

Exchange Adsorption by Clays of Large Organic Cations

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Introductory Remarks by the Chairman: Scientific study of the exchange adsorption on clays of large organic cations goes back to the early thirties of this century. The results of these studies are presently employed with great success in the manufacture of paints, lacquers, stains and lubricants to give superior consistency properties of these materials and improved resistance of the protective films formed by them.

It should be a source of satisfaction to the highway engineer that his own study and practical application of the exchange reactions of large organic cations also go back to the early thirties and that present limitations in general use are due not to lack of success but to the economic factor of lower unit prices of stabilized soils and other structural materials as compared with those of paints, lacquers, and greases.

Gieseking, a pioneer in the study and practical application of these reactions, has prepared an authoritative and precise paper on this subject which promises to become of increasing importance in the field of soil stabilization.

● Clays and clayey soils having high cation-exchange capacities also have high water-adsorbing capacities. These clayey materials normally become gelatinous when associated with large amounts of water. They retard the flow of water through soil materials, they swell when they become wet, they shrink upon drying, and when wet, they tend to flow and shear when stresses are applied to them.

The above properties are useful in a few engineering applications, but there are many engineering applications where the above properties would make a material unfit for use. Saturation of clays with large organic cations destroys the forces that attract water molecules and may possibly be a means of ameliorating clays for certain types of engineering uses.

ALTERATION OF THE PROPERTIES OF CLAYS BY ORGANIC CATION ADSORPTION

The clays in natural soil materials are normally saturated with exchangeable calcium, magnesium, hydrogen, or sodium or any combination of these cations. These cations can be exchanged by any other cation. Such reactions are equilibria reactions which can be forced to completion by any of the chemical methods used in forcing equilibria reactions to completion.

Cernescu (1) was the first to show that the exchangeable calcium in Grossalmer-

oder clay could be exchanged by large organic cations. In 1933 Gieseking (4) noted that a number of large colored cations (positive dyes) were strongly adsorbed by clays and that clays saturated with these cations no longer associated with water to form gels.

During the time these organic cationic clay complexes were being prepared, Winterkorn (12) demonstrated to the author that clayey soils saturated with large organic cations associated readily with asphaltic materials to give soil materials which could be formed in strong, somewhat resilient masses which were resistant to the attack of water. The observations of Winterkorn were in line with the observations of Harkins (7) in which he showed that "like dissolves like."

Gieseking and Jenny (6), Gieseking (5), Hendricks (8), Jordan (9, 10) and Jordan, Hook, and Findlayson (11) have presented sufficient data to show that any soluble organic cationic compound can be expected to be strongly adsorbed by clays by exchanging the organic cation for the inorganic cations on the clays. Jordan and his associates have published many data to show that clays saturated with organic cations have hydrophobic (water-hating) yet organophilic (organic-loving) complexes.

The cheapest and by far the most-common organic cationic compounds are the amines. The amine cations are ammonium ions in which one, two, three, or four of

the hydrogens of the NH_4 ion have been replaced by organic radicals. The radicals may be single carbon methyl radicals, they may be (within the limits of solubility, geometric or steric compatibility, and reactivity) composed of long chains of carbon atoms, or they may be composed of various combinations of phenyl, benzyl, or naphthyl rings.

The analogy of the exchange between a natural sodium clay and the ammonium ion and the completely substituted organic ammonium ion can be shown by the following reactions:



Jordan (10) has shown that the more completely the clay particles are covered with organic cationic material the more organophilic the clay becomes. He has

calculated that $\text{N} \begin{matrix} \text{CH}_3 + \\ \text{CH}_3 \\ \text{C}_{16}\text{H}_{33} \\ \text{C}_{16}\text{N}_{33} \end{matrix}$ gives 40 percent

in excess of the amount of organic material necessary to completely cover the surfaces of Wyoming bentonite crystals when saturated with this organic ammonium ion. At

saturation with $\text{N} \begin{matrix} \text{H} + \\ \text{H} \\ \text{H} \\ \text{C}_{16}\text{H}_{33} \end{matrix}$ his calculations

show only 72 percent of the surface covered with organic material.

Jordan and associates (11) have shown that, when the surfaces of Wyoming bentonite are completely covered by large adsorbed organic cations, the bentonite readily forms gels with toluene a nonpolar liquid. Other observations showed that bentonite incompletely covered with organic cations requires the addition of a small amount of a polar substance, such as an alcohol, to the toluene before good gelation is obtained. Similar systems gave poor gelation when large amounts of alcohol were added to the toluene. These observations show that organic ammonium bentonites can be prepared that are extremely organophilic.

Winterkorn (13) has shown that a number of soils were stabilized against the effects of alternate wetting and drying and alternate freezing and thawing by treating the soils with a mixture of 70 parts aniline to 30 parts furfural. Under the weakly acid

conditions which he used, it would be expected that his postulation of the formation of a Stenhouse dye is correct. Since the Stenhouse dye tends to act like a divalent cation in acid solutions, Winterkorn's 6-percent treatments should have been sufficient to saturate all of the soils which he used with this organic cation and the 2-percent treatments should have been sufficient to saturate all of the soils except those with the very highest cation-exchange capacities.

