THE COLLOID SCIENCE OF IMPORTANT CLAY MINERALS

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INTRODUCTION

A few days after Dr. Rudolf Wegscheider of the University of Vienna celebrated his sixtieth birthday in October, 1919, he began his next class with the following words:

> "Today I intend to start discussing with you the physico- and colloid-chemistry of the element silicon. It is not only the most abundant of all the nonmetallic solid elements which occur on this earth, but it is also, in combination with other elements, by far the most widely distributed one, with the exception of oxygen. Its only real competitor in this respect is the element carbon. Carbon differs from silicon above all by its property of combining with itself, thereby forming a great variety of compounds. With our increasing knowledge of the chemical composition of these carbon compounds the foundation for organic chemistry was laid. Science is never at a standstill, however. I refer here to physico-chemistry and to the even more recent addition to the specialized branches of chemistry, colloid chemistry.
>
> "I probably will not live to witness the importance that the colloid chemistry of siliceous matter will play in the not too distant future. In my opinion the physico- and colloid-chemistry of matter containing silicon as its major component will become a serious competitor to organic chemistry."

Our knowledge of the properties of siliceous matter has been tremendously enlarged during the last thirty years. This was possible only after it was realized that knowledge of the chemical composition of matter alone is insufficient information if it is present in the colloidal range of dimensions. In this connection it might be added that the term *colloid science* is now used, since *colloid chemistry* is inadequate to explain all the phenomena involved in colloidal research.

ULTRA- AND ELECTRON MICROSCOPY OF CLAY MINERALS

Ultramicroscopic and, whenever possible, electron microscopic investigations of clay minerals are essential in order to evaluate their morphology.

Figure 1 diagrammatically represents the Ultropak microscope; this instrument must be considered today as being unquestionably the most appropriate for studies up to a magnification of 2,000X. It offers the great advantage of revealing an ultramicroscopic picture even if the substance investigated is of comparatively coarse structure. In this respect the Ultropak differs from any other type of ultramicroscope, due to its lens construction, and is therefore also superior to the electron microscope for this type

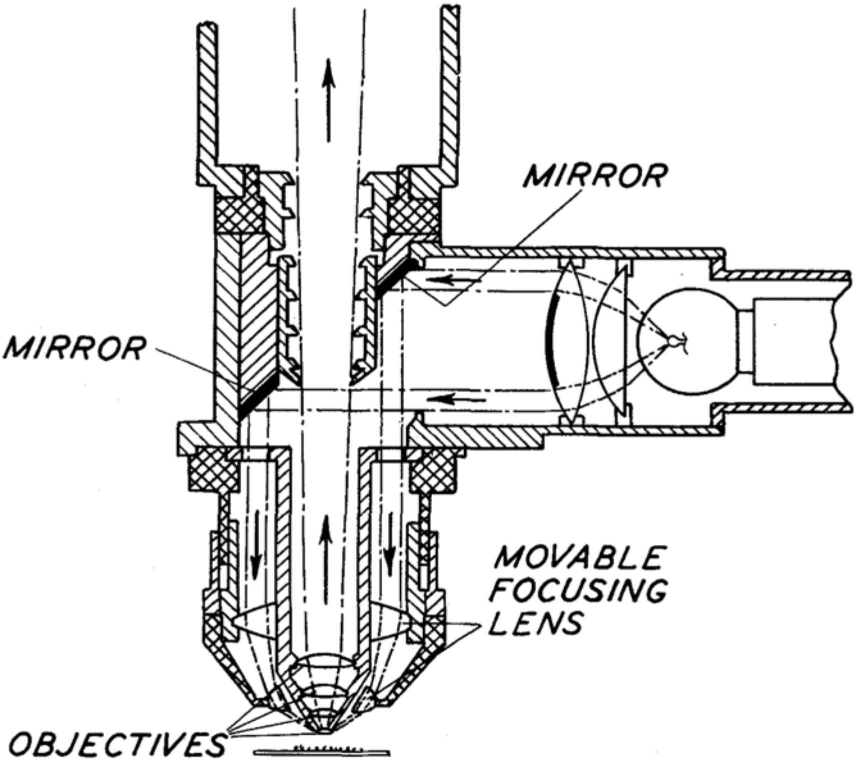


Figure 1.—The Ultropak microscope (Leitz). The light enters the microscope as an illuminating circle and is reflected down onto the preparation at an angle of 45° by a mirror located in its path through the movable focussing lenses. The circular light is then reflected from the preparation and passes through the objective of the microscope directly into the eyepiece or photographic instrument.

of work unless very high magnifications are needed. Ultraphotomicrographs may be made easily by the use of a "Mifilmca" attachment to a Leica camera casing, using the microscope eyepiece as the lens.

Samples of gibbsite reveal a structure as shown in Figure 2. The other basic constituent of all clay minerals which contain a high percentage of magnesium is brucite; Figure 3 offers an example of this product. Figure 4 is an electron micrograph of halloysite and Figure 5 shows kaolin. Figure 6 represents an electron micrograph of dickite. When studying illite we find that the electron microscope shows us a very irregular structure, and this becomes particularly noticeable when the preparation is shadowed, as is the case in Figure 7. Allophane is always found in an amorphous condition with particles which exhibit no definite or regular shape (Fig. 8). Attapulgite exhibits a fibrous structure, shown in the electron micrograph, Figure 9. Even in the electron microscope Wyoming sodium bentonite appears

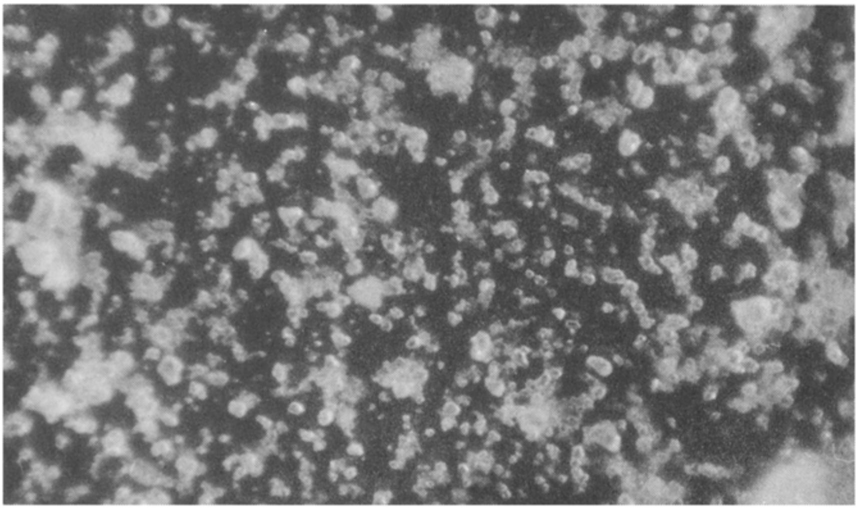


FIGURE 2. — The clay mineral gibbsite. Original magnification 550.

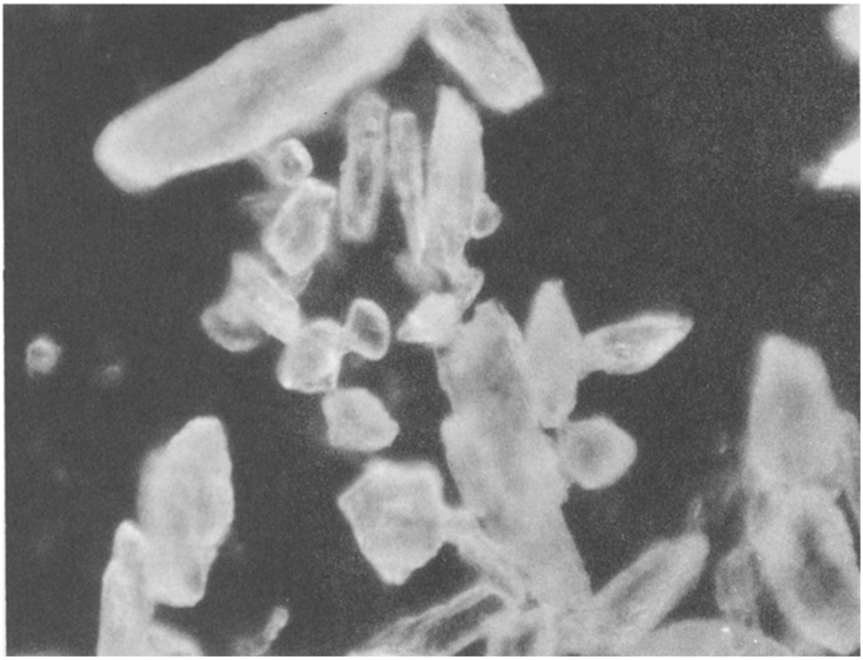


FIGURE 3. — The clay mineral brucite. Original magnification 550.

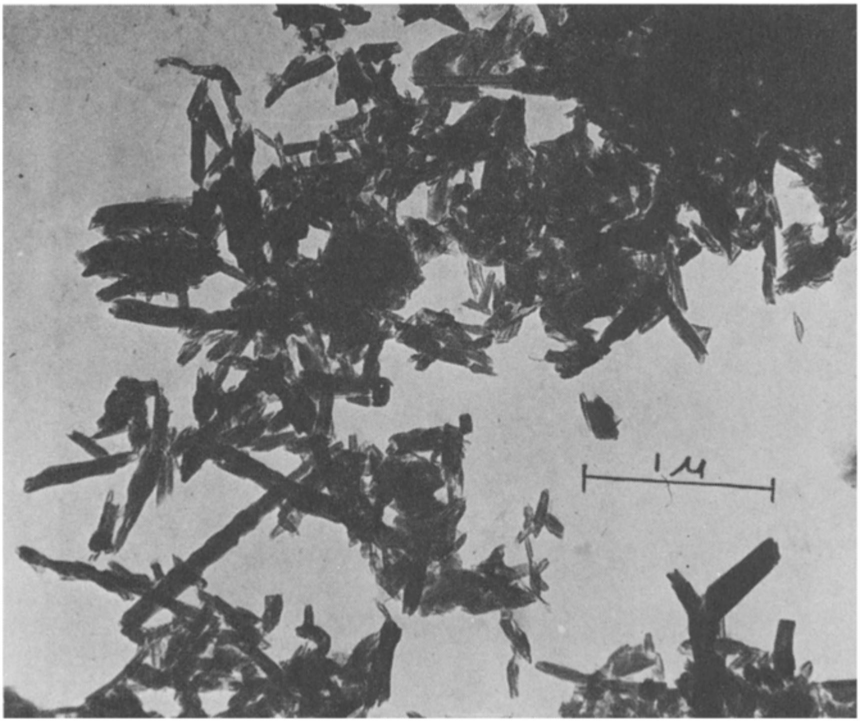


FIGURE 4. — Electron micrograph of the clay mineral halloysite ($4H_2O$) (Gardner Mine Ridge, Indiana). Magnification 35,700.

