ORGANOPHILIC CLAY-BASE THICKENERS

by

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ABSTRACT

The clay minerals, generally characterized by their small particle size, affinity for water, and response to chemical changes in their environment, are noted for their gelling and viscosity-increasing abilities in aqueous systems. Rendered organophilic by association with long-chain organic compounds, several of the clay minerals exhibit similar or even greater gelling abilities in various organic liquids.

Methods of preparing organophilic clays are discussed and data shown for ion exchange reactions between long-chain organic cations and montmorillonite minerals. Properties of modified clays in various liquid systems are illustrated, and industrial applications are cited.

INTRODUCTION

Lipsticks, you do not have to be told, are expensive grease paints which stain ladies' lips various shades of red (also green, purple, black, and sometimes gold and silver) on a more or less temporary basis. They also stain shirts, neckties, and handkerchiefs on a more or less permanent basis. Lipsticks vary chiefly as to the amount and types of dyes used and the nature of the solvent. You will probably be as alarmed as the writer was to find that historically the basic solvent for lipsticks has been castor oil. It is a shame that a man has to go through a large part of his life ignorant of the fact that there is such a pleasant way to take castor oil. Going from the sublime to the ridiculous, it is perhaps as little known that many of today's lipsticks also contain an organophilic clay-base thickener, added to provide body and to reduce the effect of elevated temperatures.

Until a relatively few years ago the building of viscosity in organic liquids was generally accomplished through use of soaps. During the same period, aqueous systems usually were thickened with inorganic materials, notably montmorillonite clay minerals. Over the past ten years there has been somewhat of a reversal in this with gums, alginates, cellulosics, and polyacrylates being used for viscosity build-up in water, and surface treated inorganic materials replacing some of the soaps in oils, solvents, and other organic liquids.

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SURFACE TREATING METHODS

A rather wide variety of surface treatments is followed in building the inorganic gelling agents. However, in restricting this discussion to the clay minerals, the technique of esterification, as applied to silica (Iler, 1953) and as proposed by Berger (1941), Deuel, Huber and Iberg (1950) and Deuel and Huber (1951), appears to be off limits for the clays (Brown, Greene-Kelley and Norrish, 1952). Ion exchange (Jordan, 1949; Hauser, 1950) has long been a useful route to follow, and long-chain organic cations have been substituted for the inorganic cations originally associated with montmorillonite, hectorite, attapulgite, and others. More recently advantage has been taken of well recognized adsorptive capabilities of the clay minerals in masking their hydrophilic nature, saturating their cohesive energy, and separating the individual laminae and thereby rendering them dispersible in low energy organic liquids (Haden and Martin, 1958; Clem, 1958). Various methods have been described for accomplishing these end results. Dispersion of clay in water, followed by adsorption of, or ion exchange with, organic surfactants, followed by direct flushing into the desired organic liquid is practiced on an industrial scale (Peterson, 1952). Clem (1961) proposes mixing dry clay with molten surfactant. At the present time the only clay base gelling agents offered industrially as dry powdered products are manufactured by an aqueous ion-exchange process (Hauser, 1950).

IONIC ENVIRONMENT AND REACTION KINETICS

Some information exists in the technical literature on the energetics of adsorption by clay minerals. A portion of this deals with adsorption of inorganics such as nitrogen, although organics have come in for attention, particularly by the catalyst groups. Slabaugh (1954) and Slabaugh and Kupka (1958) have shown that the ion exchange reaction between montmorillonite and fatty amine salts involves an appreciable energy change. The interaction of amine salts with bentonite in an aqueous system no doubt is favored by the formation of an "insoluble" hydrophobic product. Thus McAtee (1959), working in these laboratories, has shown that the monovalent organic ammonium ion quantitatively replaces sodium ion in this reaction (Fig. 1). However, divalent calcium is replaced less readily, and an excess of the organic ion is needed to complete the reaction and effectively saturate the exchange sites (Fig. 2). By converting sodium–calcium montmorillonite to the sodium salt prior to reaction complete exchange can be carried out on a stoichiometric basis (Jordan, 1960). Fig. 3 illustrates this in terms of apparent base exchange capacity of sodium montmorillonite for an organic ammonium ion in the presence of increasing concentrations of calcium ion. Apparent exchange capacity in this case is taken as the point at which the surface tension of the system shows a marked drop on a Cenco–duNouy tensiometer while the montmorillonite dispersion is being titrated with a cationic surfactant (dimethylbenzyllaurylammonium chloride).

