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COLLOID PROPERTIES OF LAYER SILICATES

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ORGANIZATION

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From the viewpoint of one interested in the structural aspects of colloids, a fortunate condition is encountered in the case of the common clay and soil minerals. It is inherent in the colloidal condition that dispersed or dispersible phases be of such low degree of crystalline perfection that x-ray (or electron) diffraction diagrams are at best less intense and less complete than those obtainable from macrocrystalline solids.

X-ray diffraction studies, first of the micas, and successively of an extended series of related layer silicates such as the brittle micas, the chlorites, talc, and pyrophyllite, have established that a highly stable complex structural unit exists which controls the varied physical properties of these related minerals. It has further developed that this same unit is the assemblage on which the crystallization of the two large groups of clay minerals, the illite group and the montmorillonite group, are based. The configuration of such a layer is illustrated in figure 1. The wide latitude of cation substitutions within this framework has recently been reviewed by Ross and Hendricks (11). For present purposes it is sufficient to observe that, whereas some certain regularity of ion distribution characterizes the macrocrystalline members, there is a range through which the magnitude of residual charge resulting from presence of lesser valent cations or from cation deficiencies gives rise to two major groups of characteristically microcrystalline clay minerals. In the one group charge deficiencies in a layer are balanced mainly by interlayer potassium ions, and the minerals are dimensionally stable and are actually varieties of micas. These are the illite group. The over-all charge deficiencies are about half as frequent as those of the crystalline micas and are considered to arise mainly from the presence of trivalent aluminum ions in tetrahedral coördination. In the other group about equally frequent charge deficiencies arise mainly from substitutions or defects in the octahedrally coördinated portion of the layer and are commonly balanced by sodium and/or calcium ions. These are the montmorillonite group of minerals, and in this group the interlayer ions are readily exchangeable and, in addition, the individual layers are subject to separation from each other by water and are readily dispersible. In nature these minerals are commonly observed to occur with one or two layers of water already interleaved between the characteristic silicate skeleton.

Base exchange is of course commonly thought of as an inorganic phenomenon, but the activity of organic bases in exchange has become a subject of proven interest, following a study by Gieseking (5), and has been utilized by Hendricks (7) to measure the van der Waals thickness of a number of large organic bases.

The water associated with montmorillonite in nature disposes itself regularly in layers between the silicate skeletons, affording characteristic interlayer spac-

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ings which are measurable by x-ray diffraction methods; in addition to the simple interlayer diffraction, some of the better specimens afford a series of integral higher orders of diffraction from the fundamental spacing which establish the fact that the alternating sequence of silicate and water layers is repeated a large number of times without irregularity. In the presence of added water additional layers penetrate between each individual silicate unit, with swelling of the specimen, and regularly constituted "hydrates" have been observed in which as many as four water layers separate successive silicate layers (3). The configuration of such layers and the likelihood of indefinite extension of the mechanism into com-

Exchange cations only on external surfaces of mica, $KAl_2(AlSi_3)O_{10}(OH)_2$

Layer in pyrophyllite, $Al_2Si_4O_{10}(OH)_2$

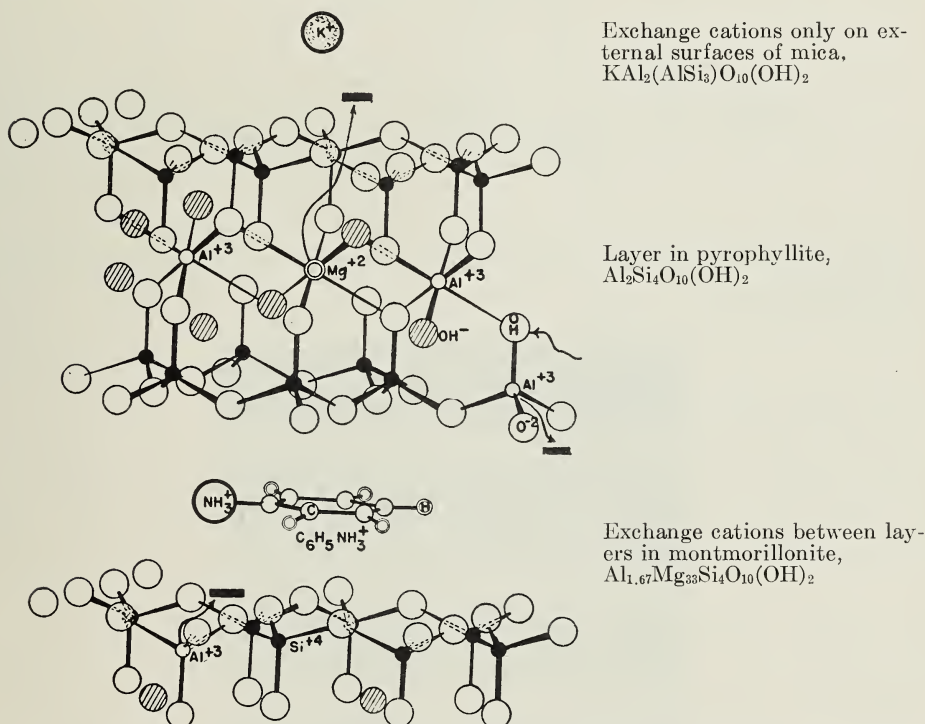Exchange cations between layers in montmorillonite, $Al_{1.67}Mg_{33}Si_4O_{10}(OH)_2$

