

Rheology of Thixotropic Montmorillonite Dispersions I

Changes on Aging of Plain and Polysorbate 80 Containing Dispersions

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The rheological characteristics of thixotropic montmorillonite dispersions are best defined on the basis of a concept of two different yield values, dynamic and static, in addition to plastic viscosity and thixotropic area. The values of these parameters were determined periodically for 10 weeks after preparation of the dispersions and were found to change at different rates. This shows that evaluation of a single rheological parameter as a function of time is not indicative of the overall rheological changes undergone by these systems. The feasibility of selective modification of certain rheological properties and aging characteristics is demonstrated by the rheograms obtained from montmorillonite dispersions to which polysorbate 80 had been added at the time of preparation.

SYSTEMS capable of isothermal gel to sol transformation upon shaking or shearing, and reversion to a gel upon rest, have considerable utility in pharmacy. Prominent among substances which can produce this property, known as thixotropy, upon dispersion in an appropriate liquid are the clays, particularly those of the montmorillonite group. The present study deals with a characterization of various rheological properties of a widely used member of the montmorillonite group, colloidal magnesium aluminum silicate (MAS), which is a refined product derived from saponite (1). Aqueous dispersions of this material exhibit complex time-dependent flow properties which are complicated further by certain irreversible changes upon aging. It has been found necessary to redefine the concept of yield value as applied to these systems, and to extend the interpretation of the obtained rheograms on the basis of the more recent rheological research results which apparently have not yet been taken into consideration by many pharmaceutical scientists. Of particular interest have been the quantitative and qualitative nature of the irreversible rheological changes of aqueous MAS dispersions upon aging, since it was hoped that subsequent studies in this series could be carried out with dispersions which have attained structural equilibrium. Since both reversible and irreversible changes of montmorillonite clays are related to the surface properties of these materials, it has been found desirable also to investigate the effect of a typical nonionic surface-active agent on the rheological and aging characteristics of the dispersions.

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EXPERIMENTAL

Preparation of Dispersions.—Three per cent w/w dispersions of colloidal magnesium aluminum silicate (Veegum)¹ were prepared in 500-Gm. portions by adding 15 Gm. of the clay to 485 ml. of distilled water, and mixing these vigorously for 3 minutes in an Arnold automatic mixer, model No. 15. The individual portions were combined while still hot and agitated with a Brookfield counter-rotating mixer in a 2-gal. beaker at a rheostat setting of 80 for 5 minutes, followed by 25 minutes of agitation at a rheostat setting of 50. The dispersion was then weighed and water lost by evaporation was replaced.

Water at room temperature was used in the preparation of dispersions by the "cold" process, while water heated to 80° was used in the "hot" process.

Polysorbate 80 was added after preparation of the dispersions by the "hot" process and incorporated by mild mixing to prevent foaming.

Storage.—The dispersions were placed in glass jars which were stored in an electric oven at a temperature of $30 \pm 1^\circ$.

Instrumentation and Methodology.—The Eprecht Rheomat 15² was used to obtain the rheograms. This instrument is a rotational viscometer having 15 different shear rate settings for a given measuring system. Changes of shear rate are discontinuous and made manually, but do not require stopping the spindle. All measurements reported in this paper were made at 30°, using the "B" measuring system. The 15 shear rate settings were 3.110, 4.177, 5.496, 7.334, 9.674, 13.94, 18.72, 24.64, 32.87, 43.36, 62.94, 84.51, 111.2, 148.3, and 195.7 sec.⁻¹. Each experimental point in Figs. 1-3 represents an average value obtained from three rheograms of different samples of the dispersion. These samples were not returned to the stock dispersion, but discarded after use.

To obtain data for a rheogram, the viscometer cup was filled with an appropriate quantity of the dispersion and the spindle was immersed. Both were then attached to the instrument which was

¹ Manufactured by R. T. Vanderbilt Co., New York, N. Y.