McAtee (1963) has taken a further step and demonstrated a replacement of one ionic organic species by another on an organic ammonium montmorillonite dispersed in an organic liquid medium. The extent of this exchange appears relatively slight, and it is probable that the energy changes involved are low.
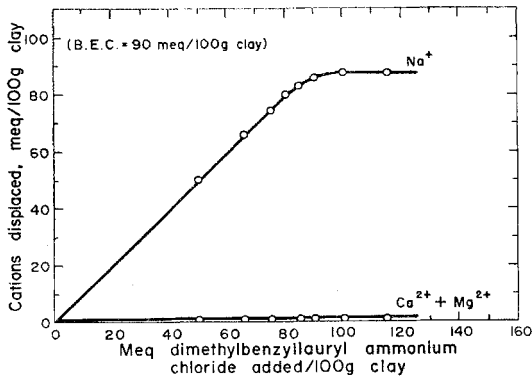
FIGURE 1.—Dimethylbenzyllauryl ammonium chloride added to homoionic Wyoming sodium bentonite.
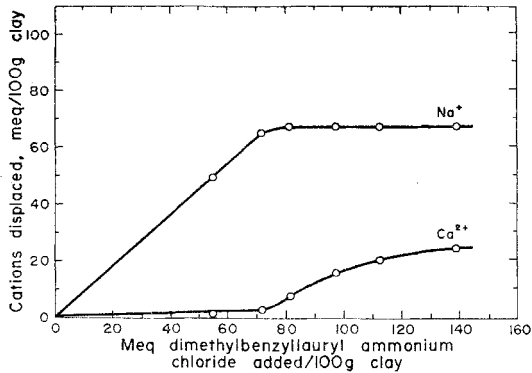
FIGURE 2.—Dimethylbenzyllauryl ammonium chloride added to centrifuged Wyoming bentonite.

Even with materials prepared under ideal conditions, including pre-conversion of bentonite to sodium montmorillonite prior to exchange with organic cations, a small proportion of organic material can be removed by extraction techniques. Starting with the dimethyldioctadecylammonium complex a low polarity solvent, n-hexane, will remove up to 4 meq/100 g, while a high polarity liquid, isopropanol, will remove 10 to 12 additional
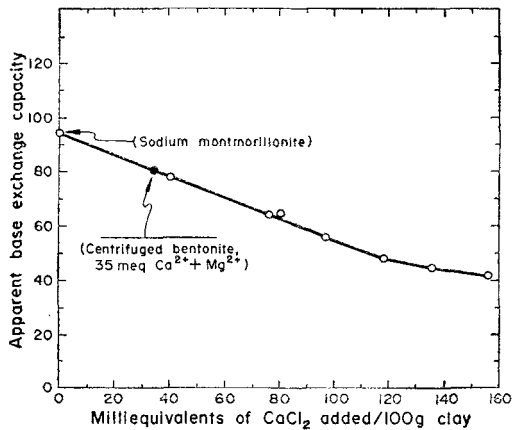
Figure 3.—Exchange capacity by surface tension method. Effect of divalent cations on the apparent exchange capacity of montmorillonite for dimethylbenzyllauryl-ammonium ion as observed from surface tension titrations.
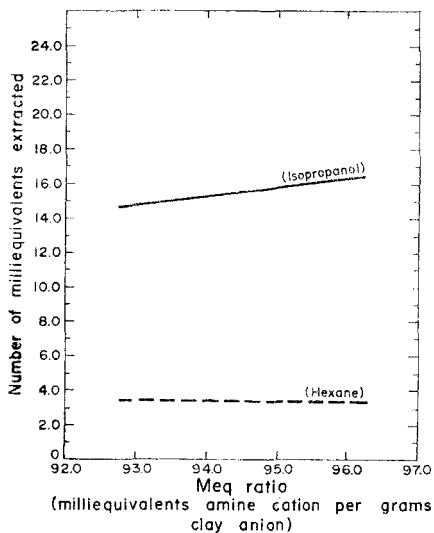

