Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Loft, B. C. and Solomon, D. H.(1972) 'Acid-Base Interactions and the Rheology of Kaolinite Dispersions in Paraffin Oil', Journal of Macromolecular Science, Part A, 6: 4, 831 — 837

To link to this Article: DOI: 10.1080/10601327208056879

URL: http://dx.doi.org/10.1080/10601327208056879

J. MACROMOL. SCI.—CHEM., A6(4), pp. 831-837 (1972)

Acid-Base Interactions and the Rheology of Kaolinite Dispersions in Paraffin Oil

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ABSTRACT

Kaolinite is commonly used as a filler in paints, elastomers, and plastics. The processing behavior of these compositions depends upon the interactions between the filler and the polymeric medium. The presence of small amounts of basic compounds can dramatically alter the flow properties of kaolinite dispersions in oils or polymer solutions. With monofunctional aliphatic additives the effectiveness of the substance depends upon the basicity of the functional groups, on the alkyl chain length, and on the quantity of additive. The effect of these factors on yield stress indicates that the additives are adsorbed on the surface via acid-base interactions to form a layer which decreases particle/particle attractions by entropic repulsion.

INTRODUCTION

Dispersions of kaolinite in nonpolar media are of practical importance in the rubber, paint, lubricant, plastics, and pharmaceutical industries. The flow of any particulate dispersion of this type is very dependent upon particle/medium and particle/particle interactions;

therefore, as well as being industrially important, the rheology of particulate dispersions is a sensitive tool for the scientific study of these interactions. A small change in each interaction is magnified exponentially by the large number of interactions to produce a large change in viscosity and/or yield stress.

A number of possible types of interaction sites on kaolinite each play their part in determining the flow properties of the final dispersion. Many authors [1-4] have demonstrated the existence of acidic sites on kaolinite, although there is still discussion whether they are Lewis or Brønsted acids. Current work indicates that both types of site coexist, their relative proportions depending upon the extent of dehydration of the surface. In addition, the crystal edges of kaolinite are positively charged [5] while the crystal as a whole has a net negative charge arising from isomorphous substitution. Thus kaolinite particles can have either acid-base or electrostatic interactions with other particles, with the medium, or with additives.

The use of small quantities of additives to control the rheology of particulate dispersions in nonpolar media is common practice in industrial technology, e.g., water is added to increase viscosity or surfactants are added to decrease viscosity, but there is no systematic approach to the selection of the additive.

This paper is concerned with the principles underlying the action of these additives and particularly the influence of the acidic sites on kaolinite.

RESULTS

The flow properties of 20% kaolinite dispersions in medicinal paraffin oil containing 0.1 mmole/gm kaolinite of the appropriate additive were measured with a Rotovisco concentric cylinder viscometer. Although the measuring routine was designed to detect thixotropy, little thixotropy was found.

All the dispersions tested were pseudoplastic fluids with a yield stress, and their shear stress/shear rate relation fitted Casson's equation (Eq. 1) over the entire range of shear rates used (2 to 400 $\sec^{-1}$), where τ (dyne cm^{-2}) is the shear stress, τ_0 (dyne cm^{-2}) is

$$\tau^{\frac{1}{2}} = \tau_0^{\frac{1}{2}} + \eta_\infty^{\frac{1}{2}} D^{\frac{1}{2}} \qquad (1)$$

the yield stress, D ($\sec^{-1}$) is the shear rate, and η_∞ (poise) is the viscosity at infinite shear rate. Casson's equation was used in an alternative form (Eq. 2) to determine the flow curve parameters η_∞ and τ_0, by linear regression of $\eta_a^{\frac{1}{2}}$ against $D^{-\frac{1}{2}}$, where η_a (poise) is

$$\eta_a^{\frac{1}{2}} = \eta_\infty^{\frac{1}{2}} + \left(\frac{\tau_0}{D}\right)^{\frac{1}{2}} \qquad (2)$$

the apparent viscosity = τ/D. In every case the regression coefficient was greater than 0.999. The parameters obtained with additives of similar molecular weight but differing chemical types are given in Table 1.