FIG. 1. The structural relationships of the montmorillonite type mineral with mica and pyrophyllite (after Hendricks).

plete dispersion is apparent from Hendricks' model of the association of such water (figure 2), which is based upon the known hydrogen-bonding properties (8). The concept of what constitutes bound water in this colloid system is thus particularly graphic.

One important commercial utilization of montmorillonite is in the preparation of drilling muds. Figure 3 illustrates the contrasting properties of suspensions of montmorillonite with those of a conventional clay mineral, kaolinite, whose crystalline particles disperse as entities. These diagrams represent the diffraction effects observed upon irradiation of a flowing stream of suspension as discharged through a capillary nozzle. The diagram of the kaolinite suspension

includes all the lines normally observed in solid specimens superposed over the characteristic water halos. The diagrams of the Wyoming bentonite suspension and of the montmorillonite base shale include the normal diagrams for the non-clay mineral accessories in each case, and the normal diffraction effects related to the prism zone—that is, to the lateral extension of the individual silicate sheets.
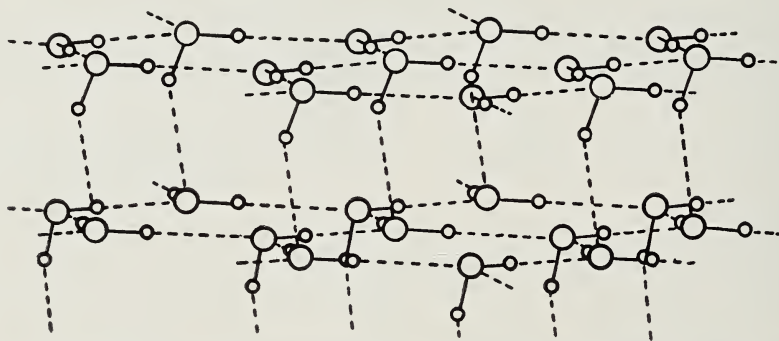

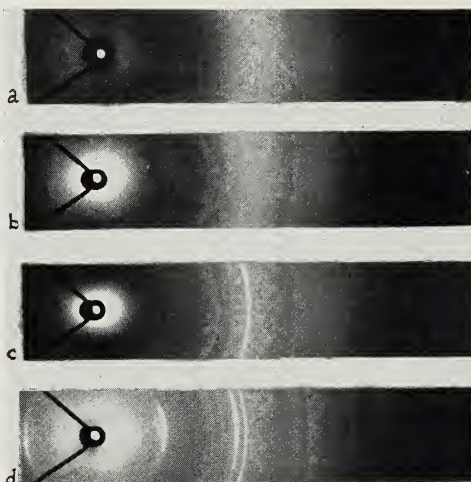FIG. 2. Probable structural arrangement of multiple water layers (after Hendricks and Jefferson).

FIG. 3. X-ray diffraction diagrams of streaming clay suspensions issuing from a nozzle: (a) water; (b) suspension of 5 per cent of Wyoming bentonite in water; (c) suspension of 20 per cent of a montmorillonite containing oligocene shale in water; (d) suspension of 30 per cent of a kaolinitic clay in water. In suspensions (c) and (d) a phosphate dispersing agent was added.

