

NLGI 1985 Annual Proceedings

52nd Anniversary

NLGI 1985 ANNUAL PROCEEDINGS
(52ND ANNIVERSARY)

HOT SPRINGS, VIRGINIA
OCTOBER 27-30 1985

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STUDIES OF THE BEHAVIOR OF DISPERSED ORGANOCCLAYS
IN GREASE SYSTEMS

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PRESENTED AT THE 52nd ANNUAL MEETING
NATIONAL LUBRICATING GREASE INSTITUTE

THE HOMESTEAD
HOT SPRINGS, VIRGINIA

OCTOBER 27-30, 1985



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STUDIES OF THE BEHAVIOR OF DISPERSED ORGANOCLAYS
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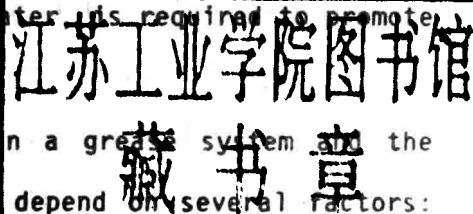
ABSTRACT

Organoclays are widely employed as rheological control agents in grease systems. If effectively dispersed and gelled in a lubricating fluid, an organoclay imparts useful rheological properties to the system. The degree of dispersion of the organoclay will dramatically influence the rheological effects via the gelation and mechanical stability of the grease system.

The role of the polar activator as a dispersant/gelation promoter has been investigated. Whereas a polar activator by definition functions as a dispersant, it may not always adequately participate in the gelled organoclay network. In this case a second species, such as water, is required to promote maximum gelation.

The ease of incorporation of an organoclay in a grease system and the resulting mechanical stability have been found to depend on several factors: organic content of the organoclay, amount of polar activator, type of oil and percent water. The relationship of the degree of organoclay dispersion and shear sensitivity to mechanical stability was also examined.

Experimental evidence to support these findings will be presented along with a description of the general rheological performance of dispersed organoclays in grease systems.



INTRODUCTION

Organoclays are widely utilized throughout the grease industry as rheological control agents for lubricating fluids^(1, 2). Four interesting phenomena are associated with an organoclay grease system: dispersion, gelation, degelation and mechanical stability. Dispersion involves the effective incorporation of the organoclay rheological control agent in the lubricating fluid via a combination of mechanical shear (work) and chemical polar activator. Gelation is achieved when the dispersed organoclay is able to impart its full rheological properties to the grease system. Degelation, a break-down in viscosity or grease consistency, occurs when the network of organoclay platelets is disrupted chemically. Mechanical stability is a measure of the tendency of greases to harden or soften when subjected to work.

Previous fundamental studies⁽³⁾ of organoclay behavior have provided definitive answers about the mechanisms by which an organoclay is able to impart rheological control to the lubricating fluid. Distinct relationships between dispersion and viscosity in organoclay grease systems were observed. For example, the dispersion of an organoclay in a grease system was related to a work (shear)/polar activator synergism. It was also observed that completely dispersed organoclay grease systems exhibit some shear sensitivity wherein the type of shear (i.e. turbulent vs laminar) affects grease consistency.

Our initial studies⁽³⁾ have been further expanded to define the role of the polar activator in the dispersion/gelation process. The role of water in the gelation process was also examined. Although mechanical stability was previously found to be influenced by a shear/viscosity relationship resulting

from the orientation of the organoclay platelets in a grease system, mechanical stability is also dependent on several other factors including the organic content of the organoclay, the amount of polar activator, the type of base stock and the water content of the grease system.

EXPERIMENTAL

The organoclay grease systems were prepared by a mixing/milling process. The experimental system was a 7% (w/w) dimethyl bis(hydrogenated tallow) ammonium bentonite (denoted as 2M2Ht organoclay) in a high viscosity solvent refined (HVI) oil. Unless noted otherwise, approximately 35% by weight of the organoclay was comprised of 2M2Ht and 65% by weight of the organoclay was bentonite clay. The 2M2Ht organoclays were prepared under experimental laboratory conditions. Variations in dispersion properties which could not readily be observed with commercial organoclays could be distinguished with these experimental organoclays since small variations in preparative properties could be maintained.