TABLE 1. Flow Curve Parameters for 20% Dried Hydrite 10 Dispersions in Paraffin Oil Containing Additives

Additive	Yield stress (τ_0, dyne cm^{-2})	Viscosity at infinite shear rate (η_∞, poise)
None	480	2.1
Methyl nonylketone	480	2.3
Methyl decanoate	460	2.3
n-Undecanol	91	1.9
n-Decylamine	49	1.9

Although the viscosities at infinite shear rate do not appear to be significantly different, the yield stresses show that there are significant differences between the effects of additives with differing functional groups. Only the basic additives decrease the yield stress, and the decrease is related to the basicity of the additive.

The effect of additive concentration is illustrated by the results in Table 2 where decylamine was the additive used. Because there was again no significant change in viscosity at infinite shear rate, the values of this parameter have been omitted. The yield stress was greatly decreased by the first 1% decylamine, but then less so until no further decrease occurs with more than 3% decylamine on the clay.

There is a similar influence of alkyl chain length on the effectiveness of an additive at a constant molar concentration. This is shown in Fig. 1 for a homologous series of amines at a concentration of 0.1 mmole/g kaolinite.

TABLE 2. Dependence of Flow Parameters on Decylamine Concentration for 20% Dispersion of Kaolinite in Paraffin Oil

Concentration of decylamine (g/100 g kaolinite)	Yield stress (τ_0, dyne cm^{-2})
None	480
1	73
2	31
3	19
4	24

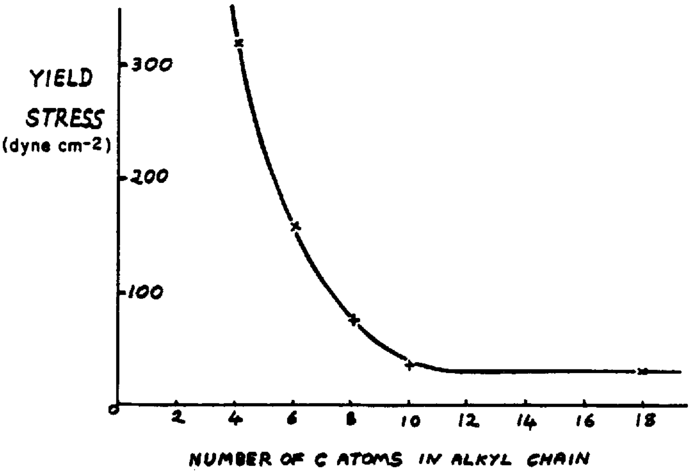

FIG. 1. Effect of alkyl chain length on the yield stress of 20% Hydrite 10 dispersions in paraffin oil containing 0.1 mmole amine/g kaolinite.

DISCUSSION

Since only the yield stress is significantly affected, the influence of these additives must be on the particle/particle interactions in the dispersion, and not on the particle size or particle/medium interactions, which control the viscosity at infinite shear rate.

Kaolinite consists of tabular particles with a positive charge at the crystal edge [5], while the crystal as a whole has a net negative charge.

The negative charge is compensated for by the presence of exchangeable cations. In a kaolinite dispersion at rest, the electrical attraction between edges and faces causes the particles to flocculate into an open 3-dimensional network structure. The yield stress of the dispersions apparently arises because of the force needed to deform and eventually destroy this "house of cards" structure.

Since the flow curves of the dispersions containing the additives all fit Casson's equation, which was derived for dispersions of mutually attractive particles [6], the additives must decrease the interparticle attractions but without eliminating them. The size of the decrease in yield stress should be a measure of the influence of the additive on the particle/particle attraction. There are two possible ways for the additive to decrease the edge/face attraction. First, by neutralization of the charges on either of the edges or the faces of crystals. Second, by the formation of a barrier of adsorbed additive which limits the distance of closest approach by entropic repulsion.

The effect of alkyl chain length shown in Fig. 1 favors the second mechanism since both a long-chain and a short-chain amine at the concentration used would have a similar ability to neutralize the electrical charges but actually give widely differing yield stresses. The effect of concentration shown in Table 2 also favors the entropic repulsion mechanism, since the decrease in yield stress with increasing concentration parallels the expected surface coverage with increasing concentration for an amine on a kaolinite of this surface area (10 m^2/g), and when the surface is saturated with additive no further change in yield stress occurs. Confirmatory evidence that an adsorption mechanism is involved is provided by the order of increasing effect of various chemical types on yield stress shown in Table 1 ($0 =$ ketone, ester $\ll$ alcohol $<$ amine) which is also the order of increasing adsorption on kaolinite determined by Dintenfass [7].