No normal reflections or higher orders of reflection related to any basal spacing are observed. Except for the water halos, there is observed only a remarkably prominent low-angle scattering feature which arises from the dissemination of solid particles in the liquid medium. It is to be noted that of the two examples illustrated the low-angle feature is somewhat more pronounced for the Wyoming

bentonite, a natural sodium bentonite, than for the shale, which is mainly calcium saturated. The sodium bentonite is considered to be rather strictly dispersed down to individual silicate layers, whereas the calcium montmorillonite apparently retains a low degree of order between small groups of a few adjacent layers. One gram of the sodium bentonite appears to furnish as many dispersed particles as 3 or 4 g. of this particular shale.

In a system in which the condition of the dispersed phase is so clearly defined, and in which the nature of the water association upon particle surfaces has been subject to demonstration, a simple graphic mechanism for the striking thixotropic properties of such suspensions is easily visualized. In a set gel most if not all of the water molecules in the system are under the influence of one or more of the silicate lamellae, which are thus both isolated from each other, and at the same time bound together, by their associated water. Under mechanical deformation, moderate disruption of the water coördination permits ready yield, and the entire system may be worked into a suspension of only moderate viscosity by simple attrition of water molecules.

In this same vein it is also clearly true that in a given suspension the partition of water molecules between the "free" and the "bound" condition would be subject to influence by heat or by chemical agents. There is a highly developed art of controlling the viscosity of drilling muds by addition agents which suitably adjust the hydration state.

The flexibility of the above water relationships and the extensive activity of organic bases in exchange suggested promise in investigating the possible relationships with various organic liquids. The nature of the stable complexes resulting from the treatment of montmorillonite with two rather highly specialized types of organic compounds, the polyamines and the polyglycols, etc., has already received some study (1) and the value of this type of reaction in mineralogy is recognized (2, 10).

It seems to be rather generally true that simple polar organic solvents also "solvate" the montmorillonite surface, some of them affording clear instances of double layer complex formation comparable in configuration to those obtained with glycol or with the polyglycols. Such double-layer complexes are probably the general case. Among the amines, which are also active in base exchange, single-layer complexes are obtained with those molecules whose flat cross-section is less than the average area per exchange position for the montmorillonite, but the larger simple amines also exhibit the double-layer configuration. Figure 4 illustrates the nature of the clear sequences of orders of diffraction from the basal spacing which are observed in those cases where a definite characteristic complex formation is realized. In general, this type of complex does not swell in the presence of an excess of the same agent. Their stability is considered to be occasioned by a quite specialized interaction between the actual aliphatic chains and the oxygen-populated clay surface, amounting to something like a C—H$\cdots$O bond. Multiple layers such as those built successively by water would thus not be anticipated.

The recently reëstablished method of thermal analysis has been used effec-

tively in qualitative estimation of the energy of association of water with mont-morillonite under various circumtances (9). For complexes with the more vola-
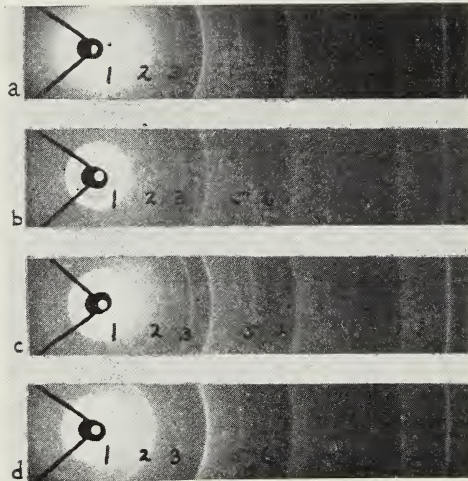

FIG. 4. Typical diffraction diagrams of montmorillonite–organic liquid complexes, (a) with ethanol; (b) with acetone; (c) with the monoethyl ether of propylene glycol; (d) with the dimethyl ether of tetraethylene glycol. The more prominent higher orders of diffraction from the base are indicated.
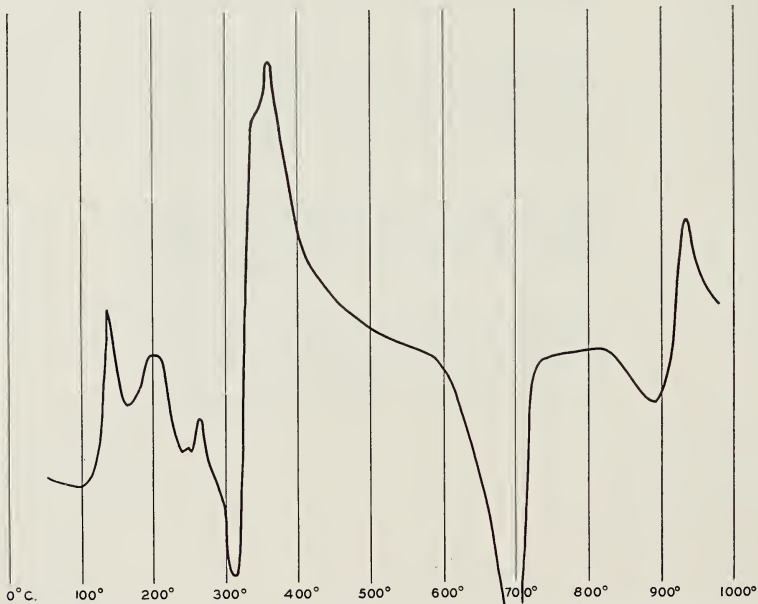