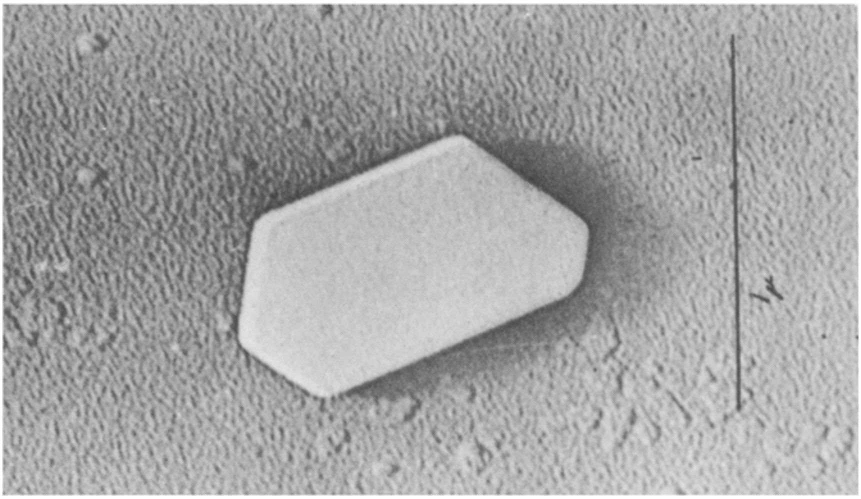


FIGURE 5. — Electron micrograph of a single kaolin crystal (shadow technique). Magnification approximately 10,000.

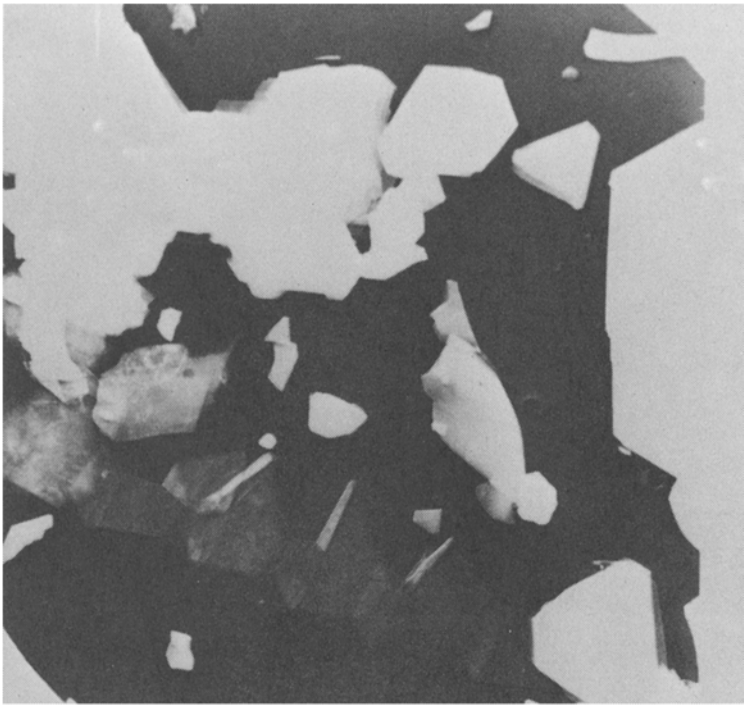


FIGURE 6. — Electron micrograph of the clay mineral dickite (San Juanito, Mexico). Original magnification 10,000.

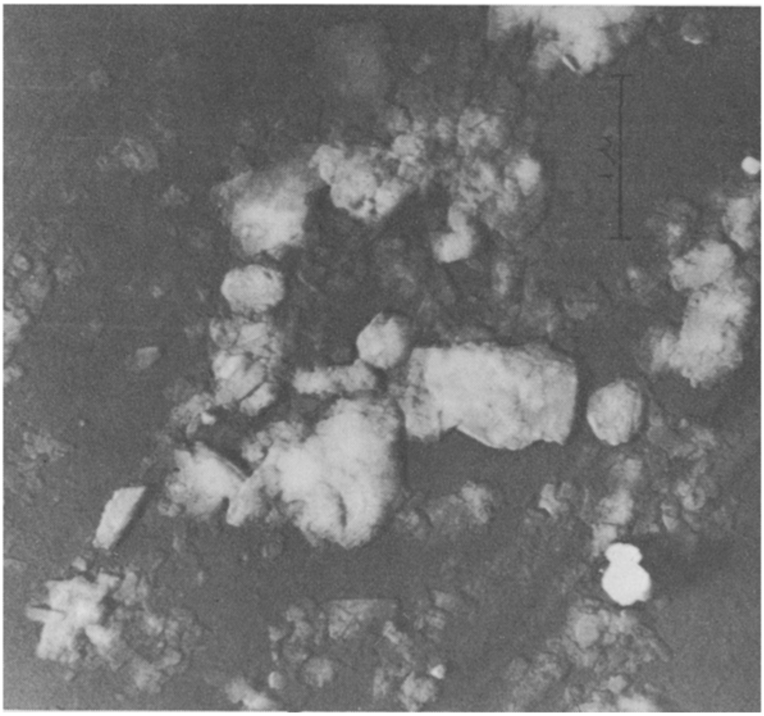


FIGURE 7. — Electron micrograph of the clay mineral illite (Morris, Illinois) (shadowed at 15°). Aggregation is clearly evident. Original magnification 40,800.

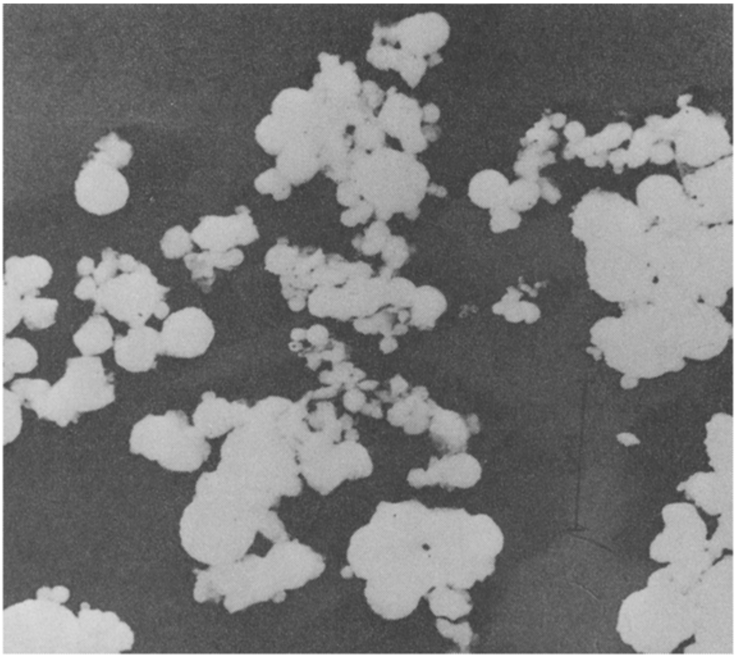


FIGURE 8. — Electron micrograph of the clay mineral allophane (Gardner Mine Ridge, Lawrence County, Indiana) (shadowed at 30°). The shape of the individual particles indicates that we deal here with an amorphous aluminum silicate. The aggregates have assumed a distinctive rounded form.

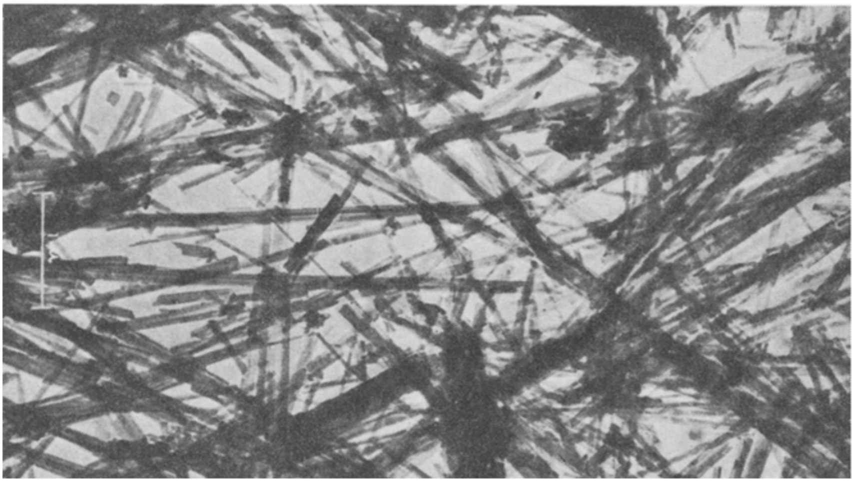


FIGURE 9. — Electron micrograph of the clay mineral attapulgite (Attapulgus, Georgia). Rods showing pronounced overlapping. Original magnification 25,000.

