thixotropy would be expected to cause considerable confusion. A control and knowledge of the shear histories of these concentrated clay–salt slurries would be vital to a correct interpretation of these data.

Table VI.—Sediment Volumes for Clay–Salt Systems

Systems		Sediment Vol., Expressed as % of Total Slurry Vol.—After 24 hr. Standing	
% Clay	% Na Benzoate	Rotated Sample	Mixed Sample
0.5	0.5	60	80
0.8	0.5	80	100
0.9	0.5	80	100
1.0	0.5	90	100

Table VII.—Clay–Salt System Filtration Rate Measurement after Various Sample Treatment

System	Treatment	Time of Filtration, sec.
1% Clay 0.4% Na benzoate	Stirring 5 min.	830
	Rotation, 15 min.	780
	Rotation, 30 min.	690
	Rotation, 1 hr.	520
	Rotation 6 hr.	360
	Rotation overnight	360

SUMMARY

The flocculated clay system has been shown to possess negative thixotropic properties. Measurements on these systems as well as on milk of magnesia have been made by both single point and high shear viscometers. In an analogous fashion to negative thixotropy, the negative rheopexy of both the flocculated clays and milk of magnesia has been demonstrated. Some information on the floccule nature has been gained by sediment volume and filtration rate measurements. The importance of the negative thixotropic behavior of the flocculated clay systems has been considered.

REFERENCES

(1) Chong, C. W., Eriksen, S. P., and Swintosky, J. V., *J. Am. Pharm. Assoc., Sci. Ed.*, **49**, 547(1960).
(2) Medalia, A. I., Hagopian, E., *Ind. Eng. Chem. Prod. Res. Develop.*, **3**, 120(1964).
(3) Fischer, E. K., "Colloidal Dispersions," John Wiley & Sons, New York, N. Y., 1950, p. 195.
(4) LaMer, V. K., and Smellie, R. H., Jr., *J. Colloid Sci.*, **11**, 710(1956).
(5) Weiser, H. B., "Colloid Chemistry," 2nd ed., John Wiley & Sons, New York, N. Y., 1949, p. 320.
(6) LaMer, V. K., Kane, J. C., and Linford, H. B., *J. Phys. Chem.*, **67**, 1977(1963).