Figure 4.—Equilibrium soxhlet extraction of dimethyldioctadecylammonium mont-morillonite. Relationships between original meq ratio and milliequivalents of organic cation extracted by a low polarity and a high polarity solvent.
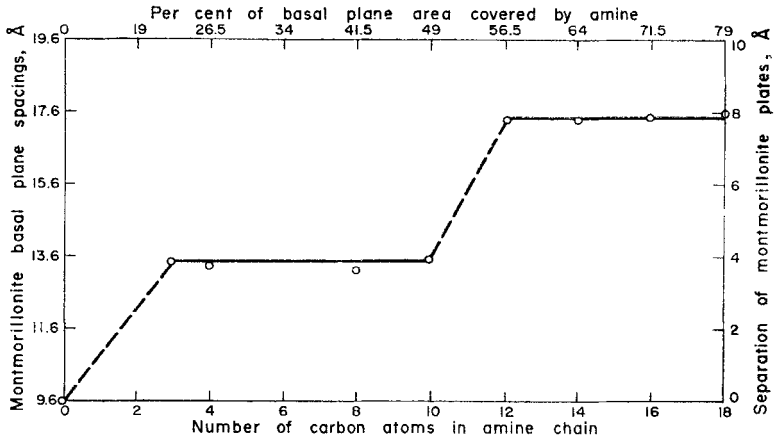
FIGURE 5.—Effect of amine chain length on montmorillonite basal plane spacings.
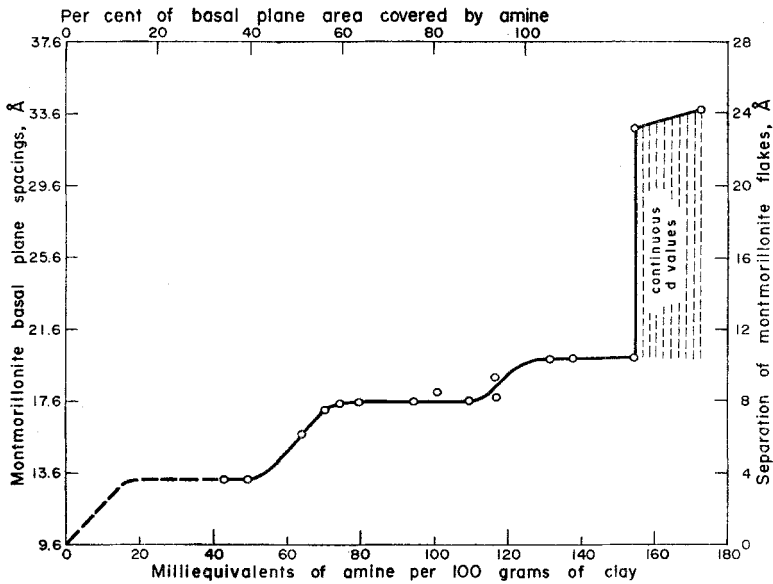
FIGURE 6.—Effect of increasing ratio of octadecylammonium ion to montmorillonite upon basal plane spacings.

milliequivalents (Fig. 4). No energy data are available for this; it may be that the extracted material represents principally adsorbed molecules that were sterically hindered from access to exchange sites toward the end of the reaction period. The alternative suggestion has been made that reaction energies diminish as the negative charges of the clay lattice become progressively neutralized, and that a minor proportion of organic cations will be removable with low energy solvents. In contrast an organophilic montmorillonite treated with a nonreactive coating can be separated to a much greater extent into its original components by similar extraction procedures. For example, equilibrium soxhlet extraction with isopropanol of an adsorption complex comprising 61.0 percent Wyoming bentonite and 39.0 percent stearic acid removed 79 percent or approximately four-fifths of the stearic acid.