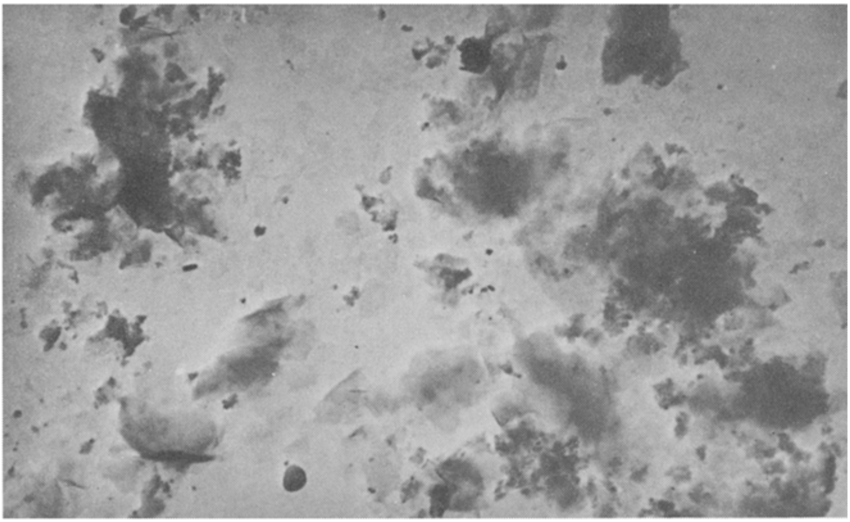


FIGURE 10. — Electron micrograph of the clay mineral bentonite (Wyoming). Original magnification 10,100.

as a very thin structure which does not permit too clear a representation (Fig. 10). In the electron microscope a true montmorillonite reveals the structure shown in Figure 11. Calcium bentonites show a pronounced difference in their structure as compared with sodium bentonites; a sample from Fayette County, Texas (Cherry Lease composite), is shown in the electron micrograph, Figure 12.

THE COMPOSITION AND STRUCTURE OF COLLOIDAL CLAYS

On the basis of laws applying only to fully ionizable simple inorganic salts, attempts have been made to classify all silicates as salts of various silicic acids. This approach can be only speculative, however, since none of the acids has ever been isolated and attempts to synthesize them have failed. Another approach has been based on laws of organic chemistry, since silicon, like carbon, belongs to Group IV of the Periodic Table. Silicon differs from carbon in many important respects, however. It is usually tetra-covalent, but since it lies in the second short period its maximum covalency is six, not four. Although silicon remains tetravalent like carbon in its organic compounds, its pronounced electropositive nature and its hexa-covalency cause vigorous reactions not found in analogous carbon compounds.

The introduction of infrared spectroscopy, X-ray diffraction studies, and differential thermal analysis have enabled the colloid scientist to evaluate the structure of siliceous matter in detail.

Infrared spectroscopy has permitted us to estimate the ratio of the ionic

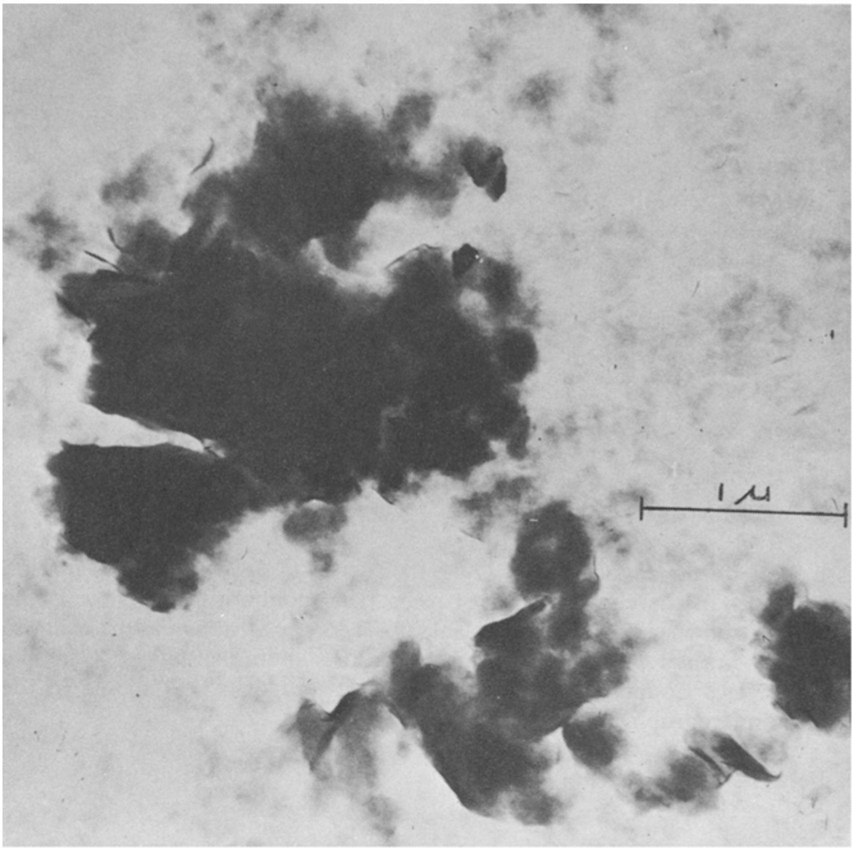


FIGURE 11. — Electron micrograph of the clay mineral montmorillonite (Combe Hay, England). Original magnification 35,700.

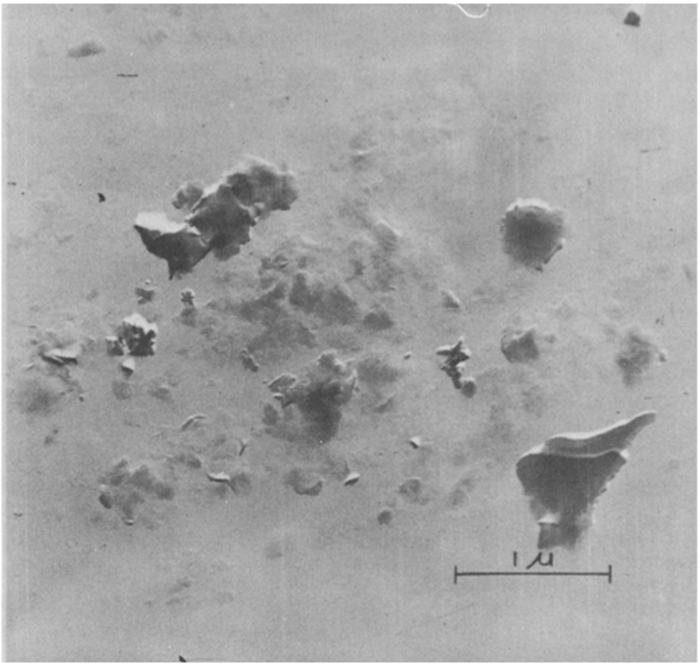


FIGURE 12. — Electron micrograph of calcium bentonite (Fayette County, Cherry Lease, Texas). Mounted dry, shadowed at 45°. Original magnification 10,100.

character of the Si-O bond to be 2.3 times that of the C-O bond. The relationship between the difference in electro-negativity and the percent ionic character has also substantiated this finding since it amounts to 51 percent for the Si-O bond, whereas it is only 22 percent for the C-O bond, a ratio of 51 to 22, or 2.3 to 1.

X-ray diffraction studies of innumerable silicates have made it clear that their basic building block is a tetrahedron with silicon in the center and four oxygen atoms at its corners. The Si-O distance has been evaluated as being about 1.6 Å and the O-O distance as about 2.6 Å (Fig. 13). The structures of the various silicates are based only on different combinations of the tetrahedral silicon-oxygen groups.

The most important clay minerals are built up from the silica sheet and the brucite or gibbsite sheets by condensation (Fig. 14). Two general possibilities exist: One of each may combine, or the gibbsite or brucite layer may be sandwiched between two silica sheets. One clay mineral does not fit into either of these groups, however; this is halloysite. The existence of sufficient data showing that halloysite is not of homogeneous structure has been overlooked so far, apparently. These data show that it is composed of units held together only by van der Waals' forces and varying from definite alignment to random orientation.

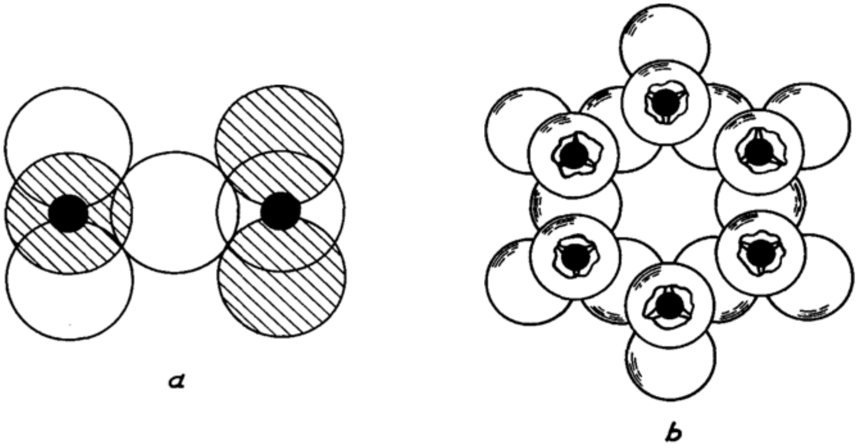


FIGURE 13. — Silicon-oxygen groupings (schematic). (a) Trisilicate $(Si_2O_7)^{6-}$. Three of the oxygen atoms have been hatched so that their location is clearly visible. (b) Hexasilicate $(Si_8O_{16})^{12-}$. The top oxygen atoms have been opened up to show the location of the silicon atoms.

