

INDUSTRIAL APPLICATIONS OF BENTONITE

by

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ABSTRACT

Bentonite is employed by industry to perform a multitude of jobs. Certain industrial applications become apparent from an understanding of the composition and structure of bentonite, and the properties they create. These properties are utilized chiefly when the material is suspended in a liquid, usually water; or as a dried powder or granule.

Most industrial applications involve the swelling property of bentonite to form viscous water suspensions. Depending upon the relative proportions of clay and water, these mixtures are used as bonding, plasticizing, and suspending agents.

Bentonites disperse into colloidal particles and, accordingly, provide large surface areas per unit weight of clay. This large surface area is a major reason why bentonite functions so well in stabilizing emulsions, or as a medium to carry other chemicals.

Bentonites react chemically with many organic materials to form compounds which are used chiefly as gelling agents in a variety of organic liquids.

Bentonites are selected for each industrial need on the basis of type and quality. This selection is based principally on physical properties, and chemistry of the bentonite becomes involved only to the extent that it influences the physical properties.

INTRODUCTION

Although the bentonite industry is slightly over 70 years old, the name bentonite was applied as early as 1848 by Knight to a highly plastic clay material occurring near Fort Benton, Wyoming (Grim, 1953, p. 361). According to Chisholm (1960, p. 30) the first commercial bentonite was shipped in 1888 under the name "Taylorite". From this modest beginning, in which production amounted to only a few tons per year, bentonite production now exceeds a million tons per year (Table 1). In fact, average annual production over the past 10 years has exceeded $1\frac{1}{4}$ million tons; 1956 was the highest production year with more than $1\frac{1}{2}$ million tons (*U.S. Bureau of Mines Minerals Yearbooks*, 1939-1960).

The bentonite industry began initially in Wyoming and South Dakota, but today Mississippi and Texas both contribute substantial tonnage to the yearly production figure.

The origin of bentonite is attributed to the alteration of volcanic ash, or glass, but common use of the term is often extended to include material of primarily a montmorillonite composition which may have formed in another manner.

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TABLE 1.—BENTONITE PRODUCTION AND USE FOR YEARS 1939-1960
(Bureau of Mines Minerals Yearbook)

Year	Production by States							Uses			
	Total tons	Mississippi	South Dakota	Texas	Wyoming	Other States	Drilling mud	Foundry	Other		
1939	219,720	*	31,528	18,132	76,133	93,927	35,880	53,872	129,968		
1940	251,032	*	40,481	14,399	91,714	104,438	45,296	74,135	131,601		
1941	354,028	*	57,139	11,593	145,574	139,722	*	*	*		
1942	374,967	*	88,149	17,651	139,410	129,757	48,745	149,384	176,838		
1943	480,202	*	124,528	25,078	159,252	171,344	68,841	181,412	229,949		
1944	546,768	*	169,893	24,081	196,138	166,656	121,237	182,410	243,121		
1945	573,998	*	178,374	24,503	199,293	171,828	162,457	160,719	250,822		
1946	601,428	*	186,707	21,576	212,530	180,615	228,542	162,385	210,301		
1947	763,889	*	186,450	18,628	259,084	299,727	236,805	206,250	320,834		
1948	921,560	*	156,701	29,926	383,815	351,118	329,752	328,799	363,009		
1949	867,243	*	137,376	27,598	350,644	351,625	313,083	178,867	375,293		
1950	973,833	*	192,591	24,574	394,939	361,729	357,315	251,716	364,802		
1951	1,218,868	*	246,585	38,425	465,254	468,604	460,261	282,753	475,854		
1952	1,317,979	*	205,934	31,386	692,853	387,806	705,280	322,746	289,953		
1953	1,269,971	189,211	205,303	47,887	670,756	156,814	583,373	347,056	339,542		
1954	1,278,393	185,554	*	105,744	742,453	244,642	548,300	295,389	434,704		
1955	1,480,205	226,852	*	155,128	825,810	272,415	595,471	419,152	465,582		
1956	1,570,610	219,216	*	160,733	847,266	343,405	628,146	408,399	534,065		
1957	1,450,867	220,313	*	126,635	822,163	281,756	556,889	376,833	517,145		
1958	1,291,414	177,041	*	121,106	702,237	291,030	425,621	361,799	503,994		
1959	1,372,286	200,256	*	133,317	763,834	274,879	483,858	470,349	418,079		
1960	1,268,800	237,564	*	115,587	782,168	133,481	404,980	464,090	399,730		

(All figures in short tons)

* Production or distribution not determined.