FIG. 5. Differential thermal analysis curve for complex of Wyoming bentonite with the dimethyl ether of tetraethylene glycol.

tile liquids, evaporation is far too ready at room temperatures to permit the application of such a method, but more stable complexes (as illustrated in figure

5 by that with the dimethyl ether of tetraethylene glycol) exhibit distinct, although not interpreted, effects. A series of amine complexes, stabilized by their activity in exchange, afford greater promise. In figure 6 are reproduced the differential curves for complexes with three normal primary amines, in the order of increasing chain lengths, and for an example of a quaternary ammonium base.

0°C. 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°
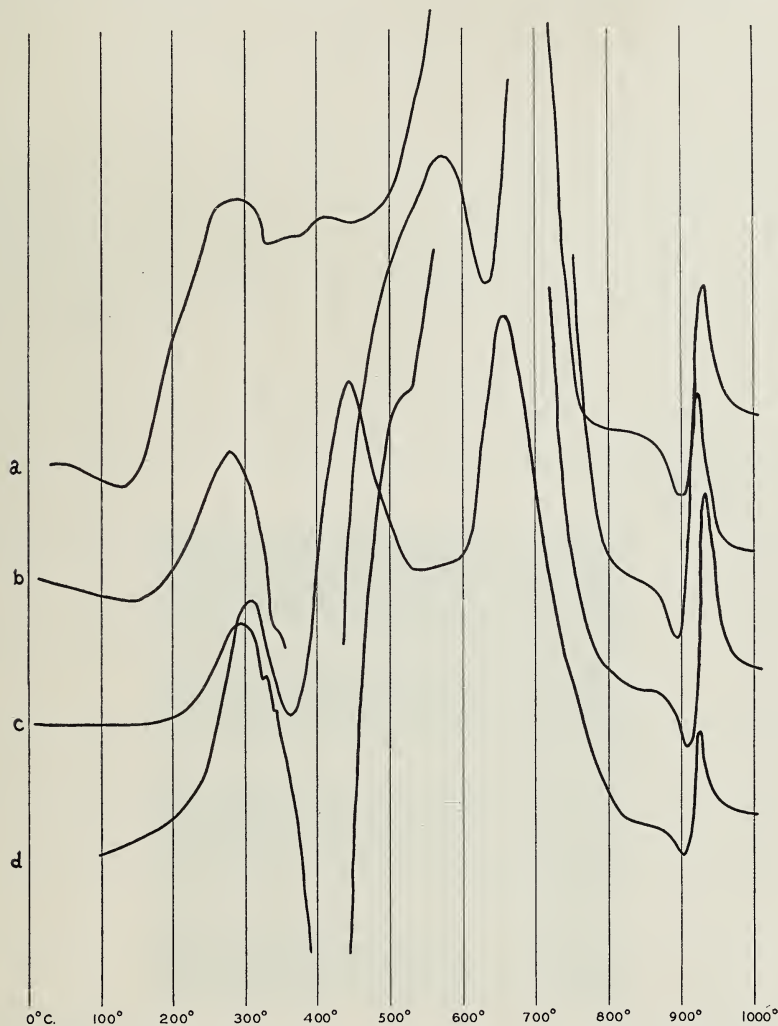
FIG. 6. Differential thermal analysis curves for dry complexes of Wyoming bentonite with amines: (a) butylamine; (b) dodecylamine; (c) octadecylamine; (d) dimethylcetyl-laurylammonium bromide.