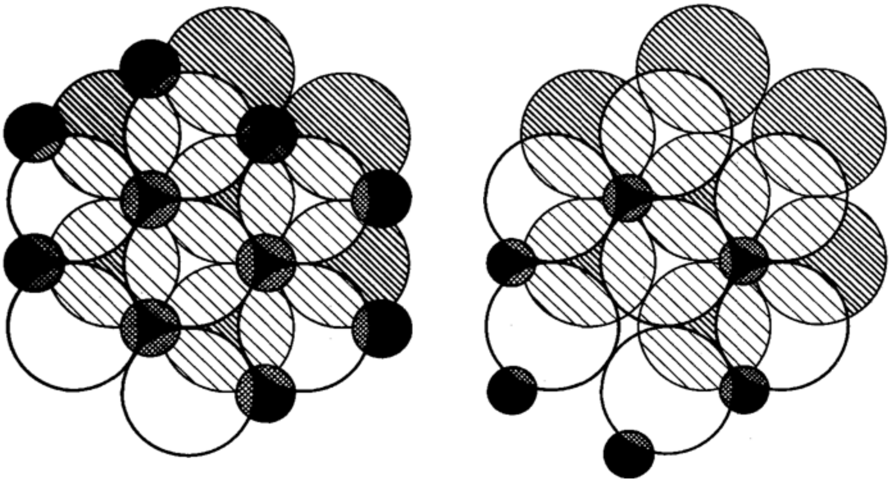


FIGURE 14. — Basic clay mineral constituents (schematic). Left, brucite, $Mg(OH)_2$. The magnesium atoms sandwiched between the two staggered layers of hydroxyl groups are now clearly visible. Right, gibbsite, $Al(OH)_3$. The hydroxyl groups in the top layer have been drawn transparent to show the location of aluminum atoms sandwiched between the two staggered layers.

In the montmorillonite group the mineral montmorillonite is most common. It consists of a gibbsite sheet sandwiched between two sheets of tetrahedral silica sheets, the individual units being held together only loosely in the direction of the c-axis with water in between (Fig. 15). Such a structure is balanced and therefore cannot explain many colloidal properties exhibited by bentonites. More recently a change in this structure has been suggested according to which every other tetrahedron of the silica sheet is inverted. In this way the previous O-position is taken up by a hydroxyl group, which would result in an unbalanced structure. The formula for the silica sheet would then be $O_2Si_4O_6(OH)^-$ and for the whole mineral $(OH)_{12}Al_4Si_4O_{16}\cdot nH_2O$. However, this theory is also unable to account for many of the colloidal properties for which montmorillonite is best known. The true montmorillonite which was originally discovered by G. Salvetat at Montmorillon, France, contains a fair amount of calcium. It has not yet been taken into sufficient consideration, however, that those bentonites exhibiting high swelling and base-exchange properties are never of the ideal composition mentioned for montmorillonites. Variations of the Al-to-Si ratio occur when some of the aluminum ions in the gibbsite layer have been replaced by magnesium (Fig. 16). Some of the Si^{++++} positions in the silica sheets may be replaced by Al^{+++}. If all the aluminum ions in the gibbsite layer in an ideal montmorillonite structure have been replaced by iron, the clay mineral nontronite is the result. Illite is similar to mont-

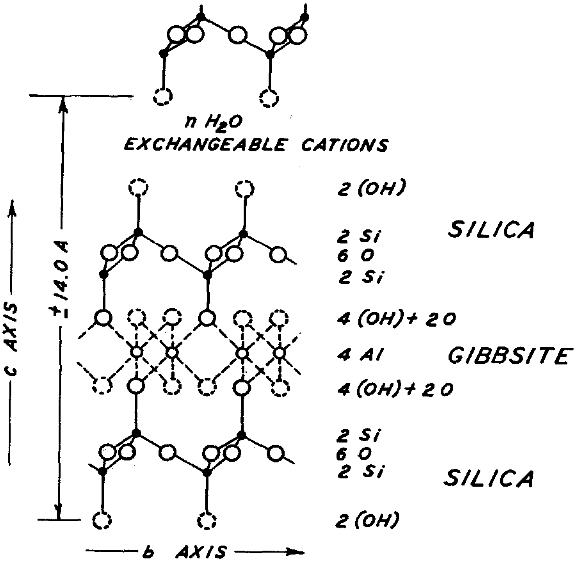
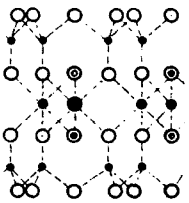


Figure 15. — Montmorillonite (schematic). A pure gibbsite layer is located in the center and no ions of lower valency than aluminum are present. The exchangeable cations depend exclusively on the unbalanced condition of the OH ions located in the surface of the colloidal crystal.



6 O	-12
4 Si	+16
4 O + 2 OH	-10
3 Al + 1 Mg	+11
4 O + 2 OH	-10
4 Si	+16
6 O	-12

• - Si
● - Al, Fe^{+++}
⬤ - Mg
○ - O
◉ - OH
● - K

FIGURE 16. — Substituted montmorillonite (bentonite) (schematic). This drawing shows the replacement of one aluminum ion by one magnesium ion in the gibbsite layer. For this reason the crystal lattice is chemically unbalanced and will therefore tend to adsorb cations as counterions.

morillonite except that about 15 percent of the silicon positions have been replaced by aluminum ions, resulting in a particle with an excess of negative charges which are compensated by K^+ ions. As in muscovite, the K^+ ions act as bridges or bonds between the silica sheets of two successive layers. The number of K^+ ions needed for neutralization is proportionally greater than in muscovite because of the larger amount of substitution of Si by Al. Furthermore, it has also been found that Mg^{++} and Fe^{+++} have been substituted for Al^{+++} in the illite lattice, but never in the muscovite lattice.

FORMATION OF CLAY MINERALS

It has been shown that montmorillonite can be produced by subjecting glass as well as a natural obsidian to high-temperature and high-pressure treatment. A devitrification phenomenon occurs whereby the alumina and silica groups are rearranged to give a crystalline structure. The alteration of the pure silica and aluminum to kaolinite or montmorillonite is therefore most probably a combination of the chemical reactions attendant upon leaching and a devitrification of the glass, the reaction then proceeding through a hydration and adsorption of ions.

Clays owe their genesis to the presence of silica and alumina or magnesia gels and the changes these undergo with time and/or temperature. Another fact which has only recently found the attention it deserves is that in spite of the inertness of most siliceous matter, the chemical reactivity of the silica surface surpasses that of most stable oxides. Systematic research on the surface chemistry of silicates has led to the discovery of unexpected chemical reactions which result from the dehydration or polymerization of silicic acid. Most important of all is the release of atomic oxygen even at room temperature and the fixation of nitrogen as ammonia at temperatures between 250° C and 350° C.

THEORIES OF GELATION AND GEL STRUCTURE

The latest theories on gelation and related phenomena are based on the application of potential energy curves. As long as potential repulsive forces only are involved, the energy will rise with decreasing distance; *e.g.,* whenever particles come into actual contact with each other, the energy will rise very pronouncedly due to strong elastic forces which prevent the particles from interpenetrating one another. A set of potential curves is shown in Figure 17. Interesting phenomena may be expected during a change which gradually carries a system represented by a curve of type R over into one represented by a curve of type A. On the same basis, however, the role of attractive and repulsive forces can also be interchanged. If we are dealing with a system in which both attractive and repulsive forces are active, then such a curve may also represent the superposition of a repulsion and an attraction.

THE CLAY PARTICLE — A COLLOIDAL MICELLE

According to a suggestion by J. Duclaux, the individual colloidal particle in a disperse system consisting of a charged solid nucleus surrounded by a diffuse ionic atmosphere is termed a colloidal micelle.

Electric charge, or the electrokinetic potential, and solvation are the predominant factors governing the stability of colloidal sols. The electrical forces associated with a given colloidal particle in electrolytic media arise from two sources. One set of forces arises either from the ions predominantly of one sign, which are rigidly adsorbed on the surface of the particle, or from those ions located in the surface which are not fully saturated. It

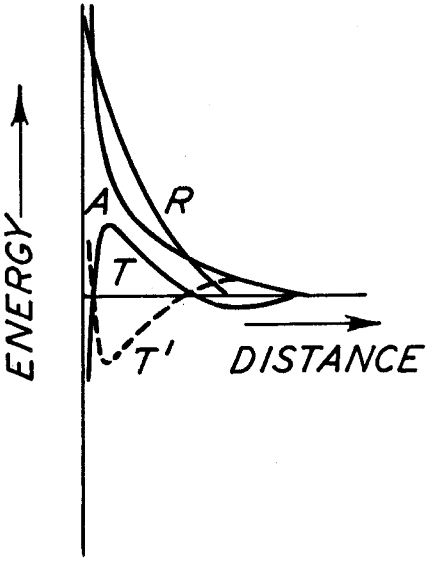


Figure 17. — Potential energy curves. Curve T represents a summation of Curves A and R; Curve T′ corresponds to the reverse. In the first case the phenomenon of thixotropy is represented. In the second case coagulation results.

is also possible, as is the case with some montmorillonites, that the colloidal particle carries a net negative charge due to an unbalance in its crystal lattice. The other source arises from the ions of opposite sign which gather about the particle in an effort to neutralize the charge which the particle carries. Since the colloidal particles in a stable sol possess a net charge, the total number of ions that gather about the particle are not sufficient to neutralize its charge. The solvation or hydration of the adsorbent surface and of the adsorbed ions must also be considered. Consequently, in hydrosols the electric double layer is really a diffuse solvated shell consisting of the bound dipoles of the dispersion medium and the accumulated ions of the solute.

When colloidal clay is dispersed in water a number of individual particles are present; they consist of a charged nucleus surrounded by a more or less extended diffuse ionic atmosphere. It is this nucleus and the bound dipoles of the dispersion medium in which the accumulated and also hydrated ions are dispersed which constitutes the colloidal micelle.