² Made by Contraves AG, Zurich, Switzerland.

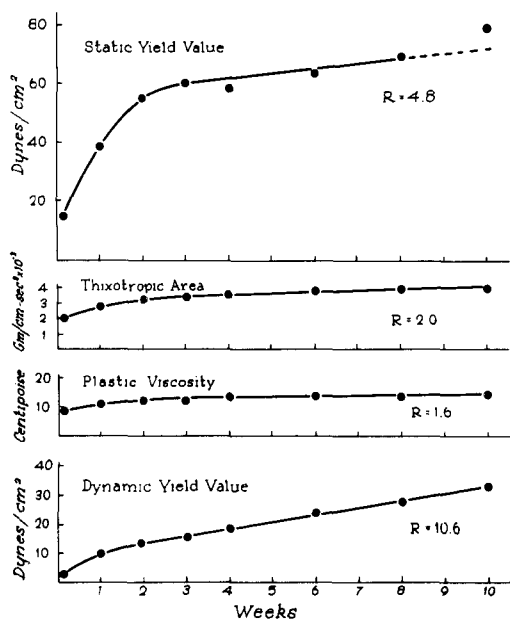


Fig. 1.—Changes in rheological properties of a 3% aqueous dispersion of MAS prepared by the "hot" process, during storage at 30° for 10 weeks.

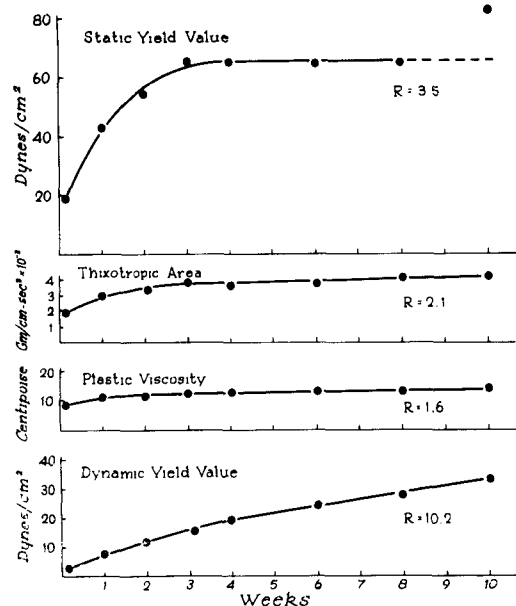


Fig. 2.—Changes in rheological properties of a 3% aqueous dispersion of MAS prepared by the "cold" process, during storage at 30° for 10 weeks.

positioned so that the cup was immersed in a constant temperature water bath set at $30 \pm 0.1^\circ$. The dispersion was sheared at a rate of 195.7 sec.^{-1} for 5 minutes and then permitted to remain undisturbed for 30 minutes. During this time, the cup was covered with a plexiglas disk to prevent significant evaporation of water from the surface of the dispersion. At the end of the 30-minute period,

the viscometer spindle was set in motion at the lowest shear rate. Characteristically, the shear stress indicator exhibited a large excursion as the spindle began to rotate. This maximum torque was noted. Another reading was made 30 seconds after the spindle had been set in motion. The shear rate was then increased to the next setting, and shear stress measured after 30 seconds. Shear rates were increased at 30-sec. intervals until the highest shear rate was reached, then decreased at the same rate to the lowest shear rate. The shear stress data obtained at the various shear rates were used to draw the rheograms.