The common feature of these curves is the shoulder indicating initiation of an endothermal reaction at around 300°C. In the registration of these thermal curves, it is also common practice to register simultaneously a record of the furnace temperature itself, such record being normally a smooth line of uniform gradient. Figure 7 is a reproduction of the composite record for the complex

with octadecylamine. On this curve it is noted that at about 400°C., where the specimen temperature is still markedly below the reference temperature, a sudden combustion has heated up the whole furnace. The same effect, but less intense, is observed with the dodecylamine complex.
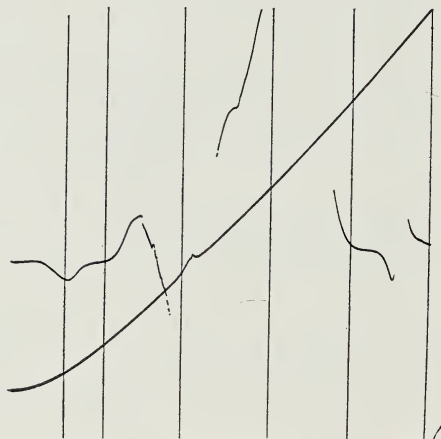
FIG. 7. Differential thermal analysis trace as in figure 6a (but not dry), showing the furnace temperature trace.
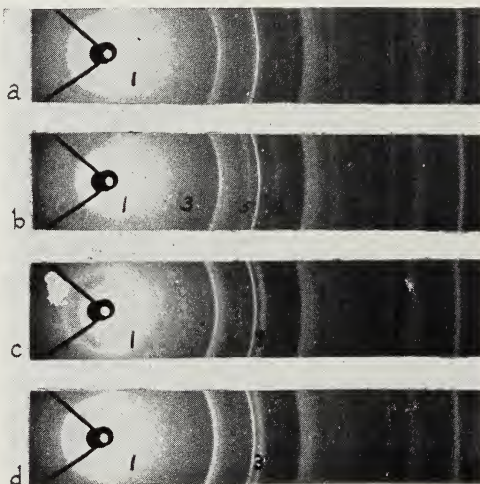
FIG. 8. X-ray diffraction diagrams of amine complexes with Wyoming bentonite: (a) complex with butylamine; (b) complex with dodecylamine; (c) butylamine complex heated to 280°C.; (d) octadecylamine complex heated to 400°C. Essentially equivalent diagrams result from heating of each complex within equivalent temperature range.

Materials being subjected to thermal analysis can, of course, be withdrawn at any chosen point and are available for examination. In figure 8 are reproduced x-ray diffraction diagrams for two amine complexes and for specimens withdrawn at about 280°C. and about 400°C. The complex cell heights have been altered

from those characteristic of the respective amines to a stable configuration of height about 12.8 Å., a figure below that which would accommodate one aliphatic chain but compatible with an alternation of montmorillonite layers with graphite. The endothermal feature remarked above can now be identified as the dehydrogenation of entire aliphatic chains; the released hydrogen ignites in the furnace atmosphere to overheat the whole specimen block sharply, and the coked carbon is left between the silicate layers, eventually burning off at higher temperatures. In table 1 are analyses of prepared coked specimens heated in an open oven to the indicated temperatures.

The carbon layers are not truly graphite. An ideal graphite layer would provide about 28 g. of carbon per 100 g. of ash. The deposit is more comparable to a single layer of petroleum coke, although it may well be partially graphitized. The hydrogen contents cited in table 1 are not subject to the degree of accuracy normally realized in hydrogen determinations because of the necessity of correction for water expelled from the silicate framework under the ignition conditions,

TABLE 1.

Analyses of prepared coked specimens

SPECIMEN	GRAMS PER 100 G. OF ASH		
	N	C	H
Octadecylamine–bentonite	1.7	26.2*	4.8*
Same heated to 275°C......................	Not determined	14	0.6
Same heated to 400°C......................	1.0	8.5	0.23

* Calculated from per cent nitrogen.

but are rather to be looked upon as maximum figures. The coke composition is clearly no more than one hydrogen atom to two carbon atoms.

The degradation of hydrocarbon chains of this sort to coke is presumably the ultimate in catalytic cracking. The activation treatment of natural montmorillonite clays for cracking seems only to be a suitable preparation of the oxygen-populated clay mineral surface to afford this dehydrogenation to only a useful degree.