The location of organic surfactant on planar surfaces has been described (Gieseking, 1939; Hendricks, 1941; Erbring and Lehmann, 1944). Occupation of interlaminar surfaces as a function of organic chain length is straightforward (Jordan, 1949). Figure 5 demonstrates the stepwise separation of montmorillonite laminae as alkylammonium salts of increasing chain length are reacted by ion exchange with sodium montmorillonite at full exchange saturation. If we stick to one molecular species and vary the ratio of organic to clay mineral the spacing again varies in an orderly fashion (Jordan, Hook and Finlayson, 1950). Figure 6 shows the stepwise change in spacing which follows the addition to sodium montmorillonite of increasing amounts of octadecylammonium chloride up to double the exchange capacity. Orientation of organic matter on clay surfaces progresses from a horizontal position of the zigzag chains (4 Å effective thickness) to a position in which the chains are lying on edge (5 Å effective thickness) to the final stage in which the organic chains are crowded into an upright position (23–24 Å).

INDUSTRIAL APPLICATION

Widespread industrial application has been made of surface-treated clays. A mere summary of distinctly different end uses runs into several dozens and includes such things as lubricating greases, paints, putties, gelled paint removers, printing inks, plastisols, epoxy resins, potting compounds, rubber, waterless foundry sands, and oil base drilling fluids. Many of these applications take advantage of the ability of treated clays to form thixotropic gels in organic liquids. In a typical paint formulation the apparent viscosity imparted by dimethyldioctadecylammonium montmorillonite depends upon the rate of shear of the instrument used in making the observation. Thus a thixotropic index can be determined for a gelling agent based upon area bounded by a curve (Fig. 7). Various types of "loop" can be obtained depending on the nature of the gelling agent.

Gelling mechanisms have come in for much discussion. It appears likely that dispersion in low energy organic liquids depends upon reduction of the cohesive forces between clay flakes or particles by the physical separation
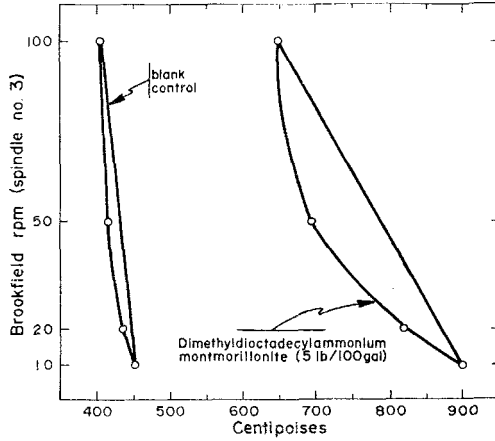
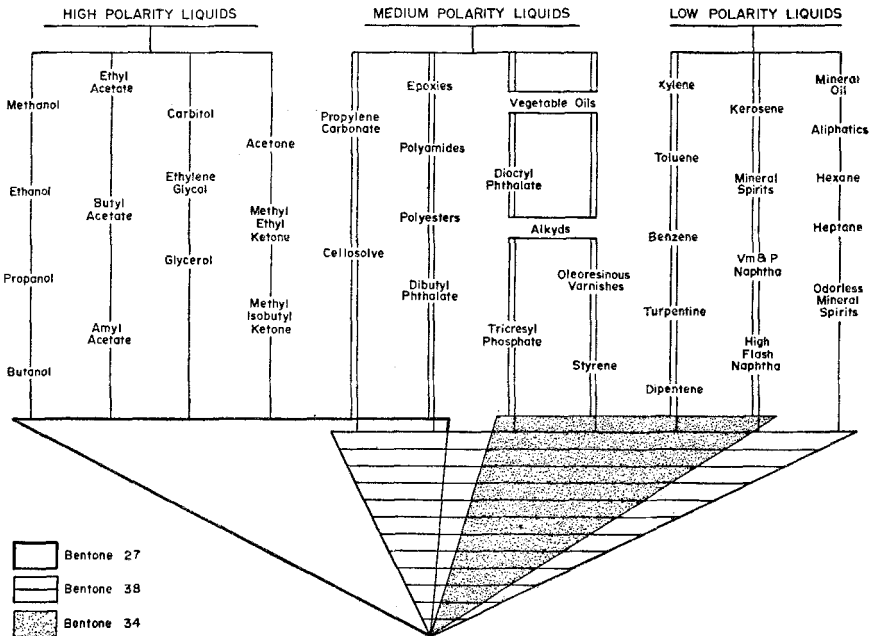FIGURE 7.—Brookfield viscosities of semi-gloss alkyd enamels.

