THE DIVERSE USES OF MONTMORILLONITE

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ABSTRACT: The industrial applications of Fullers' Earth are discussed including those of the clay in its natural form, calcium montmorillonite, and after modification by acid activation or sodium exchange. Special consideration is given to uses in oil refining, foundry bonding, civil engineering, and agriculture.

The deposits of montmorillonite clay found in Britain have calcium as the exchangeable ion. These deposits have been excavated and used commercially for a considerable number of years. The Romans used the clay for 'fulling' which was a method for degreasing wool or woollen cloth by treating it with a clay-water slurry.

Although the natural calcium montmorillonite has many applications, ways of improving and increasing its uses have been developed. First it was found that acid treatment increased the ability of the mineral to remove colour bodies from oils and other liquids. This led to the development of a new type of fullers' earth, the acid activated clay. More recently the discovery of a commercially economic process for converting the clay, by ion exchange, into the sodium form, brought all the applications of this swelling clay within the scope of what was originally calcium montmorillonite. The applications of British montmorillonites are therefore considered in three parts, those of the natural calcium fullers' earth, of the acid activated clay and of the sodium exchanged form.

NATURAL CLAY

Pharmaceutical preparations

The best known and possibly the smallest use of montmorillonite is in pharmaceutical preparations where the clay is used in some creams and powders, baby powders, and as face packs and therapeutic muds. This is an extremely small use but it seems to be the one best known to the public.

Oil refining

The main use of the natural clay is in liquid refining, especially for oils, although it has been largely replaced by acid activated forms. In glyceride oil refining, natural fullers' earth is used for bleaching very sensitive oils, such as coconut, where an acidic clay might damage the oil, or for polishing very light oils when all that is
required is the removal of some impurities and, because of the light colour of the oil, no bleach is needed.

Perhaps conversely, natural fullers' earth is used in conjunction with strong sulphuric acid to refine low grade tallow which are very difficult to bleach. In this method the acid actually does much of the bleaching, whilst the clay mineral removes the degradation products and generally tidies up the oil.

Again in oil refineries it is used for soap scavenging. Soaps are formed during the neutralization with caustic soda of the free fatty acids present in the oil and these soaps are washed out before the oil is bleached. In cases where the oil is not completely washed and some soaps remain, the refiners pre-treat the oil with natural montmorillonite before bleaching with activated clay. The natural clay absorbs the aqueous soaps which would impair the efficiency of the activated bleaching earths.

Some mineral oils are refined with natural fullers' earth but again only when very little bleach is needed; the clay acts as a mild bleaching agent, with certain amount of adsorption of impurities, and to a certain extent as a filter aid.

Sugar refining

Sugar refiners use quite a lot of montmorillonite for scavenging and clarifying aqueous sugar solutions. The turbidity of raw sugars is frequently due to colloidal protein particles. These particles carry large negative charges which prevent flocculation, and the addition of montmorillonite can bring about neutralization of these charges and so coagulation. The mechanism of the neutralization might be due to the high valence cations such as aluminium which are part of the clay structure, but the pH of the sugar solution being treated is often quite low and the offending colloidal particles may be removed by being mechanically entrained with the flocculated clay.

Iron compounds present in sugar solutions cause oxidative breakdown and discoloration. These iron complexes can often be removed by ion exchange onto the clay surface.

Catalysts

Natural calcium montmorillonite is used as a catalyst for organic reactions such as the dimerization of α-methyl styrene. Although here again many of the applications have been taken over by acid activated clay.

The large surface area of the clay mineral makes it a suitable support for other catalysts. An example of this is its use, when impregnated with copper chloride, for the sweetening of kerosene. Here the copper salt converts the evil-smelling mercaptans present in the kerosene into odourless disulphides. The clay simply acts as a convenient vehicle for the chemical catalyst.

Other uses

Calcium montmorillonite finds use in a variety of minor applications such as in polishes, especially where a mild abrasive action is required, as a binder for pencil graphite, and as a filter aid for recovering dry cleaning fluid or removing solid particles from used chip oils.
ACTIVATED CLAY

Although, as mentioned previously, natural calcium montmorillonite has some bleaching action, its decolourizing power can be increased manifold by treatment with strong mineral acids such as hydrochloric or sulphuric.