Bentonites are typically strip-mined, that is, the overburden is removed initially in order to expose the bentonite. The clay normally occurs as lenses which are a few feet thick.

After mining, the bentonite is generally stockpiled, dried, separated with respect to particle size or ground to a powder, bagged, and shipped.

BENTONITE COMPOSITION AND PROPERTIES

It is desirable at this point to understand the nature of bentonite. Various definitions of bentonite have been given in the literature, but generally all agree that bentonite is a rock term used to designate a naturally occurring,

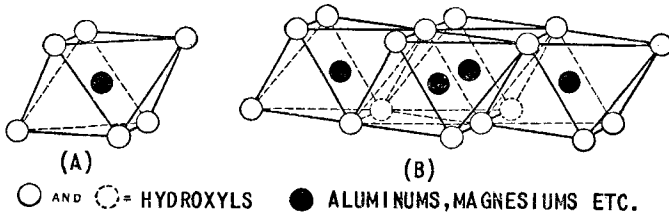


FIGURE 1.—Diagrammatic sketch showing (A) single octahedral unit, and (B) portion of an octahedral sheet structure.

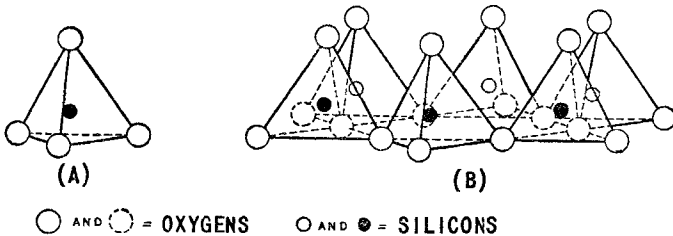


FIGURE 2.—Diagrammatic sketch showing (A) single silica tetrahedron, and (B) portion of a silica tetrahedral sheet structure.

very fine grained material largely composed of the clay mineral, montmorillonite. Accordingly, a description and discussion of montmorillonite is applicable to bentonite as well. Bentonite, in addition to montmorillonite, contains a small portion of other mineral matter, usually quartz, feldspar, volcanic glass, organic matter, gypsum, or pyrite.

Chemically, montmorillonite is described as a hydrous aluminum silicate containing small amounts of alkali and alkaline-earth metals. Structurally, montmorillonite is made of two basic building blocks, the aluminum octahedral sheet and the silica tetrahedral sheet (Figs. 1 and 2). A single montmorillonite unit cell consists of two silica tetrahedral sheets, between which

is an aluminum octahedral sheet (Fig. 3). Lengths and widths of montmorillonite flakes are from 10 to 100 times the thicknesses. The montmorillonite lattice is negative in charge, owing primarily to isomorphous replacements of ions within the structure. This negative character is balanced by cations which are held on the surface of the flakes. Cations held in this fashion by the clay can be readily exchanged; the cations most commonly found in nature are sodium and calcium.

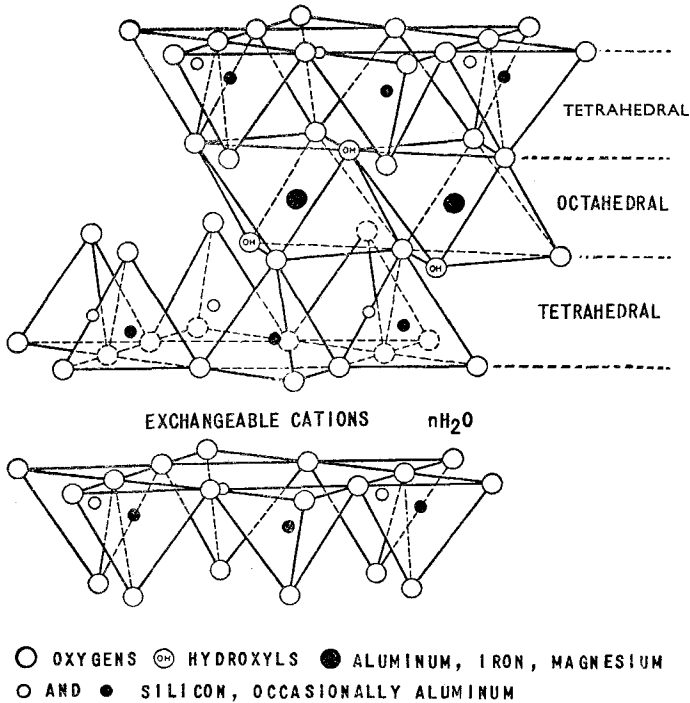


FIGURE 3.—Diagrammatic sketch of the structure of montmorillonite (after Grim, 1953).