A typical grease pregel was prepared by mixing the 2M2Ht organoclay and HVI oil for 5 minutes with a drill press stirrer operating at 450 rpm. The polar activator was introduced and the pregel mixed an additional 25 minutes with a drill press stirrer at 450 rpm. Depth of penetration measurements were measured on the resulting pregel at 25°C according to ASTM Method D217-82. Viscosities for relatively fluid samples were measured with a Brookfield RVT viscometer. The grease pregel was passed through a laboratory Tri-homo mill with a rotor-to-stator gap of 0.003 inch at a rate of 230 g/min. The grease was cooled to 25°C and a penetration measurement was made.

To determine consistencies of worked greases, the milled grease was placed in a grease worker and penetration values were recorded after 60 and 10K strokes. Worked or mechanical stability of greases was evaluated as the difference in penetration measurements at 10K and 60 strokes, i.e., penetration value at 10K strokes minus penetration value at 60 strokes.

RESULTS

Dispersion

Organoclays, as a result of their preparation, exist as tightly bound stacks of clay platelets where the organic quaternary ions are located on the faces of the clay platelets. The organic portion of the organoclay, the quaternary amine, is chosen such that the organoclay will have good affinity with the fluid system. A combination of mechanical shear and a chemical polar activator is employed to disperse the organoclay additive in the base fluid. A dispersed state occurs when the stacked organoclay platelets become fully separated from each other and are thus incorporated within the lubricating fluid. This process is schematically represented in Fig. 1.



Figure 1 Organoclay platelet dispersion via mechanical milling and polar activation.

The polar activator associates with the clay surface and induces an increased spacing between the platelets as a result of steric changes in the quaternary amine located on the faces of the clay platelets. This action drastically lessens the attractive forces between the platelets and allows mechanical shear to easily separate the platelets, resulting in dispersion of the organoclay in the lubricating fluid. When extensive shear is applied to the polar activated organoclay system, a complete dispersion of the organoclay platelets within the grease system occurs. At this point the organoclay is able, in principle, to impart its full rheological control to the system if a network of bonds between platelets can be established. The formation of a hydrogen-bond network between adjacent dispersed clay platelets is commonly advanced to describe the gelled state⁽⁴⁾.

The dispersion or separation of the organoclay platelets within an oil system can be monitored analytically with infrared (IR) spectroscopy (3,5). Infrared spectroscopy can be used to study the motion of atoms within a material. The motion of the atoms occurs with discrete frequencies and causes an absorption of energy at those frequencies. Other sets of atoms in close proximity will perturb or alter the frequencies leading to changes in the absorption pattern measured by infrared spectroscopy. For example, an absorption at 1040 cm^{-1} in the infrared arises from Si-O-Si stretching motions within the clay platelets. The relationship of the band width of the IR absorption band to the degree of dispersion of the organoclay platelets arises from the effects of vibrational coupling, i.e., the interaction of sets of silicate moieties between the stacked clay platelets. As the clay platelets separate, the vibrational coupling between platelets is diminished

and the IR clay band width collapses. The collapse of the 1040 cm^{-1} band width can be seen in Fig. 2⁽⁶⁾ where the combined effect of milling and the addition of a polar activator (acetone) to a 10% (w/w) 2M2Ht organoclay in mineral oil on clay band width is presented. The collapse of the IR clay band width indicates extensive dispersion of the organoclay platelets in the base oil.