This acid treatment extends the surface and alters the pore size distribution by removing aluminium and other ions from the octahedral layer. It also modifies the clay surface by replacing the exchangeable ions with hydrogen and aluminium.

By varying the amount of acid attack, a series of grades of bleaching clays can be produced which are used to bleach or refine many liquids. Phenolic fractions distilled from coal tar can be bleached by these clays, and sulphur recovered from the purification of domestic gas, can when molten, be refined by clay treatment. There are many others but the major use for activated clays is for the refining of oils.

Glyceride oil refining

Glyceride oils, that is oils from vegetable and animal sources, are used in vast quantities for a number of purposes and the majority of this oil has to be bleached before use. Soyabean, olive, cottonseed oil, and lard are the oils most commonly refined for edible purposes, although there are many more. Those such as palm and tallow, are bleached before being used for soap manufacture, and drying oils like linseed are refined for the paint industry.

Mechanically the bleaching process is a simple operation; the clay and the oil are usually brought together under vacuum at the required temperature and are then separated in a filter press. The exact conditions and the grade of bleaching clay are selected for each particular oil. Generally temperatures in the range 65–105°C are used and the total time of bleach and filtration will be about 1½ hr. The clay dose may vary from ½ to 4% depending on the oil (Andersen, 1953).

Whilst the process of bleaching is simple, the complex mechanism by which the clay removes or reduces colour is not completely understood (Rich, 1964). Among the common pigments in glyceride oils are the yellow-red carotenoids, chlorophylls, xanthophyll, and gossypol. However, the colour bodies may vary with the type of oil, its origin, age, and how it has been processed from seed (Ames, Raymond & Ward, 1960). Damage to the seed during picking or to the extracted oil during pre-treatments such as neutralization, can cause degradation products of very complicated structure. Darkening on aging can be due to the formation of colour bodies by the oxidation of previously colourless precursors. A much quoted example of this is the formation of dark red chroman 5,6-quinone from colourless \( \gamma \)-tocopherol, which is an anti-oxidant present in most vegetable oils (Rich, 1964). Colour formed in this way is very difficult to remove.

Bleaching clays are most effective for removing carotenoids such as \( \alpha \)- and \( \beta \)-carotene. The colour bodies are removed by sorption onto the clay surface although it is possible that oxidation plays some part in bleaching. Unfortunately oxidation may also promote additional colour formation and fix colours already present (King & Wharton, 1949).
Mineral oil refining

Mineral oils such as lubricating oils and other hydrocarbons are refined by treatment with activated bleaching clays. A wider temperature range is used for these oils, some being bleached at 40°C whilst others require temperatures of the order of 200–250°C. At these higher temperatures it is necessary to maintain an inert atmosphere above the oil to prevent oxidation. Steam or nitrogen is used for this purpose and this also strips off any volatiles present.

These hydrocarbon oils can be re-refined after use by a similar treatment with activated bleaching clay. Lubricating oils recovered from the sumps of internal combustion engines make up the bulk of the oil recovered in this way and such oils contain contaminants which are not present in the original crude oil. These contaminants are the oxidation and degradation products of the lubricating oil and its additives. The solid impurities and water are removed by simple filtration, by settling, or by centrifuging. Unburnt fuel is stripped off by steam, and the oil-soluble impurities, which are corrosive and gum-forming, are removed by the bleaching earth.

Many liquids other than those I have mentioned can be bleached by treatment with activated bleaching clays.

Catalysts

Activated montmorillonites are used to catalyse various chemical reactions. The activation process is similar to that used for the bleaching clays. An early example of their use was for the catalytic cracking of petroleum. This process, which is used for increasing the yield and quality of gasoline from petroleum, involves splitting the heavier molecular weight hydrocarbons into lighter ones with lower boiling points. The catalyst used must promote rupture of the carbon to carbon bond near the middle of the hydrocarbon chain. The first cracking catalysts were montmorillonite but synthetic catalysts have now mainly replaced them.

Present uses of activated clays are as alkylation catalysts, particularly for the alkylation of phenols. These alkylated phenols have many uses and are intermediaries in the formation of detergents. Clays are also used to promote polymerization, dehydration and various other chemical reactions.

In addition, the activated clays are used as delicate pH adjusters where the last traces of alkalinity have to be removed from organic liquids. The natural clay is similarly used for the removal of traces of acidity.