Montmorillonite has a cation-exchange capacity of about 70 to 110 meq/100 g of clay. Generally the laws of mass action dictate which will be present as exchangeable ions on the clay. The exchangeable cations, both by type and amount, that are associated with the montmorillonite are of great importance since they largely control its physical properties.

Montmorillonite adsorbs water whenever it is available. Water adsorption occurs to the greatest extent on the basal surfaces of the clay and in this fashion pries adjacent flakes apart, resulting in an overall volume increase of the clay. Evidence of this swelling mechanism is seen as an increase in the *c*-axis dimension of the clay (Fig. 4). The water which is adsorbed primarily on the basal surfaces of the clay (frequently referred to as "bound" or

"oriented" water) consists of a regular, rather than a random, arrangement of water molecules; the energy with which the water orients and is bonded to the clay flake is measured as heat of wetting.

Many types of organic materials are adsorbed by montmorillonite, and this adsorption is somewhat similar in manner and orientation to that of water. Organic material adsorbed on basal surfaces also increases the *c*-axis

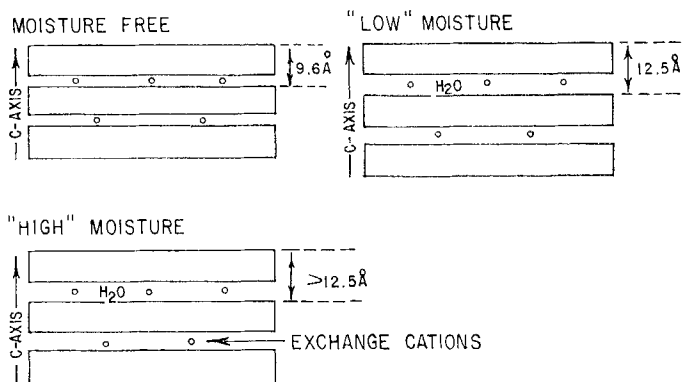


FIGURE 4.—Diagrammatic sketch which shows swelling action of montmorillonite with increasing moisture content.

dimension of the clay. Some of the parameters governing organic adsorption include type and composition of the organic material, the organic concentration, pH, and the presence or absence of water in the system.

INDUSTRIALLY ATTRACTIVE PROPERTIES OF BENTONITE

The greatest use of bentonite in industry results from its swelling action in water. Combinations of water and bentonite can perform a multitude of jobs in industry because physical properties of the mixtures change as the water-to-clay ratio changes. The swelling capacity of the clay is of prime importance: this property is controlled in large part by the types of associated exchange ions.

Let us consider only the two most common montmorillonite varieties. The sodium bentonites expand or swell in aqueous suspensions more than the calcium. At relatively low moisture contents, a stable hydrated form of sodium montmorillonite has one adsorbed molecular layer of water between adjacent layers. At this same moisture content, calcium montmorillonite is stable with two molecular layers of water. At higher moisture contents, or even in suspension, a comparison of the calcium and sodium montmorillonites shows that the calcium variety has fewer, more tightly bound water layers

associated with it, whereas the sodium variety has many water layers, but bound less tightly.

When a relatively small amount of water is mixed with a large amount of bentonite, the mixture forms a sticky mass which has adhesive properties. This physical state results when the water content is inadequate to fulfill the oriented water requirement by the montmorillonite. The plastic properties of a clay-water system increase as the ratio of water to clay increases. When each montmorillonite flake has adsorbed its maximum amount of water, additional water in the system acts as a lubricant for the hydrated particles. It frequently takes a period of time or ageing for the clay to develop a completely hydrated state, even if the necessary water is available. Aggregates of clay flakes are disaggregated by agitation or stirring in suspension, and this substantially aids the clay swelling or hydration. Usually, however, swelling proceeds with additional time as water pries its way between neighboring clay flakes which agitation has been unable to separate.

When bentonite disaggregates in water and swelling takes place, the average clay particle size decreases. As a function of decreasing particle size, the number of particles per unit weight of clay increases, and consequently also the available surface area. Grim (1953, p. 311) states that a theoretical value for the surface area of sodium montmorillonite, disaggregated to unit cell dimensions, is of the order of $800 \text{ m}^2/\text{g}$ of clay.