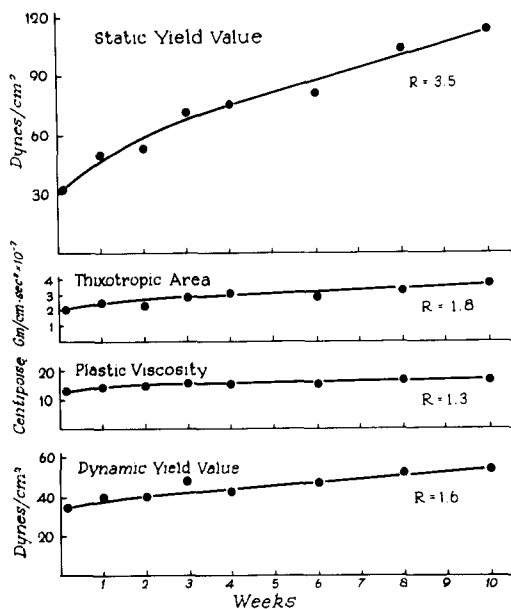


Fig. 3.—Changes in rheological properties of a 3% aqueous dispersion of MAS prepared by the "hot" process and containing 0.1% polysorbate 80, during storage at 30° for 10 weeks.

Yield value corrections were made according to Epprecht (2), using a K_f factor of 0.80, which is based on an R^2/r^2 value of 1.58. Thixotropic areas were determined by means of a compensating polar planimeter from a graph where the shear rate axis represented 7.75 sec.^{-1} per cm. and the shear stress axis 24.9 dynes/cm.^2 per cm. Accordingly, a thixotropic area of 1 cm.^2 was equal to $193 \text{ Gm./cm. sec.}^3$. The thixotropic area was taken as the area enclosed by the ascending and descending shear rate *vs.* shear stress curves, and the horizontal line connecting the experimental points of both curves at a shear rate of 3.110 sec.^{-1} , as shown in Fig. 4.

RESULTS AND DISCUSSION

Flow curves of thixotropic systems are defined usually on the basis of plastic viscosity, thixotropic area, or index, and the value of the shear-stress intercept of the extrapolated linear portion of the down curve at zero shear rate. The latter value is referred to as the yield point or yield value. The rheograms of the MAS dispersions yielded up curves having characteristic shear stress maxima at the

beginning of measurement, followed by shear stress minima at a relatively low shear rate (Fig. 4). The shear stress maxima have been observed only in re-

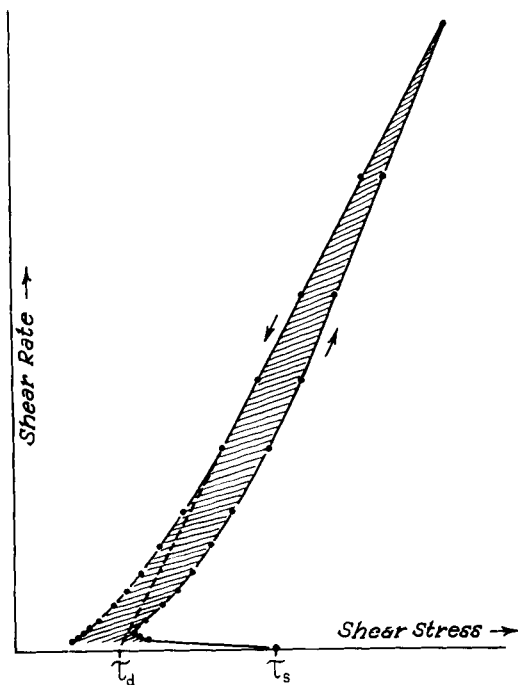


Fig. 4.—Typical rheogram of an aqueous dispersion of MAS. τ_d , dynamic yield value; τ_s , static yield value. Shaded section represents the thixotropic area.

cent years when continuous recording viscometers and more refined and sensitive multiple-point instruments have come into use. However, there is already evidence that these maxima reflect a rheological property of direct pharmaceutical pertinence; for example, it has been found that the persistence of penicillin levels in the blood after administration of procaine penicillin depot preparations is directly related to the value of the initial shear stress maximum of these suspensions (3). Thus, it is desirable to consider the initial shear rate maximum as one of the several rheologic properties which must be measured in order to describe a thixotropic system adequately. This necessitates a redefinition of the concept of yield value as well as a consideration of the significance of the shear stress minimum on the up curve of the rheogram.