FIGURE 8.—Bentone gellant selection fan.

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occasioned by the presence of surfactant molecules. Gel structure is then built up by edge to edge or edge to face interactions, or both, between flakes or particles. Damerell (1956a; 1956b) pictures water bridges between flakes, these bridges depending upon hydrogen bonding for their existence. The picture deserves considerable credence, because such gel systems can be broken down rather completely by elimination of the last traces of water, providing all other bridging agents, organic or inorganic, are absent.

A partial listing (*Handbook on "Bentone Gellants"*, 1960) of applications of surface-treated clays follows:

Lubricating greases
Exterior primers
Exterior topcoats
Shake and shingle paints
Sash and trim paints
Wall primer-sealers
Interior enamels
Enamel undercoaters
Interior flats
Interior flats of low solids content
Thixotropic stipple paints
Multicolor finishes
Water-based metal protective primers
Light metal alloy primers
Complete vinyl metal protective paint system
Two-package wash primers
Intermediate vinyl anti-corrosive paint
Vinyl topcoat
Vinyl anti-fouling paint
Synthetic resin adhesives
Epoxy resins
Hydraulic fluids
Drawing compounds
Buffing and cutting compounds
Colors-in-oil
Silk-screen printing inks
Ball point pen ink
Pencil lead
Shoe dressings
Polishes and cleaners
Plastic foams
Textile lubricants

Rubber-base paints (solvent type)
Finishes based on chlorosulfonated polyethylene
Asphalt paints
Flatted clear finishes
Pigmented lacquers
Traffic paints
Maintenance paints
Interior wood stains
Exterior wood stains
Epoxy finishes
Baking finishes
Polyurethane finishes
Polyester finishes
Putty
Caulking compounds
Wood fillers
Printing inks (non-misting)
Plastisols
Organosols
Emulsion systems
Gas chromatography
Transformer potting compounds
Lipsticks
Cosmetic creams
Pharmaceutical ointments
Wood-treating pastes
Oil base and oil emulsion well drilling fluids
Waterless foundry sand bonding agents
Modeling clays
Wax crayons

Figure 8 illustrates the rather wide applicability of one group of organophilic clays to the gelling of various organic liquids.

CONCLUSIONS

Surface coating of the clay minerals montmorillonite, hectorite, and attapulgite with polar organic molecules renders them organophilic and capable of gelling various organic liquids. Although coating may be achieved

by ion exchange techniques or by adsorption, the ion-exchanged coating appears to be more tenacious than the adsorbed type in organic liquids. X-ray diffraction data indicate regular interlamellar distribution of alkyl-ammonium cations reacted with montmorillonite by ion exchange. The thixotropic gelation achieved by alkylammonium montmorillonites is widely applied to diverse industrial usages.

ACKNOWLEDGMENT

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