If we now look at the structure of a clay mineral of the montmorillonite group exhibiting, as is common, a substituted lattice (Fig. 16) and not the ideal structure, we find that these substitutions result in establishing net residual negative charges in certain sections of the lattice, which in turn cause attraction of counter ions or cations. If the concentrations, valency, or hydration of the counter ions is such that the magnitude of the net charges of the colloidal micelle or the thickness of the diffuse double layer is so reduced that van der Waals' attraction forces come into play, coagulation results.

With these concepts as a basis the most important properties of colloidal clays may now be far better understood than has been possible so far.

THIXOTROPY

All colloidal particles of siliceous systems are of anisometric shape and therefore their orientation must be taken into consideration, specifically in the process of gelation and in dealing with the related phenomenon of thixotropy. Clay dispersions exhibiting thixotropy are characterized by such a distribution of ions in their diffuse double layers (resulting either from adsorption of added electrolytes or from surface dissociation) that the particles with their solvated hulls will take on equilibrium positions if left undisturbed. If agitated, however, the solvated hulls are disrupted and the particles may then move about freely. This concept is further substantiated by the sudden change in light transmission when a bentonite sol sets to a gel, and it is also in line with the mathematical treatment of thixotropic systems, which concludes that the particles in the gel are placed like ions in a crystal lattice and lie at considerable distances from each other (up to 5,000 Å). They are locked into position by the balance of far-reaching attraction forces and appropriate repulsion forces set up by the interplay of the surface ions of the clay crystal and the free ions in the dispersion medium.

An important and interesting property exhibited by "Bentone," an organophilic bentonite, is that of setting to a thixotropic gel in organic liquids. This proves that the phenomenon of thixotropy is not unique to the electrical properties of colloidal systems that swell in water, like natural bentonite, but that far-reaching van der Waals' attraction forces can substitute for the electrical forces.

RHEOPEXY

The first time that this phenomenon was recorded with colloidal clays was based on research using the finest supercentrifuged fractions of natural Wyoming bentonite. The phenomenon occurs only in an extremely narrow range of electrolyte concentration, and the higher the valence of the cation of the electrolyte the lower will be the concentration needed to produce a rheopectic gel. Systematic ultramicroscopic observations have revealed a distinct layer arrangement of the anisometric particles when gelation occurs. The phenomenon is even more striking with dispersions which exhibit aggregation and pronounced syneresis upon standing and never set to a thixotropic gel.

DILATANCY

The phenomenon of the dilatancy of suspensoidal systems depends on a strong repulsion between the particles upon their close approach. This is due to the presence of a thin layer of liquid between the particles. If quick deformation of the dilatant system is attempted, the external force will cause an unequal distribution of the particles; they pile up locally, thus preventing the liquid from following these movements, so that further displacements are inhibited; the liquid which has been removed from the thin layers originally surrounding the particles will not fill the cavities which have been formed and the system behaves more or less like a solid. In other words, the lyosphere surrounding the individual particle permits it to slip past another one easily, but when the dilatant system is deformed very rapidly, a displacement of the ions located in the lyosphere takes place; now London-van der Waals' attraction forces become predominant and a clustering or aggregration of the particles results.

STREAMING DOUBLE REFRACTION

The particles of colloidal clays, *e.g.*, of sodium bentonite, are of a platey shape and therefore anisometric; thus they exhibit stream double refraction if present in the form of a sol which is put into motion. A systematic study of the double refraction of monodisperse fractions of bentonite sols revealed that the stream double refraction decreases with decreasing particle size.

Because the colloidal particles of a sodium bentonite sol are electrically charged, it is also possible to induce double refraction of the sol by applying an electric field to the system. By putting the large electro-optical effect of sodium bentonite sols to use it has been possible to study and measure nonhomogeneous electric fields surrounding an object by an optical method analogous to that of photoelasticity.

PLASTICITY

The significant difference between a system exhibiting truly viscous flow and one exhibiting truly plastic flow is the initial expenditure of force before the occurrence of shear in the latter system; some force exerting its influence in a plastic system must first be overcome before the proportional relationship of applied force to shear, which is characteristic of a truly viscous system, can apply. The point at which this relationship is finally achieved is called the "yield point" and, by definition, it constitutes a measure of plasticity.

Systematic studies of the properties exhibited by clay-water systems have offered strong evidence that the character of initially adsorbed water differs from that of liquid water. Grim and Cuthbert have suggested a theory for the bonding action of clay and water in molding sands which is based on the nonliquid nature of the initially adsorbed water. On the basis of analyzing the phase relations of water Winterkorn concluded that the water held directly on the clay mineral surface must be solid and not liquid and that the change in the state of the water with distance from the surface is an exponential one.

When ceramic problems are taken into consideration several colloidal problems based on the adsorption of water or electrolytes on the clay particles must also be considered.

In the case of kaolinite, for example, hydroxyl ions are preferentially adsorbed. The kaolinite particle therefore takes on a net negative surface charge and an attraction for positive ions located in its vicinity is the result. The repulsion forces which are associated with the colloidal micelle originate with the counter ions which swarm about the colloidal particle in an effort to neutralize its surface charge. The amount of repulsive force existing in the system depends on the type, valency, and hydration of the cation serving as the counter ion. If a small trace of an electrolyte of low valency is added to the system, the forces connected with the micelle will undergo profound changes as a result of the preferential ion adsorption on the particle and a rearrangement of the counter charges. This causes the formation of a considerable repulsion force at the edge of the lyosphere. Such a system is called deflocculated or dispersed, and it is this condition which should be attained for commercial casting processes in the ceramic industry.

The addition of an acid to a kaolinite slip will cause a pronounced decrease in its repulsive energy, since the hydrogen ion is not hydrated as such. Now all the counter charges are located within the hypothetical water hull and the adsorbed hydroxyl ions are discharged. Repulsion forces consequently do not exist beyond the lyosphere and from a colloidal viewpoint the system is unstable or flocculated.

BASE-EXCHANGE CAPACITY

Among many methods for determining the total base-exchange capacity of clay minerals, one applies the chemical "Versenate." The main disadvantage of the method is that soils rich in organic matter give highly colored solutions; this difficulty may be overcome to a considerable extent, however, by dilution or by increasing the amount of indicator used and, if necessary, by carrying out the titration by the use of soft white light or a daylight fluorescent bulb. Versenate will quantitatively titrate calcum carbonate and magnesium carbonate; a soil contaminated with free lime will show a high cation-exchange capacity unless the proper correction is made. When base-exchange reactions are determined by the Versenate method it is advisable that only pure clay be used and that only particles of a given size be subjected to investigation. Wyoming sodium bentonite and the calcium bentonite of Fayette County, Texas (Cherry Lease composite), for example, reveal a pronounced change in base-exchange capacity depending on the pH present or used, as shown in Figures 18 and 19.

DIFFERENTIAL THERMAL ANALYSIS

A standard Wyoming sodium bentonite offers a differential thermal analysis curve as shown in Figure 20. A pronounced minimum appears at about 175° C and an endothermic peak occurs at about 725° C. The clay

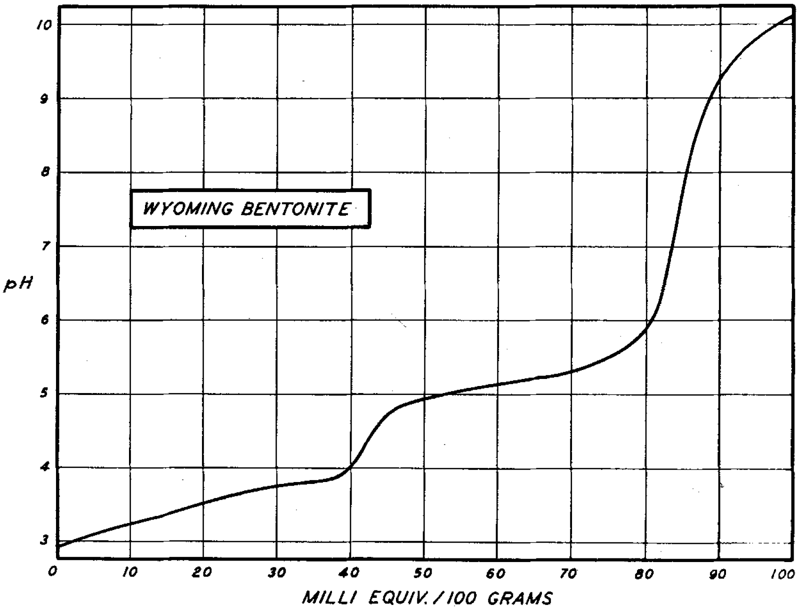


FIGURE 18. — Base-exchange capacity of Wyoming Na-bentonite vs. hydrogen ion concentration.

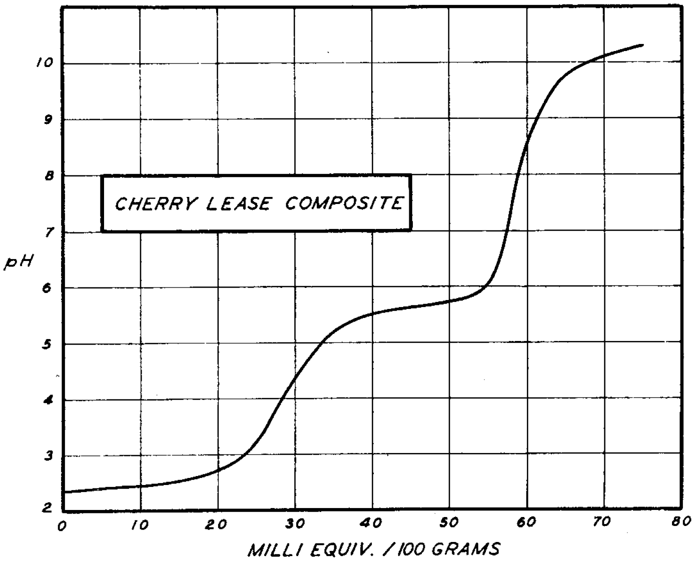


FIGURE 19. — Base-exchange capacity of Fayette County, Texas, Ca-bentonite (Cherry Lease composite) vs. hydrogen ion concentration.