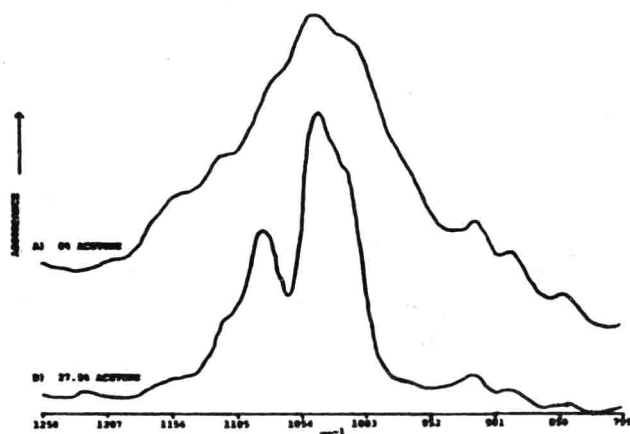


Figure 2 Infrared spectra of the Si-O-Si stretching region for a 10% (w/w) 2M2Ht organoclay/mineral oil system milled 5 minutes in a Spec shutterbox: (A) with no acetone and (B) with 27.5% acetone (the % acetone is based on the weight of the organoclay). The band width narrowing observed in (B) is indicative of organoclay dispersion.

There is an extensive list of polar activators widely used throughout the grease industry for the activation of organoclays. Some commonly used polar activators include acetone, propylene carbonate, methanol, and ethanol. A feature that these and all polar activators have in common is the presence of functional groups, such as hydroxyls and carbonyls, which are available for hydrogen bond participation. When any of these polar activators are added to a 7% (w/w) 2M2Ht organoclay/HVI oil system which is subsequently subjected to

shear, a dramatic decrease in the IR clay band width is observed, indicative of dispersion of the organoclay platelets throughout the oil media. Simultaneously, the gelling or thickening of the grease system is observed as the dispersed organoclay imparts its rheological control to the system via a network of hydrogen bonded clay platelets. Although the role of the polar activator in the dispersion process is understood, its role in the establishment or disruption of the hydrogen bonding scheme involved in the gel network is not well known.

It would be expected that any chemical species which contained functional groups that were available for hydrogen bonding could be used as a polar activator provided the species exhibited sufficient solubility in the base oil to interact with the surfaces of the clay platelets. Not all chemicals which have these functional groups and exhibit solvent compatibility appear to behave in the same manner as the more widely used polar activators. For example, several chemical additives have been examined which are effective dispersants of organoclays in oil, but play a minimal role in the gelling mechanism. These types of dispersants include glycols, aromatic ketones and nitrated alcohols. For example, when a glycol is added to a 7% (w/w) 2M2Ht organoclay/HVI oil during the formation of a pregel, a narrowing of the 1040 cm^{-1} IR clay band width is observed, signifying dispersion is occurring. Furthermore, this collapse of the IR clay band width is very similar in magnitude to that observed for an acetone activated pregel, signifying a similar degree of dispersion. The narrowing of the IR clay band width for

non-activated, acetone activated and glycol activated 7% (w/w) 2M2Ht organoclay/HVI oil systems is displayed in Fig. 3.

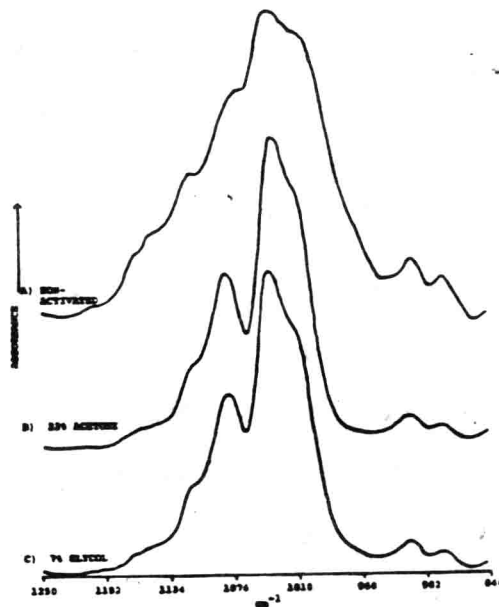


Figure 3 Infrared spectra of the Si-O-Si stretching region for a 7% (w/w) 2M2Ht organoclay/HVI oil system pregel: (A) non-activated, (B) activated with 22% acetone, and (C) activated with 7% glycol (the polar activator is based on the weight of the organoclay). The narrow band width observed in (C) indicates that the glycol has dispersed the organoclay.

A similar observation (Fig. 4) is noted for IR clay band widths after Tri-homo milling. In this case, the non-activated system has a slightly more narrow IR clay band width compared to the non-activated pregel IR clay band width because the extensive shear introduced by milling somewhat separates the clay platelet stacks.