Unlike many other materials that possess a large surface area, the surfaces of montmorillonite are essentially populated by oxygen atoms which promote a high degree of reactivity with other compounds. Accordingly, bentonite thoroughly dispersed in water has a high potential to carry on other reactions.

Disaggregation or dispersion of bentonite in water is aided by the addition of a small amount of an electrolyte. Like other colloidal materials, however, a high ion concentration can flocculate bentonite. Furthermore, if initial hydration is attempted in a strong electrolyte, such as a concentrated sodium chloride solution, there is essentially no swelling. This phenomenon is explained by repulsion of like ions associated with the clay and also available in the suspending medium.

INDUSTRIAL USES

Clay-Water Mixtures

Bentonite-water mixtures are used for bonding, plasticizing, and suspending. This versatility is made possible chiefly by adjusting the quantities of the two components.

A bonding agent must have certain adhesive properties, and these are developed when bentonite is mixed with only a small amount of water. When oriented water is shared by adjacent clay flakes, and this mixture is added as a constituent to a combination of materials, rigidity rather than plasticity is developed in the final product. For a bonding agent, generally both water and clay are mixed into the finished product in amounts less than 5 percent by weight.

In this fashion bentonite is used as a bonding agent in foundry molding sand, as a binder for rock wool and asbestos fiber in producing industrial insulation products, as an ingredient to create pellets of animal feed from coarse ground components, and in the pelleting of finely divided magnetite concentrates recovered from taconite ore.

The ideal properties of foundry sands may vary considerably as the result of several factors. Some considerations include the casting of metals of different compositions, the desire for a particular surface characteristic of the castings, and the need for a formula which will accommodate a variety of casting sizes. The development of adequate strengths is of primary importance in foundry sands when these sands are in the green (moist), dry, and hot states. Sand characteristics are then matched to suit a particular foundry product. Calcium bentonite as the clay member develops relatively higher green compression strengths, and sodium bentonite higher dry and hot compression strengths in the sand mixture. Accordingly, both common natural forms of bentonite are used by foundries; the strengths of the sand mixtures, whether green, hot, or dry, can be adjusted by varying the mixtures of the clay types.

The bonding properties that are ideal for use with insulation materials, feeds, and taconite ore, are generally comparable to those in foundry sands. Each industry has strength requirements for its products at various stages of processing, and in each case the raw materials consist of a large number of particles which need to be bound together. The bentonite that binds these products well is one which disaggregates into extremely small particles, provides a large available surface area, and allows maximum contact with other product components.

The taconite industry provides an interesting example of the use of bentonite as a bonding agent. The processing of low-grade iron ore, taconite, is made into an economic operation by the following process. The ore is crushed into a fine powder, and the iron particles are separated from other rock particles by means of a magnetic separator. The up-graded iron ore is difficult to handle in powder form. Accordingly, the material is pelletized to aid further processing. Excellent results are obtained when bentonite is used to bond the pellets, and only 12–18 lb of bentonite is needed to pelletize a ton of ore.

A clay-water mixture becomes highly plastic when there is water in excess of that which is bound as "oriented" water by the bentonite. An ingredient capable of developing high plasticity is often added to formulae for ceramic and concrete products. In these cases, the requirement is for the development of a plastic state adequate to allow the raw materials to be easily shaped or molded into the form of the finished product. Frequently a material is needed which will also act as a bonding agent or binder of other ingredients. Therefore, small bentonite additions, which constitute a small percentage of the entire product, function both as plasticizing and bonding agents. Applied in this fashion, the beneficial properties of bentonite are utilized; however, the addition is sufficiently small so that there is no adverse effect on the finished products.

Suspensions of bentonite in water are widely used in industry. The viscosity of an aqueous medium is increased substantially when bentonite is added and mixed in amounts generally less than 10 percent by weight. These suspensions contain bentonite particles which have disaggregated into the colloidal particle range. Therefore, they have similar properties, and respond like other colloidal suspensions. Some of the many uses of bentonite suspensions include application as drilling mud for rotary drills, as fire retardant gel, and as media for suspending materials which range from medicines that are taken internally, to lumps of coal as part of a float-sink or separatory process. The consistencies or viscosities of suspensions best suited for any application are easily controlled by adjusting the amounts of bentonite in water. The largest and also the best known use of bentonite suspensions is as drilling mud. The functions of drilling mud include removal of cuttings from the bore hole, prevention of blow-outs, strengthening of the well bore and reduction of fluid loss from the mud, prevention of weighting agents and cuttings from settling down the well when circulation stops, and lubrication and cooling of the drilling bit and string. The development of these favorable properties in the mud depends on the viscosity and gel characteristics that are contributed by the bentonite. Impermeability of the filter cake is due in part to the fact that the adsorbed water on bentonite is very tightly bonded; also because the many small clay flakes act together to form a nearly perfect lining of the bore hole.