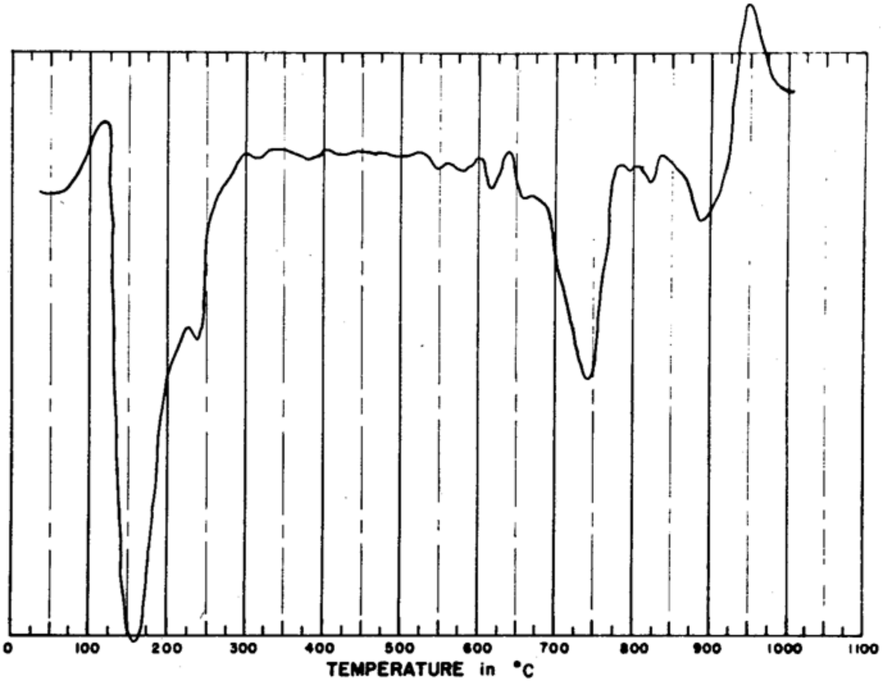


FIGURE 20. — Differential thermal analysis curve of Wyoming bentonite.

shows a pronounced exothermic peak between 900° C and 950° C; in all probability this is due to the formation of the mineral spinel. The initial endothermic peak is due to adsorbed water on the surface of the clay mineral; the most pronounced second endothermic peaks refer to the loss of lattice water; and the last endothermic peak corresponds to the breakdown of the lattice itself.

INFRARED ABSORPTION SPECTRA

The infrared absorption spectra of sodium bentonite (Fig. 21) show distinct absorption bands at a reciprocal wave length of 3,700 cm.$^{-1}$ due to free hydroxyl groups, and between 3,600 and 3,200 cm.$^{-1}$ due to associated hydroxyl groups. If the drying temperature of the films is increased, the second absorption band is pronouncedly reduced, whereas the first remains almost unchanged. With calcium bentonites (Fig. 22) the relatively sharp band near 3,700 cm.$^{-1}$ is characteristic of an OH band such as is found in alcohols, hydroxides, and water vapor. The broad band extending from 3,200 to 3,600 cm.$^{-1}$ is characteristic of liquid water and a small amount of hydroxide. Heating to 150° C does not remove much of the adsorbed water, but heating to 500° C removes the largest part of it.

X-RAY DIFFRACTION

Many X-ray diffraction diagrams of clays have been reported. Most of this work was carried out by the use of the standard Debye-Scherrer technique. More recently, X-ray diffraction research has been carried out

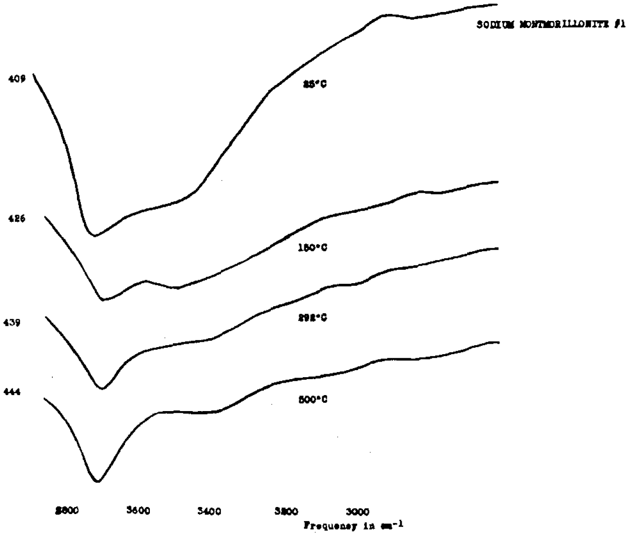


FIGURE 21. — Infrared absorption spectra of sodium montmorillonite.

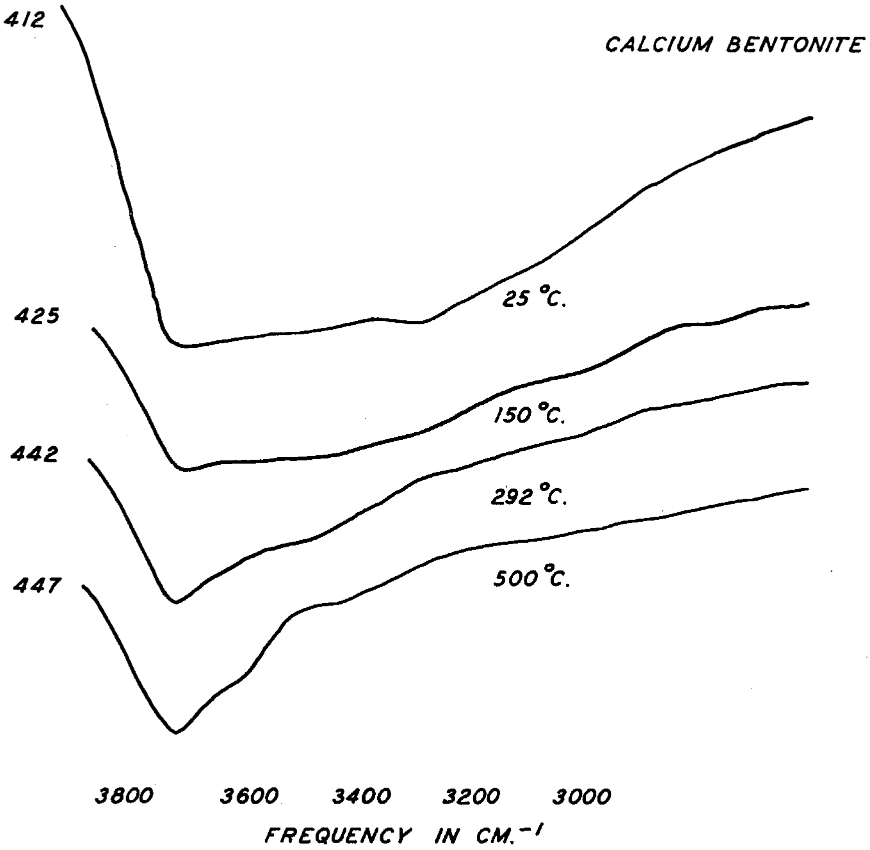


FIGURE 22. — Infrared absorption spectra of calcium bentonite.

with the Norelco Geiger-Mueller X-Ray Spectrometer. A typical result is shown in Figure 23.

ELECTROPHORETIC PROPERTIES OF MONTMORILLONITE

The electric double layer of a sodium bentonite which exhibits high base-exchange capacity is due to the negatively charged surface of the crystallite of the inner rigid layer, the adsorbed hydrated sodium ions representing the counter ions in the diffuse outer layer. In the case of calcium bentonite the calcium ions are much more strongly adsorbed and held closer to the surface of the negatively charged clay particle, and therefore the chances of dissociation are reduced. This is shown in a much lower base-exchange capacity. If pure water is used as a dispersion medium, osmotic imbibition of water occurs and the clay swells to its maximum.

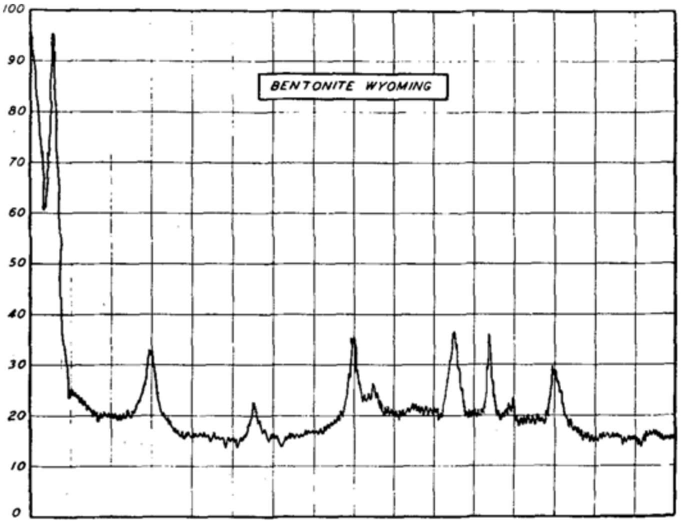


FIGURE 23. — X-ray diffraction analysis of Wyoming bentonite using the Norelco Geiger-Mueller X-Ray Spectrometer.

The cataphoretic velocity of purified, colloidal, monodisperse fractions of sodium bentonite increases with decreasing particle size. With constant particle size it decreases with increasing concentration, the drop being most pronounced with the smallest particles. In extreme dilutions (up to 0.5 percent) the cataphoretic velocity remains constant for a given particle size.

It is interesting to compare the mobility of bentonite and of aluminum oxide against hydrogen ion concentration. While aluminum oxide shows a pronounced drop in mobility with increasing pH, the bentonite does not, as shown in Figure 24.