Conventional or Dynamic Yield Value.—The shear-stress intercept of the linear portion of the down curve of a rheogram at zero shear rate, referred to conventionally as the yield value, is usually defined as the minimum tangential shearing force necessary to cause flow (4). Experimentally, however, it can be shown that the shearing force necessary to initiate flow of thixotropic montmorillonite dispersions is considerably higher than the conventional yield value. This is reflected by the initial shear stress maximum characteristic of such dispersions. Furthermore, if the conventional yield value really has the meaning assigned to it by the above definition, it should be independent of the maximum shear rate to which the system is ex-

posed in the course of measurement. Such is not the case since the yield value frequently increases upon increasing the top shear rate used in the determination of the flow curve (4, 5). It is well appreciated that the need for some minimum shear stress to initiate the flow of thixotropic systems is predicated upon the presence of a continuous structure whose interparticle bonds must be broken in the process of inducing flow. Thus it should be clear that any measurement based solely on a thixotropic system in flow cannot provide information concerning the shear stress necessary to cause this flow. Upon examination of a typical rheogram, the real significance of the conventional yield value becomes quite clear; it is the energy-input necessary to maintain a constant ratio of shear rate to shear stress (that is, total shear stress minus the yield stress referred to) in a system whose structure has been destroyed, totally or in part, by previous shear (in the course of determining the up curve of the rheogram). Expressed in a different way, the conventional yield value reflects the energy input required to maintain the degree of structural breakdown which exists at the maximum shear rate, just before shear rate is reduced for the determination of the down curve. This is reasonably analogous to the concept of a coefficient of dynamic friction as opposed to the coefficient of static friction of solids. Accordingly, it is proposed that the conventional or Bingham yield value be referred to as the dynamic yield value, unless it can be shown experimentally that this value does not differ from the yield value necessary to cause flow (which would be the case in plastic systems). Apart from the purely mathematical usefulness of quantitating the dynamic yield value, it should also be indicative of the degree to which the internal structure of a system has been destroyed by a given shear stress and duration of shear. At some point, a further increase in shear stress and/or duration should cause no further increase in dynamic yield value; namely, when all the weak secondary bonds between particles have been broken and the dispersed units consist solely of primary particles.

Static Yield Value.—This term evolves as a logical consequence of accepting the concept of a dynamic yield value. It may be defined as the minimum tangential shearing force necessary to initiate flow. Unfortunately, this value is not independent of time. Houwink has pointed out the necessity of including a specification about the rate of increasing shear stress when defining yield value (6).³ McVean and Mattocks (7) could demonstrate that the static yield value is a function of rate of strain, since it is evident that their rising sphere rheometer measures static rather than dynamic yield value at the "flow" point. The time dependency stems from the viscoelastic and relaxation behavior of most gels. In stating that the force required to break down structure and cause flow of thixotropic suspensions is time-dependent and must be represented by a curve with time as one of the parameters, Dintenfass points out that it is not a case of no flow occurring below a given shear stress value, but rather that the time taken for measurable flow to take place would be abnormally long (8). In addition, the time effect

³ Within the context of Houwink's discussion it is clear that he was referring to the "static" yield value.

applies also to the rest period of the thixotropic system. In the act of charging the viscometer, structure is destroyed and requires time to rebuild, as indicated by data reported in the following paper (9). Moreover, there are indications that the structural recovery rate is affected by the diameter of the annulus of the viscometer (9). The static yield value is, therefore, far from an absolute value and is related not only to the previous history of the measured material, but also to measurement conditions and instrument characteristics. While the concept of a dynamic and a static yield value has, to the best of our knowledge, not previously been applied experimentally within the strict definition of these terms as presently proposed, it is of interest to note that the idea is not new. A review of the literature has shown that Green and Weltmann suggested these terms in 1946 but evidently did not follow upon their suggestion with experimental data, possibly due to lack of appropriate instrumentation (5).