A newer application of bentonite suspensions is as fire retardant material, particularly in combating forest fires. When a stream of water is directed at vegetation, such as a tree, much of the water ricochets off and is lost owing to its high fluidity. When the viscosity of the water stream is increased with bentonite, a greater proportion of liquid is retained on the vegetation. Because of the thicker consistency, suspensions can be dropped from planes to aid fire-fighting. The advantages obviously are greater coverage in a shorter period of time, and accessibility to virtually all locations.

Because of its water-adsorption characteristics, bentonite is used as a material to impede or stop the flow of water. The clay can control flow of water by two methods. In the first case, when dry clay comes in contact with a source of water, the water becomes adsorbed by the clay so that it no longer is free to flow. By this method there is a limit to the amount of water which can be controlled by a given amount of clay. A second water-impedance mechanism is effected, however, after the bentonite adsorbs water. The hydrated or swollen clay becomes impermeable to the flow of additional water. In this fashion it is possible for small amount of clay to impede a large amount of water if the clay is applied advantageously.

Surface Area

Certain industrial problems can be solved best by use of materials that possess a large surface area, and therefore bentonite is frequently used. Carrier materials for chemicals, such as insecticides, are examples of this

application. When the carrier material provides an adequate surface area for the adsorption of the insecticide, the application of the insecticide-carrier mixture has several advantages which include a more even distribution of the insecticide when scattered over a large area, increased durability or life of the insecticide, and also increased effectiveness by keeping the insecticide in the most advantageous position; that is, on the vegetation rather than on the ground.

Another example in which the surface area supplied by bentonite is applied in industry is as an emulsion stabilizer. Briefly, emulsions are formed by mixing and agitation of two immiscible liquids, such as oil and water. One liquid becomes a continuous phase, and the other liquid forms as droplets or globules within it. The ratio in which the two liquids are mixed determines the role of each in the emulsion. When the oil-water interface is strengthened, the stability of the emulsion is increased. Bentonite has a stabilizing effect on emulsions when it is added to the mixture prior to agitation. Apparently, the clay flakes form a thin film at the oil-water interface, and the large surface area of the clay aids in the entrapment of the oily globules as they are broken down by mechanical agitation.

Reactivity

There are applications of bentonite in industry which depend upon its ability to react with materials other than water. This is not to say, however, that reactions do not occur in the uses discussed thus far, because when bentonite is used as an insecticide carrier, for example, there probably are reactions which occur in addition to the "plating-out" of the insecticide on the clay mineral surfaces. The reactions discussed here unquestionably occur between organic materials and clay. These reactions are primary to the bentonite application, whereas reactions between clay and other materials may be considered as secondary in some of the applications discussed earlier.

Reactions between bentonite, or montmorillonite, and amines were initially investigated by Hauser and Leggett (1940) and later by Jordan (1949). They showed that bentonite surfaces could be entirely coated with organic material by substitution of inorganic cations by the amine. When this was accomplished, the clay lost its ability to swell in water. The clay-organic product, however, does swell in a number of organic solvents, and because of this property, a market in industry was created. These products are used as gelling agents in paints, greases and lubricants, and other oil-base media.

Bentonites are also used commercially as decolorizers of oils. The process is fairly simple. Certain oils are clarified by allowing percolation through beds of bentonite in which a selective adsorption of some organic types onto the clay mineral surfaces takes place. The portions of the oil which are darkest in color are removed preferentially by the clay.

Bentonites are also used in industry for their beneficial properties as clarifying agents for products such as wines and beers. Many of the "impurities", or sediment, present in these liquids during their manufacture

are proteins or protein-related compounds. The sediment reacts with the bentonite, and thus can be removed from the liquid either by filtration or sedimentation.

BENTONITE TYPES VS. APPLICATION

Industry uses bentonite more for the physical properties it can develop than for its chemical composition. Accordingly, the greatest tonnage of bentonite is used annually for bonding, plasticizing, or suspending purposes. In these applications, the bentonite is usually in contact with water. Thus the clay-water characteristics are of primary importance to industry. The chemical composition of the bentonite is a consideration only because changes in physical properties accompany changes in chemical composition. There are some exceptions, and generally these can be described as instances where the clay chemistry, as a component in a product, could be a complicating factor.