GELATION

A negatively charged bentonite sol will set to a gel by the use of lithium, sodium, potassium, hydrogen, etc., and it should be noted that the effectiveness of adsorption of the ion in the diffuse layer increases as we travel from lithium to hydrogen in the Hofmeister series. This indicates that the less strongly the ion carrying the charge opposite to that of the sol particle is adsorbed in the diffuse layer, the more powerful it is in forming gels. The electrocratic behavior of a sol depends in general upon the individual adsorption characteristics of the ions in the surface of the system and the adsorption behavior of the colloidal clay particles.

THE ATOMIC STRUCTURE OF COLLOIDAL CLAYS

The atomic structure of all silicates is governed by three basic principles: The tetravalency of silicon in the solid state, the four-fold coordination of

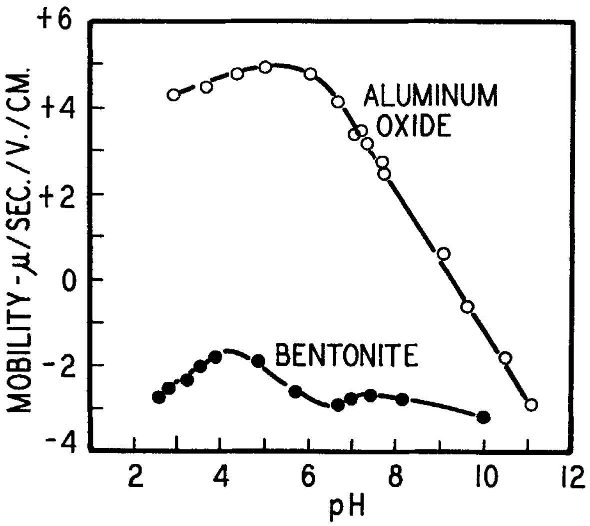


FIGURE 24. — Mobility of aluminum oxide and bentonite vs. hydrogen ion concentration.

silicon with respect to oxygen ions, and the strong repulsion forces between the two silicon ions located in the neighboring SiO_4 tetrahedra which prevent these units from sharing edges and faces. A phenomenon accompanying the formation of a free silica surface is the cleaving of O_2 molecules, which leads to the formation of atomic oxygen.

WETTABILITY

When sodium bentonite exhibiting high base-exchange capacity is reacted with water-soluble calcium or lead salts, the sodium counter ion of the natural clay is immediately exchanged for the calcium ion or for the lead ion in an amount corresponding to the respective valency of the cation involved. By this procedure calcium or lead clays may be obtained from sodium bentonite of the Wyoming or Montana type. If clay slips are made from all three types and are sprayed onto unglazed ceramic tiles, allowed to dry in a drying oven, and the wettability of these tiles is then studied, the following results will be obtained: The sodium clay will adsorb a drop of water immediately; the calcium clay will adsorb a drop of water much more slowly and will exhibit a much poorer wettability; and the lead clay will not be wetted with water at all, even after a prolonged time. Since the calcium ion is more polarizable than the sodium ion and the lead ion even more than the calcium, these experiments offer proof of the effect which surface polarization exerts on the properties of siliceous matter.

SURFACE TENSION OF BENTONITES

This work was carried out using the pendent drop method; all measurements were made on drop surfaces ten seconds old, at 25° C.

A 3 percent (dry weight) dispersion of Wyoming bentonite gives a surface tension of 78.20 dynes/cm. After only a few seconds the formed drop shows the phenomenon of thixotropy. Thixotropy becomes even more pronounced if a few drops of a 50 percent solution of sodium hydroxide is added to a 1 percent dispersion of bentonite in water. The surface tension also shows a pronounced change; it is now reduced to 61.5 dynes/cm.

The surface tension of a 3 percent dispersion of the montmorillonitic clay known as Hectorite is 81.5 dynes/cm. This product also reveals the phenomenon of thixotropy to some extent. In contrast to Wyoming bentonite, the addition of a few drops of a 50 percent sodium hydroxide solution to a 1 percent dispersion of Hectorite increases the surface tension to 88.72 dynes/cm.

The surface tension of pure benzene, determined in a benzene-saturated atmosphere to avoid any evaporation of the drop, amounts to 12.79 dynes/cm. When a very dilute solution of the organophilic clay mineral known as "Bentone" is tested in benzene, the surface tension amounts to 14.92 dynes/cm. This shows that the addition of Bentones even at such low concentrations (0.5 percent) increases the surface tension slightly over 2 dynes/cm. With a concentration of Bentone amounting to 3 percent in benzene, the surface tension of the pendent drop is 14.14 dynes/cm.

INDUSTRIAL USES OF COLLOIDAL CLAYS

The colloidal nature of many clays and the properties depending thereon are not only of paramount importance for the ceramic industry but they also play an important part in oil well drilling operations, they may no longer be overlooked in modern agriculture, highway construction and soil solidification quite generally, and they are equally important for the rubber and plastics industry. The colloid science of silicates is just as important in medicine, and "silicic science" is essential for an up-to-date understanding of the fundamentals involved in problems pertaining to geology; it is necessary also in order to explain catalytic reactions which involve the use of silica.

CERAMICS

Only since the day when the concept of the clay particle as a colloidal micelle was introduced has it become possible to offer a better understanding of such properties as plasticity, dry strength, shrinkage, and several others. This changed ceramics from an art to a science.

Plasticity refers to the property of a moistened material to be deformed when pressure is applied, the deformed shape being retained even when the deforming pressure has been released. The input of force without resulting shear (yield point) is a characteristic of plastic flow.

The plasticity of kaolinite slips, as exemplified by the yield point, depends on the attraction force present at the edge of the hypothetical lyosphere or water hull of the colloidal micelle. The most important single cause for the yield value of the kaolinite-water system is probably the diffuse electric double layer associated with the solid particles or nuclei. It is therefore possible to improve the plasticity of the kaolinite-water system by adjusting the counter ions in the diffuse double layer and the ions of the medium, which ultimately control the attraction forces in the system. A consideration of the plastic properties of any mineral should thus include a careful analysis of the characteristics of the double layer formed by the particular substance in question.

Because most industrial clays which contain kaolinite as the principle mineralogic constituent contain calcium in exchange positions, these clays are relatively plastic. If it were necessary to enhance the yield point of a kaolinitic clay, the exchange of the calcium ions for aluminum or hydrogen ions would be the most economical method. Because the introduction of the hydrogen ion or of trivalent ions causes a further reduction of the charge on the particles, the attraction forces acting between the micelles are increased, thereby increasing the plasticity of the system. A reduction of plasticity can be accomplished by adding to the system such ions as will tend to cause deflocculation when adsorbed on the clay particle, *e.g.*, sodium phosphate; the phosphate ions will replace the OH ions located on the surface of the clay particle.

THE PAPER INDUSTRY

In the manufacture of paper a large quantity of kaolinite is consumed every year. To obtain the best results, however, more attention should be paid to the surface phenomena exhibited by this product. The use of other colloidal clays, specifically calcium bentonite, would also aid in the production of fairly transparent papers of high tensile strength. By appropriate knowledge of the colloidal phenomena involved, it is possible to overcome the loss of such clay even in the equipment now applied.

CATALYSIS

The greatest use of siliceous matter in catalytic reactions is as a carrier for metal ions. Siliceous matter has also been used as a catalyst itself in the catalytic oxidation of hydrocarbons and in catalytic cracking processes. In heterogeneous catalysis silica gels, silicic acid gels, quartz, and silicates like clay minerals with low base-exchange capacity are being used onto which metals are attached, preferably in oxide form. Since rough surfaces are better adapted for catalytic reactions than smooth ones, it is understandable why the use of such clays as a carrier has an advantage over the use of pure metals. The use of siliceous matter as a carrier also has economic advantages because a far smaller amount of selected metal catalyst can now be applied which would still offer at least the same surface area needed for the reactions to take place. This is particularly important since the reactivity of the catalyst is inversely proportional to the number and type of metal ions adsorbed on the carrier.

AGRICULTURE

In the field of agriculture the adsorptive power of clays is of specific importance; by virtue of this property the loss of valuable plant nutrients by leaching is largely prevented. This is especially important when soils are being treated with fertilizers. In this case the nutrient is adsorbed by the clay in such a form that it becomes readily avalible to the plant.

Most clays exhibit the property of base exchange to a more or less pronounced degree. Potassium, calcium, and magnesium generally, and sodium in arid-region soils, are adsorbed by the clay constituents in an exchangeable form. The growth of plants, the decay of organic matter, and the life processes of microorganisms produce hydrogen ions which are now made available for plant growth.

In arid regions the clay constitutent of the soil is rich in adsorbed sodium. Since the sodium ion hydrates pronouncedly, the clay constituent of such soil has the property of swelling appreciably, causing the formation of a soil which resists the percolation of water. To make such a sodium clay more amenable to plant growth, the sodium ions must be exchanged with higher valent ions, preferably calcium, thus forming a calcium clay.

A phenomenon which may not be overlooked is the anion-exchange capacity of some clay minerals. In kaolinite and halloysite the OH ions can be readily exchanged for PO_4 ions. This explains the pronounced phosphate adsorbing power of these clays and also explains why soils rich in kaolinite can be very much improved for agricultural purposes when they are treated with phosphates.

BENTONITE FILMS AND BENTONITE PLASTICS

One of the most interesting discoveries in the field of the applied colloid science of bentonites is their use in the production of coherent, self-supporting, flexible films and their applicability as the basic material for moldable plastics.