Shear Stress Minimum.—Prominent in the beginning portion of the up curve of the thixotropic rheogram shown in Fig. 4 is a shear stress minimum, which may occur at shear rates significantly higher than zero. This phenomenon has been explained recently by Enneking (10). He found that the shear stress minimum occurred at higher shear rates when the annular width of the viscometer was increased. As the spindle begins to move (*i.e.*, the point at which static yield value is determined), the measured material flows only at the spindle surface and not throughout the annular space. Upon increasing the spindle velocity, further breakdown of structure occurs and the effective annular distance increases. Since shear rate is inversely proportional to the distance between annular boundaries, the actual shear rate to which the thixotropic material is subjected is decreased, despite the higher speed of rotation of the spindle. Naturally, the shear stress will be less at this lower shear rate. This process continues until flow occurs throughout the space between cup and spindle. At that point, the shear stress minimum is reached and any further increase in spindle r.p.m. reflects a true increase in shear rate and, therefore, requires higher shear stresses. The narrower the annulus, the lower the shear rate at which the stress minimum will occur. Thus, this factor is primarily an instrumental characteristic rather than a property of the material, although the rate of thixotropic breakdown is a contributing factor under the usual nonequilibrium experimental conditions. The experimental points on the up curve of the rheogram between the static yield value and the shear stress minimum have, therefore, no absolute physical meaning since they are plotted on the basis of apparent, but not actual, shear rates.

Rheological Changes of Montmorillonite Dispersions on Aging.—Figure 1 shows the changes in static yield value, thixotropic area, plastic viscosity, and dynamic yield value of a 3% MAS dispersion prepared by the "hot" method during a period of 10 weeks after preparation. Static yield value increased quite rapidly during the first 3 weeks and then leveled off. The *R* value in the graph is the ratio of the 10-wk. value to the 24-hr. value.⁴ For

this calculation, the 10-wk. value indicated by the extrapolated curve was used, since the actual experimental points in Figs. 1 and 2 are unusually high and appear to be artifacts. Thixotropic area also increased most rapidly during the first 3 weeks and very slightly from then on. Over the 10-wk. period, the thixotropic area increased only twofold, as opposed to an almost fivefold increase in static yield value. The plastic viscosity exhibited an even smaller change, and essentially reached equilibrium after 4 weeks when it had increased by 60% over the 24-hr. value. This rather small increase is readily understandable if it is assumed that the thixotropic suspension, at the time of measurement of the down curve, consists of individual particles (not necessarily primary particles) suspended in a Newtonian liquid (water). This assumption is reasonable since interparticle bonds have been broken by previous shear and are prevented from reforming as long as the down curve remains linear. As a first approximation, the viscosity of such a liquid should follow the Einstein equation

$$\eta = \eta_0 (1 + 2.5\phi)$$

where η is the viscosity of the suspension, η_0 the viscosity of the medium, and ϕ the volume fraction of the dispersed phase. The latter value would increase somewhat in an aging clay dispersion due to lattice expansion, the degree of this expansion being a function (among others) of the moisture content of the solid clay just prior to use.

Dynamic yield value increased over tenfold during 10 weeks. This is remarkable, especially since the dispersion was agitated quite intensively in the course of preparation. The increase in dynamic yield value signifies that a greater energy input is necessary to prevent structure reformation as the dispersion ages. This may be due to the ultimate dispersion into primary particles of what were originally face-to-face aggregates of numerous clay particles. These primary particles should be capable of individual participation in the formation of the typical scaffolding structure of clay dispersions at rest.

The rheological changes during aging of MAS dispersions prepared by the "cold" method did not differ significantly from those of the dispersions prepared by the "hot" process (Fig. 2). This result was somewhat surprising since the use of heat is generally recommended for the preparation of montmorillonite dispersions. Reference to the literature indicates, however, that another worker also observed only small temperature effects with MAS (11). It may be that the temperature effect is greater when the dispersions are subjected to lower agitation intensities and shorter agitation periods during preparation.