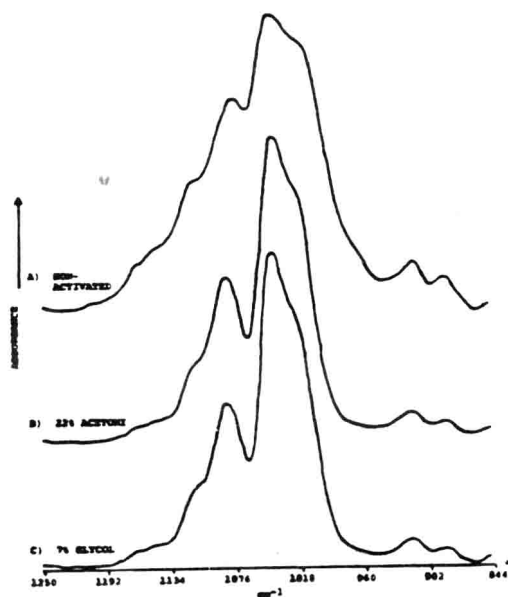


Figure 4 Infrared spectra of the Si-O-Si stretching region for a 7% (w/w) 2M2H organoclay/EVI oil system milled in the Tri-horn mill: (A) non-activated, (B) activated with 22% acetone, and (C) activated with 7% glycol (the 1 polar activator is based on the weight of the organoclay). The slight band width narrowing observed in (A) is due to a minor separation of the clay platelet stacks caused by the extensive mechanical shear employed.

Examination of the viscosity and penetration data, Table 1, for the systems displayed in Figures 3 and 4 clearly indicates that the glycol is an effective dispersant but is not a good gel promoter. One can conclude therefore that some chemicals are capable of simultaneously causing dispersion and participating in a network, i.e., polar activators, and others, such as glycols, are primarily dispersants and play a much less effective role in the network formation.

Table 1: 7% (w/w) 2M2Ht Organoclay/HVI Oil. Acetone versus Various Dispersants

Polar Activator ^a	Pregel		Milled Grease			IR Band Width
	Viscosity cP @ 5 RPM ^b	IR Band Width	Penetration			
			0	60	10K	
Non-activated	160	25.5	2100 cps ^b	--	--	22
Acetone (22.2%)	[284] ^c	15.5	201	230	242	15.5
Glycol (6.2%)	576	16.5	239	278	270	15.5

(a) % polar activator based on weight of organoclay

(b) Brookfield Viscosity (cps)

(c) Penetration Measurement

One of the ways to contrast the behavior of polar activators and dispersants is to study the role that water plays in grease systems. The question was posed that if a hydrogen bonding species such as water was added to a dispersed but not gelled system, would gelation occur? The choice of water was a logical selection since water is an excellent hydrogen bond former and gelation has been theorized to result from the formation of hydrogen-bond bridges between the edges of the clay platelets. Additionally, previous experiments demonstrated that when a milled 7% (w/w) 2M2Ht organoclay/HVI oil activated with 22% acetone (penetration = 278) was heated above 100°C to volatilize the polar activator, the grease quickly lost consistency. When 0.1% water was introduced to the grease, gelation rapidly occurred with hand mixing.

If water is added in a quantity of 0.1% (the % water based on the weight of the grease) to the organoclays dispersed with nitrated alcohols, glycols or aromatic ketones, grease consistencies are now obtained which are similar to those observed for an acetone activated system, Table 2. Thus, water

functions to promote gelation in dispersed systems in which the initial gel promoting agent has been volatilized or in systems where the dispersant itself does not adequately promote gelation.