SODIUM MONTMORILLONITE

The third type of montmorillonite to be considered is the sodium-exchanged clay. Once an economic method was found for exchanging the natural calcium clay into one which has sodium as the predominant exchangeable cation, all the applications of the sodium clay come within the scope of the original calcium clay. Sodium montmorillonite forms stable suspensions in water at very low solids content which,
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when allowed to stand, form thixotropic gels. These colloidal properties find wide application in industry as binding agents, suspension aids, and plasticizers, and find many uses in civil engineering methods.

**Binding and pelleting**

The foundry industry uses sodium montmorillonite as a binder in foundry moulding sands (Grim, 1962). These sands which are essentially a mixture of sand and clay are used in metal foundries for casting metal shapes. The moistened sand is formed, by ramming, around a pattern. When the pattern is removed, it leaves a cavity of the required shape, into which the molten metal is poured.

The nature of the exchangeable ions and the impurity minerals present affect the fusion temperature of the clay and although some clays are suitable for use in steel foundries, most British clays are used with cast iron and non-ferrous metals, such as aluminium and brass, which have lower melting points than steel.

Natural moulding sands, which contain clay, are used but synthetic mixes of clean quartz sand with sodium montmorillonite are widely employed because their properties can be varied to meet different specifications and because the clay has to be replaced after each casting to maintain the sand properties at the required level, owing to the destruction of the clay by the high temperature of the molten metal.

The montmorillonite imparts green strength, dry strength and many other important properties to the sand. The binding of the sand grains is brought about by milling the sand with the sodium clay and water. The clay breaks down to colloidal or almost colloidal particles which coat the sand grains forming wedges at their points of contact. These wedges hold the sand grains firmly in position and are responsible for both green and dry strength. About 5% of clay is used and 3\textendash{}5% of water.

The water closely associated with the sodium clay (about three molecular layers) is held relatively rigid. Thus, for maximum green strength the water content should be equal to that needed to give only rigid water. A slight increase in the water content leads to the formation of non-rigid layers, giving a certain amount of lubrication and allowing the sand to be formed around the pattern more easily and with the minimum of ramming.

Another use as a binding agent is in the preparation of animal feed cubes and pellets. Here the feed mixtures containing oats, barley, and other cereals mixed with molasses are extruded under pressure into cubes and pellets. These pellets are used for feeding cattle, pigs, and chickens under intensive farming methods or as winter feeds for animals being farmed normally. The feed mixtures have a certain amount of natural binding so that the amount of clay added is not critical as it is with foundry sands. However, the addition of 1 or 2% of sodium montmorillonite gives a hard pellet able to withstand bulk handling. The inclusion of clay in the mixture also makes the extrusion process easier and occasionally serves as a carrier for essential trace metals in the feed.

Similar to its use as a binder, it is used for pelleting iron ore concentrates. Some iron ores have to be ground to very fine powders to aid their separation and con-
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concentration; other ores often contain quite appreciable amounts of fines. Before being fed to the furnaces, these fine powders must, therefore, be formed into larger particles by sintering or pelleting. The pellets are formed by mixing $\frac{1}{4}$–$\frac{1}{2}$% of sodium montmorillonite into the powdered ore and tumbling the mixture in a drum until the pellets build up to the required size.

A similar application brings seeds too small to be handled by seed planting machinery up to the correct size so that the plants do not have to be thinned out later.

**Suspension aids**

Thixotropic dispersions of the sodium clay will keep fine particles in suspension by holding them in the net-like structure of the gel. This property is used in oil well drilling and in less complex, shallower drilling to make up the fresh-water drilling mud (Rogers, 1963).

The drilling mud has many functions. It is pumped down the centre of the drilling pipe to emerge at the bit and returns up the outside. It cools and lubricates the pipe and bit and brings the cuttings to the surface. The mud also forms an impermeable wall cake which stops loss of drilling fluid into the strata and prevents caving-in of the sides. The column of mud must also exert sufficient hydrostatic head to overcome the pressure in the strata thus preventing the formation fluids breaking into the drill hole. For this purpose the drilling mud density can be increased by adding ground barytes or other weighting agents.

Another suspension application is with some fertilizer preparations. These are suspension fertilizers which are liquids containing the active salts in excess of their solubility, the excess being held in suspension by the clay. The requirements of a suspension fertilizer are that it must contain a proportion of the active ingredients, nitrogen, phosphorous, and potassium similar to that found in solid fertilizers. The resultant preparations should be stable and have a viscosity low enough to allow them to be sprayed by simple agricultural equipment.