If a gel of grit-free bentonite, preferably one exhibiting a high base-exchange capacity, is spread onto a smooth surface and subjected to careful drying, a film will form which, being coherent and self-supporting, may be easily removed from its support. An ultramicroscopic reproduction of this film is seen in Figure 25. By using conventional spreading machines, the process may be made continuous and the formed film wound up on a mandrel just as in the production of paper or other organic film or sheet-

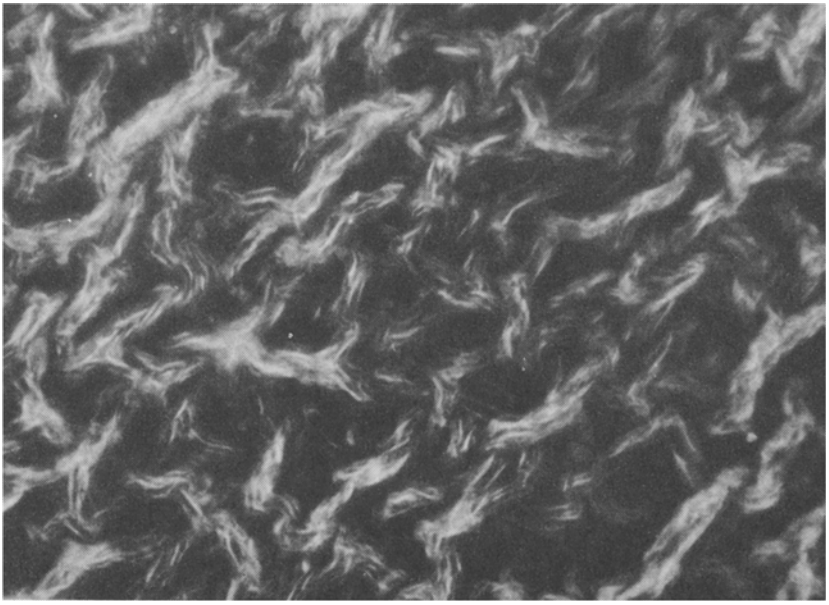


FIGURE 25. — Self-supporting, coherent sodium bentonite clay film known as Alsifilm. Original magnification 550.

forming substances. Clay films which have been rendered water-insoluble are excellent electric insulators, approaching the best types of mica in this respect. This can be accomplished by causing a base-exchange reaction of the clay mineral, using ions of such dimensions that they cannot penetrate the crystal lattice and therefore remain simply adsorbed on the surface layer of the clay particle.

DRILLING FLUIDS

The drill pipe used for all modern drilling operations is hollow and conducts the "drilling mud" to the bottom of the hole, where it passes out through holes in the bit and then upward through the annular space between the drill pipe and the wall of the hole to the surface, where it is then recirculated by the use of pumps.

The main function of the mud is to transport the cuttings made by the bit to the surface. The mud must be dense enough to provide adequate hydrostatic pressure, but must be fluid enough at the same time to permit easy pumping. It must also exhibit the property of thixotropy so that cuttings remain suspended in the bore hole whenever circulation must be stopped.

Sodium bentonite, if added to the drilling mud in concentrations not exceeding 2-3 percent by weight, will cause the formation of a thixotropic system and therefore solve the most important problem, namely, to retain cuttings, shales, and the like while the system is not in motion, but permit their immediate release when the top of the well is reached and the water is kept in slow motion.

BENTONES

The optimum condition for the production of the organophilic clays known as "Bentones" is to totally cover the surface with organic ammonium salts or other onium compositions. The most important properties of Bentones are swelling, the formation of gels, and even of thixotropic gels, in organic liquids, and perfect dispersion in organic systems (Figs. 26 and 27).

Bentones are successfully used today for lubricating greases and for multi-purpose greases where the Bentone acts as a highly efficient gelling agent, exerts unusually high mechanical stability under the most severe working conditions, will not melt even in extreme heat, is water-resistant, and provides longer, trouble-free service life in comparison to any other known agents used in the formulation of greases.

Bentones have also found satisfactory applications as compounding ingredients for elastomers and plastics; they may be incorporated into any type of elastomer, including Silastics, where, due to their organic surface structure, they chemically combine with the organic polymer. Vulcanization of the elastomers is not affected by the use of the Bentones; on the contrary, they offer superior aging properties and higher tear resistance to the polymer than would the addition of an inorganic filler.

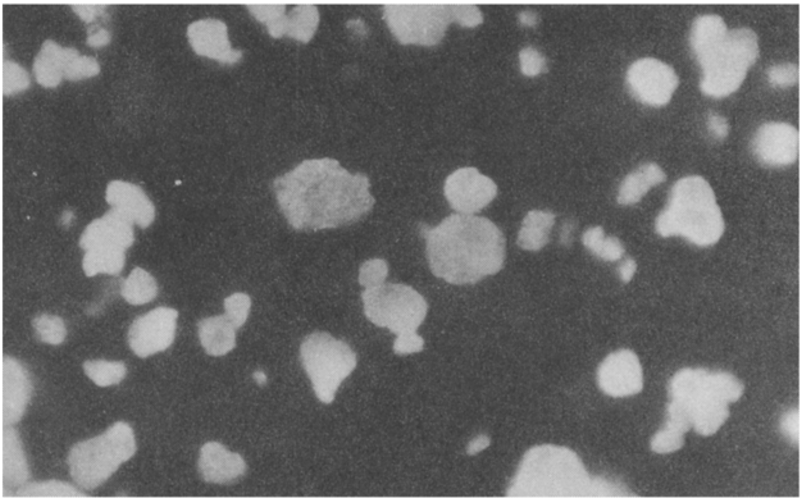


Figure 26. — "Bentone" dispersed in water. The particles are strongly aggregated and float at the surface. Original magnification 550.

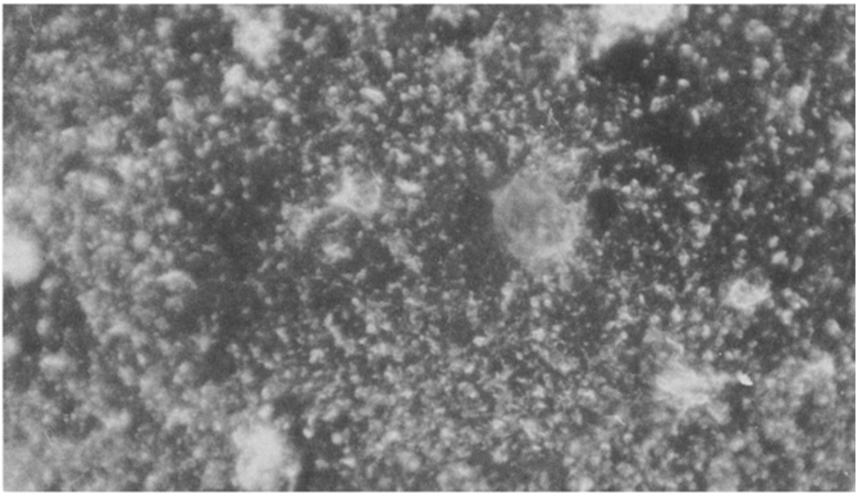


FIGURE 27. — "Bentone" dispersed in benzene at a concentration of 3% (dry weight). Perfect dispersion in the organic solvent is clearly evident. Original magnification 550.

WATER SOFTENING

Clays which possess a high ion-exchange capacity may be used successfully for water softening. If hard water, which contains calcium and magnesium salts, is percolated through a bed filled with sodium bentonite, the sodium ions will be replaced by the calcium or magnesium ions until all the free and therefore accessible negative valencies of the clay particles have been compensated by the concentration and valency of the cations originally present in the water. Then, simply by applying the mass-action law, the clay can be regenerated by using a high concentration of a sodium salt solution, like brine, and a sodium clay is formed again. This process is still in use today, although synthetic ion-exchange resins are being used more and more, primarily because they do not involve the swelling problems characteristic of sodium bentonites.

THIXOTROPIC RUBBER COMPOUNDS

The viscosity of the natural milk sap or latex of the rubber tree is very low as compared with that of a solution of rubber in an organic solvent, even if the concentration of rubber in latex is many times that of the organic solution. Although this low viscosity has many advantages for the use of latex, it can be a serious drawback whenever too great a fluidity of the system hampers its use. For example, it is easier to squirt a latex compound through a fine nozzle than a highly viscous solution of rubber in benzene, and the concentration of rubber will be much greater for any given volume. However, the latex tends to spread out when deposited on a surface, owing to its low viscosity. If a thixotropy-inducing bentonite dispersion is added to the latex, however, the compound will set up to a thixotropic gel as soon as the dispersion has come to rest, and spreading will be avoided.

PHARMACEUTICAL APPLICATIONS

For generations the Red Indians of the United States have been applying crude bentonite gels for the healing of cuts and other skin injuries. With our increasing knowledge of the colloidal properties of these natural products, they are now being used for the production of salves and ointments. The most important problem is how the foreign matter present in these clays may be best removed; this has been solved by the use of appropriate supercentrifuges. Today salves and ointments for the treatment of burns, weeping of wounds, and the like are available and are being used by members of the medical and veterinary professions. In this connection it should be stated that calcium bentonites have proved to be of special value because they will not form gels so readily as the sodium bentonites do, thus permitting the use of much higher concentrations of clay.

SUMMARY

On the basis of our latest information the chemical composition and structure of the most important clay minerals are discussed in detail. The need for a knowledge of colloid science to understand the properties of colloidal clays is emphasized, and specific examples are offered to illustrate this. Since colloid science deals with typical surface phenomena exhibited by matter present in the colloidal range of dimensions, the reasons for them need to be discussed in detail; such explanations are offered throughout.

The application of the ultramicroscope and electron microscope, differential thermal analysis, infrared diffraction studies, X-ray investigations, stream double refraction, thixotropy, and several other methods and phenomena of colloid science are explained and discussed.

A profound knowledge of the colloid science of clay minerals is necessary to make it possible to better understand their properties, their versatile reactivity, and the still unexplored possibilities this comparatively new branch of science has to offer.

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All the literature references pertaining to this article appear in three books and in a paper presented at the Second National Clay Minerals Conference (Columbia, Missouri, October, 1953). For this reason no other specific references are listed here.

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