The additives in Table 1 are all bases, and the order of their effectiveness is the accepted order of their basic strength. The existence of acidic sites on dehydrated kaolinite in dry systems has been demonstrated by the use of Hammett indicators [1]. Hence it is reasonable to accept that the adsorption is via an acid/base interaction to give particles coated with the additive. The alkyl chain of the additive would be solvated by the paraffin oil, thus becoming fully extended and forming a barrier of entropic stabilizer around the particles.

EXPERIMENTAL

Materials

The kaolinite used was from a single batch of Hydrite 10 kindly donated by Georgia Kaolin Co., Elizabeth, New Jersey. The mean particle size is 0.55 μ e.s.d. with 95% of the particles less than 2 μ e.s.d. The specific gravity of Hydrite 10 is 2.58. The surface has Brønsted acidity in water, and the pH of a 20% aqueous slurry is 4.6. The oil adsorption of the dry material measured under anhydrous conditions was 54 g linseed oil/100 g clay. The paraffin oil used was Ondina 33 supplied by Shell Petroleum Co. This is a colorless medicinal paraffin oil meeting the specifications of the British Pharmacopeia 1968 with a density 0.888 g/ml, a viscosity of 79 cSt at 100° F (1.52 P at 25°C), an acid number of 0.006 mg KOH/g. It is free of aromatics as evidenced by an extinction coefficient of < 4 between 240 and 280 mμ.

The additives were all pure grade materials shown by GLC to be >99% pure.

Procedure

The suspensions were made by first dissolving the required weight of additive in 80.0 g of paraffin oil; then 20.0 g of dried Hydrite 10 was rapidly added and mixed in to ensure minimum contact of the clay with the atmosphere. The Hydrite 10 which was dried for at least 2 hr at 110° C was stored in the drying oven until needed and consequently was hot when added to the paraffin oil. This procedure ensured that water adsorption from the atmosphere was minimal. Dissolution of the additive in the paraffin oil ensured that it was distributed uniformly throughout the suspension and hence gave uniform adsorption. This method also avoids the high torque needed to incorporate the pigment without additive.

After the preliminary mixing the final dispersion was performed on a Sorvall Omni-mix high-shear mixer. The completed dispersion was kept in a 25.0° C water bath before transfer to the viscometer.

The flow properties were measured with a Haake Rotovisco using the MV II concentric cylinder measuring system. Thixotropic loops were measured using the routine of 60 sec at each of 10 shear rate steps increasing from 2.72 to 441 $\sec^{-1}$, then at decreasing shear rates back to 2.72 $\sec^{-1}$. This routine was adhered to although little thixotropy was found.

The use of a Rikadenki model B-140 potentiometric recorder to record instantaneous shear stresses enabled structure breakdown or build-up to be easily detected. However, in all cases the shear stress reading was taken at the end of the period of constant shear rate.

The flow curves plotted as log shear stress = f(log shear rate) were all similar, with an initial low slope gradually increasing with increasing shear rates. The major differences were at low shear rates, reflecting the wide variation in yield stresses. The flow curves did not fit the power law equation (log shear stress = const × log shear rate) but did fit Casson's equation (Eq. 1) very well.

$\eta_a^{\frac{1}{2}}$ and $D^{-\frac{1}{2}}$ were calculated from the τ,D data, and linear regression of $\eta_a^{\frac{1}{2}}$ as a function of $D^{-\frac{1}{2}}$ was performed on a Hewlett Packard 9100 calculator to yield values of $(\tau_0)^{\frac{1}{2}}$, $\eta_\infty^{\frac{1}{2}}$, and the coefficient of regression. No attempt was made to correct for the variation of shear rate across the sample caused by its non-Newtonian behavior; the large differences between the samples made this unnecessary.

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Received for publication February 7, 1972