Sodium bentonite swells or expands to a greater degree than its calcium equivalent. The greatest swelling, however, is not achieved by the pure sodium end-member. Apparently when a small percentage of cation exchange sites are occupied by another ion, such as calcium, a state is developed in the clay which promotes both optimum swelling and fastest hydration.

Comparison of swelling characteristics of sodium and calcium bentonite introduces another factor in addition to that which deals directly with the exchange ion. That other factor is the environment in which the bentonite formed initially. If conditions favored formation of a sodium bentonite, certain structural features were included or excluded in that clay which are different from those that formed when conditions favored calcium bentonite. This is to say that the physical properties of a natural sodium bentonite cannot be developed in a natural calcium bentonite merely by exchanging the associated cation.

Since sodium bentonite has higher swelling capacity, this property necessarily develops higher viscosity in suspensions, greater state of disaggregation, formation of smaller clay particles or greater colloidal properties, and finally larger available surface area when compared with calcium bentonite.

The highest swelling sodium bentonites are used in industry as drilling muds, fire retardant gels, and emulsion stabilizers, where the maximum in viscosity and gel characteristics are required. Many natural bentonites, however, which are primarily the sodium form, disaggregate almost as completely, but have a somewhat reduced swelling capacity. There is only partial correlation between swelling capacity and type and amount of exchange cations associated with the clay. This variety of sodium bentonite, lower swelling than drilling mud quality, but higher swelling than calcium bentonite, has applications such as bonding and plasticizing. Since the clay disaggregation is adequate, as a binder this clay gives excellent strengths to inert material mixtures and provides adequate plasticity by simple adjustment of the clay-to-water ratio.

Calcium bentonites have the greatest market as bonding agents in foundry molding sands. Their higher green strengths are unique among mineral binders considering the small amount of bentonite necessary to impart adequate strengths. By blending both calcium and sodium bentonite, foundrymen develop favorable strength characteristics throughout all phases of the casting procedure and keep a mixture which is compatible with other sand additives such as the cellulose products.

Calcium bentonites have also been used for many years for their ability to decolorize oils. The exact reasons for calcium being better than sodium bentonite for this use are not fully understood.

SUMMARY

Industry uses bentonite for its inherent physical properties, or for the physical properties it can develop in another material or product. A thorough understanding of the chemistry and structure of bentonite, or more appropriately montmorillonite, is helpful when discussing bentonite applications because its physical properties are so closely related to these parameters.

The greatest applications of bentonite are those that involve mixture with water. By adjusting the water content in combination with a given quantity of clay, properties of the mixture can be developed which are utilized by industry for bonding, plasticizing, and suspending applications.

When the water-to-clay ratio is low, this combination is used as a bonding agent for a variety of materials because the consistency of the mixture is more rigid than plastic, and it possesses adhesive properties. Accordingly, bentonites are used to bond foundry molding sands, animal feeds, insulation materials, and taconite.

When the water-to-clay ratio is increased, plasticity develops in the mixture as the water adsorption capacity of the bentonite is just exceeded. This clay-water combination is used as a plasticizing agent in certain ceramic wares and concrete.

Very high water-to-clay ratios ultimately form suspensions which have a multitude of industrial applications, the largest of which is as drilling muds or fluids for the rotary drilling industry. That bentonite suspensions are versatile is shown by such varied applications as in medicines and as fire retardant material in combating forest fires.

The large surface area of bentonite is utilized by application as a chemical, or in particular, insecticide carrier. Surface area is also of primary importance to bentonite application as an emulsifier and emulsion stabilizer.

Bentonite enters into chemical reactions with many organic materials, and certain of these clay-organic products have favorable properties as gelling agents in organic solvents. Bentonite-organic material reactions, however, are also used where the clay acts to decolorize oils and to coagulate sediment in such liquids as beers and wines.

Certain industrial jobs are performed best by particular bentonites in regard to type and quality and attempts are made to match the bentonite

with a particular application. The two most common natural forms of bentonite are sodium saturated and calcium saturated. These two forms have different physical properties, and accordingly are applied differently. Generally, the sodium variety is more versatile and is used for essentially all of the applications discussed here. The calcium variety is directed largely toward the bonding of foundry sands and decolorization of oils.

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