Effect of Polysorbate 80.—The addition of 0.1% polysorbate 80, immediately after preparation, to 3% MAS dispersions prepared by the "hot" method results in a profound modification of flow and aging characteristics (Fig. 3). The static yield value at 24 hours is about 50% higher than in the absence of surfactant. It increases at practically constant rate throughout the 10-wk. period. The thixotropic area is somewhat smaller in the polysorbate 80-containing dispersions. This could be due either to a smaller degree of thixotropy or to a more rapid

⁴ This *R* should not be confused with the coefficient of thixotropic recovery, also designated as *R*, in the following paper (9).

structural recovery. Subsequent studies described in the following paper (9) indicate that a more rapid structural recovery rate is probably the reason for the smaller thixotropic area. The plastic viscosity is slightly higher in the presence of polysorbate 80. Since polar but otherwise neutral molecules, such as the glycols, are known to be adsorbed between the silicate laminae of montmorillonite clays (12, 13), it is probable that the higher plastic viscosity of polysorbate 80-containing dispersions is due to an increased volume of the dispersed phase caused by lattice expansion upon adsorption of the surfactant. The most significant effect of surfactant was, however, a tenfold increase in dynamic yield value at 24 hours. The subsequent increase upon aging was only 60%, compared with a tenfold increase in the dispersions without surfactant. The presence of polysorbate 80 thus affects, primarily, the dynamic and static yield values, and only slightly the thixotropic area and plastic viscosity of aqueous MAS dispersions. This demonstrates the possibility of a selective modification of certain rheological properties by means of additives capable of modifying the surface properties of montmorillonites. Interpretation of the mechanism of the polysorbate 80 effect is complicated by the fact that the montmorillonite was neither dialyzed nor homoionic. It is known that neutral but polar molecules adsorb on the surface of montmorillonite, orient parallel to that surface, and are capable of displacing hydrogen-bonded water (13). It was found in the course of studies of the adsorption of nonionic aliphatic molecules from aqueous solutions on montmorillonite, that mixtures with high molar adsorption tend to form gels while mixtures with low molar adsorption settle out on standing (14). Of interest, also, are the observations by Samyn that small concentrations of polysorbate 40 increase the apparent viscosity of MAS dispersions but that higher surfactant concentrations reverse this increase (15). It is possible that the surfactant effect is due to partial displacement of inorganic cations from the surface of the clay, although such displacement need not necessarily occur when organic molecules are adsorbed (16). It has been suggested also that surfactant micelles can serve as a locus for the attachment of individual colloidal particles (17). The surfactant may, therefore, have a bridging effect. The high initial yield values and smaller subsequent changes (as compared with those of suspensions without the surfactant) indicate that the lowering of interfacial tension by the surfactant could have increased the rate of dissociation of face-to-face aggregates of the clay. This would make a larger number of particles available for face-to-edge or edge-to-edge association which leads to the scaffolding structure responsible

for high yield values. Experiments are currently under way to elucidate the mechanism or mechanisms of the surfactant effect.

CONCLUSIONS

The experimental data show that aqueous dispersions of a representative montmorillonite clay undergo large rheological changes on aging. It has not been possible under our experimental conditions to attain structural equilibrium during 10 weeks of aging at 30°. Other studies in this laboratory indicate that even considerably longer aging periods are inadequate for equilibration of rheological properties of montmorillonite dispersions. The changes in rheological properties of montmorillonite dispersions on aging or due to additives can be characterized adequately only if all the various rheological parameters are determined individually, since they change to different extents. Comparative studies on montmorillonite dispersions must be standardized rigidly with respect to time in order to exclude the aging period as one of the variables. The effect of polysorbate 80 on the rheological and aging properties of MAS dispersions illustrates the feasibility of a relatively selective modification of these properties by means of additives for the purpose of obtaining optimum flow and aging characteristics in a pharmaceutical system.

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