**Paints and emulsions**

Small amounts of montmorillonite are used in paints to impart some degree of structure but the colour of the clay limits its use for this purpose. They are also used in some bituminous emulsions and mastics and ceramic glazes.

**Civil engineering**

Small amounts of calcium montmorillonite are used in civil engineering but it is the properties of the sodium clay that find wide application (see *Grouts and Drilling Muds in Engineering Practice*, 1963, Butterworths). The sodium montmorillonite suspensions have two principle uses. These are the formation of a water impermeable barrier and the support of the walls of trenches and other excavations. There are many methods used in civil engineering that take advantage of these properties.

(a) Construction of diaphragm walls. This method was introduced into this
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country by the Italian firm I.C.O.S. It is used to construct load bearing concrete walls below ground level. The trench is excavated under a 3–6% clay suspension and provided there is a pressure difference between the slurry and the ground water, a layer of sodium montmorillonite builds up on the sides of the trench. The slurry prevents the sides of the trench from caving in by exerting hydrostatic pressure against this wall cake and shuttering is, therefore, not needed.

When the trench has been excavated to the required depth, the steel reinforcement cage is lowered in and concrete is placed through a tremie pipe into the bottom of the trench. The concrete displaces the clay slurry into the next section where it is re-used.

The alternative methods involve the driving of sheet piles to hold up the sides of the trench and this method with its attendant noise and vibration is often unsuitable in a built-up area. Diaphragm walls are used to lay load bearing walls such as building foundations and were used for constructing the foundations of the Post Office Tower. This method was also used to place the side diaphragm walls of the Hyde Park Underpass before the actual underpass was excavated from between them.

(b) Membrane cut-offs. In this method a water-tight subsurface screen or membrane of a clay–cement grout is formed. The cavity is prepared by driving a series of steel piles into the ground shoulder to shoulder. The rear pile is removed and driven in again at the head of the line whilst the cavity remaining is filled with grout. This procedure is repeated until the complete cut-off membrane has been finished.

(c) Slurry cut-offs. This is another method of preventing the access of water. The trench is excavated under a sodium montmorillonite slurry which prevents the walls from falling in. Then a suitable filler is mixed with the slurry in the trench and this acts as a water-tight cut-off which has no structural strength. This technique was first used in this country to construct a cut-off 7800 ft long around a gravel pit at Harmondsworth. Here the trench was cut down to the impermeable clay at an average depth of 15 ft whilst the water table was at approximately 3 ft. The gravel pit was consequently worked in the dry without lowering the water table outside the cut-off.

(d) Grouting. This is a method of consolidating the ground and making it impervious to water. Clay or clay chemical grouts are pumped under pressure into the ground through injection tubes inserted into previously drilled holes. The grout penetrates the strata and on gelling forms a barrier to water.

When sodium montmorillonite grouts are used alone the gelling depends on the formation of the edge-to-face structure and this can be broken down by vibration or a high hydrostatic head. When irreversible gels with higher shear strength are needed the sodium clay is used in combination with cement or sodium silicate. Grouting has been used on many projects including the tunnels at Blackwall and at Whiteinch under the Clyde. It is also used to prevent seepage from reservoirs.

(e) Other uses. The sodium clay is used as an aid for driving piles into difficult ground and as a sealing blanket for the floors of ponds, reservoirs, and canals.
(Kulkarni & Narain, 1965). It is also used as an additive to concrete and in other smaller engineering applications (Endell, 1950). It is used as a water treatment aid for industrial water, trade effluents, and sewage discharge. Generally speaking, it is used for specialized or difficult cases or when rapid sedimentation is required.

**MISCELLANEOUS USES**

There are numerous other small uses for the various types of montmorillonite. Usually they employ one or other of the properties already considered such as binding or bleaching. A use which takes advantage of a new property is for binding insulating material. Here lithium montmorillonite, formed by ion exchange of the natural calcium clay, is irreversibly dehydrated at temperatures above 200° C (Fullers' Earth Union, 1960). This property, which is due to the small size of the lithium ion, is used to bind fibrous insulating materials such as glass fibre and asbestos which are to be exposed to temperatures too high for organic bonding agents such as starch or resins.

**REFERENCES**