The aspects of the colloid chemistry of this type of silicate layer which are outlined above are consequences of the phenomenon of "bound water" and the analogous concept "bound solvent." The same silicate skeleton exhibits another separate degree of water association in that part of the skeleton which includes hydroxyl ions. Far less is understood about these hydroxyl water relationships, and there is apparently less latitude of possible variation, but it is at least readily apparent that the dehydroxylated silicate skeleton is capable of reassociating with itself hydroxyl water of markedly lesser association energy than that of the natural structure. Figure 9 is a series of thermal analysis curves taken from a recent study of this feature (6). Illustrated are the thermal curves of a Wyoming bentonite and curves of the same bentonite after firing to various temperatures
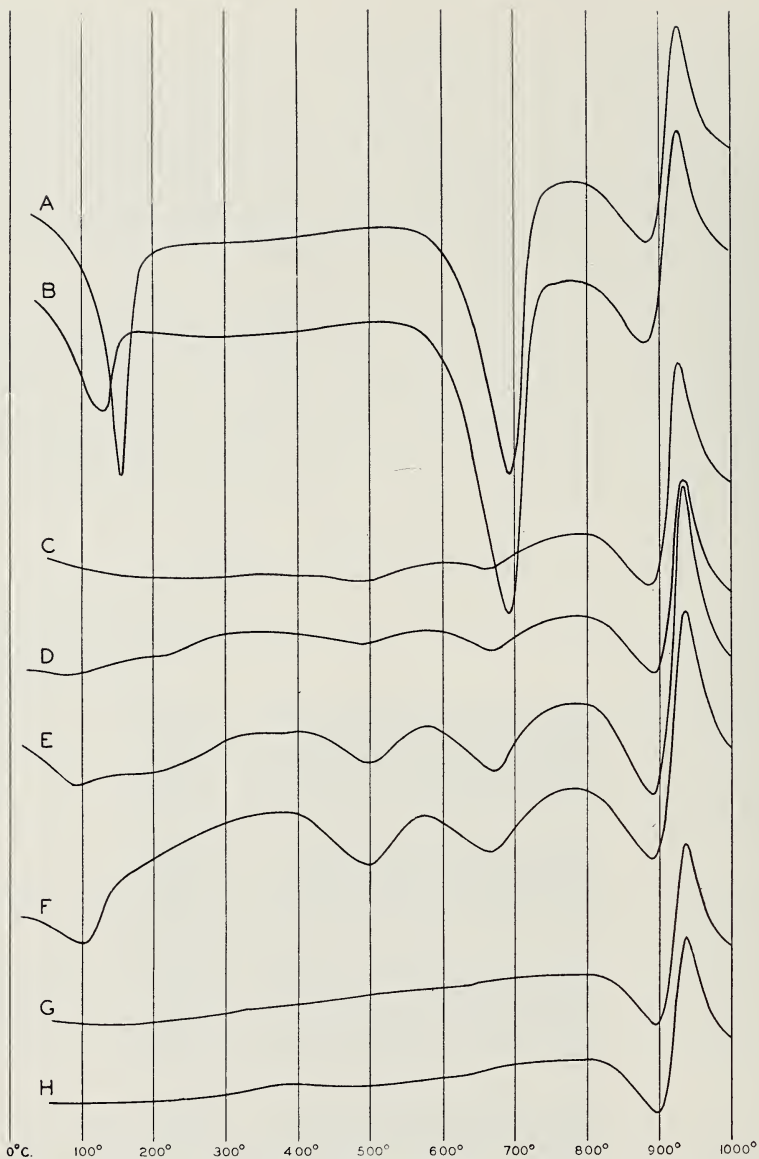
Fig. 9. Differential thermal analysis curves of dehydrated and rehydrated Wyoming bentonite.

A. Mill-run Wyoming bentonite
B. Heated to 500°C. for 1 hr.; curve run after standing 13 days
C. Heated to 600°C. for 1 hr.; curve run after standing 11 days
D. Heated to 600°C. for 1 hr.; curve run after standing 68 days
E. Heated to 600°C. for 1 hr.; curve run after standing 146 days
F. Heated to 600°C. for 1 hr.; curve run after standing 268 days
G. Heated to 800°C. for 1 hr.; curve run after standing 76 days
H. Heated to 800°C. for 1 hr.; curve run after standing 268 days

with rehydration under laboratory conditions.   It is perhaps significant that it
has been found in catalyst activation and regeneration that the use of steam to
maintain a hydroxylated active product is effective in preventing the suscepti-
bility of catalysts to sulfur poisoning (4).

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