Table 2: 7% (w/w) 2M2Ht Organoclay/HVI Oil; Acetone versus Various Dispersants + 0.1% Water

Polar Activator ^a	% H ₂ O ^b	Pregel		Milled Grease			
		Viscosity cP @ 5 RPM ^c	IR Band Width	Penetration			IR Band Width
				0	60	10K	
Non-activated	0.0	160	25.5	2100 cps ^c	--	--	22
Non-activated	0.1	200	25.5	410	431	--	18
Acetone (22.2%)	0.0	[284] ^d	15.5	201	230	242	15.5
Nitrated Alcohol (9.6%)	0.0	360	--	324	352	363	--
Nitrated Alcohol (9.6%)	0.1	2200	--	218	235	227	--
Aromatic Ketone (9.5%)	0.0	1360	--	280	319	340	--
Aromatic Ketone (9.5%)	0.1	15200	--	208	222	232	--
Glycol (6.2%)	0.0	576	16.5	239	278	270	15.5
Glycol (6.2%)	0.1	1304	16.5	208	224	209	15.5

(a) % Polar activator based on weight of organoclay

(b) % Water based on weight of grease

(c) Brookfield Viscosity (cps)

(d) Penetration

It remained to be determined if water also contributes to organoclay dispersion. If 0.1% water is added to a 7% (w/w) 2M2Ht organoclay/HVI oil system, the IR clay band width of the pregel sample is identical to the non-activated 7% (w/w) 2M2Ht organoclay/HVI oil species. Similarly, pregel viscosity for the 7% (w/w) 2M2Ht organoclay/HVI oil with 0.1% water is comparable to the non-activated species (Table 2). Thus, although water is an effective gelation promoter, water does not appear to cause dispersion.

Comparison of greases milled in the Tri-homo mill is somewhat more complicated. A milled 7% (w/w) 2M2Ht organoclay/HVI oil with 0.1% water exhibits some narrowing of the IR clay band width and viscosity build over the unactivated 7% (w/w) 2M2Ht organoclay/HVI oil. This is not unexpected since extensive milling alone breaks apart the organoclay platelet stacks to a limited degree. Extensive milling may also force water/organoclay interaction leading to some organoclay dispersion. In no case, however, is the degree of dispersion caused by water the same as that achieved by other polar activators. From these results, it appears that water functions primarily as a key participant in the gelation mechanism and not as a dispersant.

A general conclusion can now be made for 2M2Ht organoclay/HVI oil systems. First, some chemicals function simultaneously as dispersants and network participants, others as dispersants only and a third group as network participants only.

The role of water as a dispersant of organoclays in other fluid systems cannot be discounted. The insolubility of water in HVI oil may cause it to be ineffective in this matrix since it cannot effectively bind to the surface of the clay and lead to increased spacing of the platelets. Also note that a very small amount of water (i.e., 0.1% based on the weight of grease) causes gelation but the level employed is far below that required of polar activators (i.e., 2-3% acetone based on the weight of the grease) for dispersion purposes.

One extremely important point to note is that commercial polar activators which appear to function well as dispersants and gelation promoters, such as acetone, ethanol, and methanol, contain small amounts of water, approximately 3.4%, 5%, and 5% water, respectively. It is known in the industry that propylene carbonate does not function well in this role without additional

water. An area for future studies could be to examine the dispersion/gelation promoting behavior of anhydrous acetone, ethanol, and methanol. One could postulate that these "polar activators" in the anhydrous form are actually only dispersants.

Shear Sensitivity

Once an organoclay is completely dispersed in a base fluid, the measured penetration values after working are a direct reflection of the shear sensitivity of the system. For example, consider a 7% w/w 2M2Ht organoclay activated with 16.4% nitrated alcohol (% activator based on the weight of the organoclay) in HVI oil. Although mechanical stability is poor for this particular grease, there is almost no change in the consistency profile for the organoclay grease when the grease is remilled in the Tri-homo mill, Table 3. The reproducibility of the consistency profiles indicate that the organoclay was completely dispersed after one pass through the Tri-homo mill. With the dispersion variable eliminated, attention can be focused on the shear sensitivity characteristics of the organoclay grease. The laminar shear of the grease worker causes the platelets to align resulting in grease softening. The turbulent shear of the Tri-homo mill restores the random orientation of the platelets resulting in grease hardening.

Table 3: Penetration Measurements for a 7% (w/w) 2M2Ht Organoclay/HVI Oil with 16.4% Nitrated Alcohol.

	Penetration			Δ	(10K-60)
	0	60	10K		
Milled	220	280	350	70	
Worked 10K, Remilled	216	280	337	57	