The author has found that Wyoming bentonite, nontronite and Ipava clay, when saturated with various organic cations do not adsorb as much hygroscopic moisture (25 C. and 96 percent relative humidity) as the corresponding natural clays. These clays are montmorillonitic clays. The results are shown in Table 1.

TABLE 1

HYGROSCOPIC MOISTURE ADSORBED BY UNTREATED AND ORGANIC AMMONIUM TREATED WYOMING BENTONITE, NONTRONITE, AND IPAVA CLAY. STORED AT 25°C. AT 96% RELATIVE HUMIDITY FOR 10 DAYS.

Treatment*	Wyoming bentonite	Nontronite	Ipava clay
	% H ₂ O	% H ₂ O	% H ₂ O
None	20.2	19.3	8.5
Aniline	9.5		6.2
Pyridine	10.4	11.2	5.9
B-naphthylamine	4.0	8.2	6.1
Brucine	12.9		5.7
Methylene Blue	9.2		
Malachite Green	7.1		
Janus Green	6.6		
Magdala Red	5.9		

* All of the organic substituted cations were used in association with chloride anions except magdala red which was used in association with acetate anions.

The differences between the treated and untreated Ipava clay are not as striking as those for Wyoming bentonite and nontronite. This is true because the natural Ipava clay contains organic materials and is already partly saturated with organic cations formed during the decay of nitrogenous vegetative materials.

THE RESISTANCE OF CLAY ADSORBED ORGANIC AMMONIUM CATIONS TOWARD MICROBIOLOGICAL DECOMPOSITION

If the organic ammonium cations are to be used in ameliorating clays for engineering uses, they must resist microbiological decay for a reasonable time. No definite answer is available to this problem, but the

work of Ensminger and Giesekeing (2) and Erickson (3) indicate that clay-adsorbed cations would be expected to be more resistant toward decomposition than the unadsorbed cations. Ensminger and Giesekeing found that clay-adsorbed proteins were more resistant to enzymatic hydrolysis than unadsorbed proteins.

Erickson found that clay-adsorbed amino acids are more resistant to enzymatic and chemical hydrolysis, oxidation, deamination, and decarboxylation than unadsorbed amino acids. The proteins and amino acids are organic ammonium ions. They are easily hydrolyzed and decomposed by the enzyme systems of microorganisms when not protected in some way.

The studies of Ensminger and Giesekeing and Erickson indicate that other, more-stable organic ammonium cations may possibly be still more resistant to decomposition when adsorbed on clays.

COST OF SATURATING CLAYS WITH ORGANIC AMMONIUM CATIONS

Aniline hydrochloride was quoted in the December, 1953, markets at 22 cents a pound. A clayey soil with a cation-exchange capacity of 25 milligram equivalents per 100 grams, or 25 millipound equivalents per 100 lbs. of soil requires 65 lbs. of aniline per ton to saturate the clay with this organic ammonium cation. This amounts to approximately \$14 per cubic yard. Dimethyldioctadecyl ammonium chloride, which Jordan found to be most effective in "waterproofing" clays, was quoted at 37 cents (75 percent purity) in December of 1953.

Since dimethyldioctadecyl ammonium chloride is a larger molecule, and allowing for impurities, calculations show that it takes six times as much of this compound as aniline hydrochloride to saturate a clay. From this we find that it costs approximately \$77 to saturate a cubic yard of soil with dimethyldioctadecyl ammonium chloride, if the soil has a cation-exchange capacity of 25 milliequivalents. Soils with lower exchange capacities would naturally require proportionately smaller amounts of the organic ammonium salts to saturate them.

Winterkorn's results (13) suggest that only a fraction of the exchange capacity

would need to be occupied by organic ammonium cations in order to render soils more easily stabilized with asphaltic materials. If this should be true, the cost of the combination might possibly be within practical limits, especially in cases where other materials for construction were not available.

PRESENT USES OF ORGANIC AMMONIUM CLAY COMPLEXES IN INDUSTRY

Manufacturers of paints, lacquers, and stains are using the organophilic dimethyldioctadecyl ammonium bentonite to inhibit settling of pigments and to give a tougher and more-resistant film after the paint has dried. Lubricant manufacturers are using this same organic cation: bentonite complex to thicken greases and to prevent the melting of greases at high temperatures. Asphalt manufacturers are adding this compound to asphaltic materials to make their product resistant to summer heat.

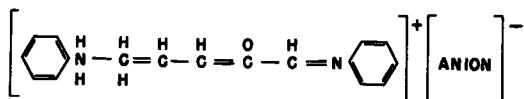
CONCLUSIONS

It is evident from the results reported by Jordan and associates, Winterkorn, and Giesekeing that organic-ammonium-saturated clays are more hydrophobic than natural clays. Jordan has shown that these complexes are more organophilic than the natural clays. Winterkorn has shown that aniline-treated soils are more stable toward alternate wetting and drying and alternate freezing and thawing than the corresponding untreated soils.

Saturation of natural clays with organic cations is an expensive operation. It appears that the presence of only small amounts of organic cations on the clay surfaces might prove to be beneficial in certain soil-stabilizing operations. Further studies should be made to show the effects of various degrees of organic-cation saturation on the clay-water relationships of a number of clayey soils. Prohibitive costs might be avoided by these treatments if only a low degree of saturation with the organic cation were required. The organic ammonium clay complexes are already in widespread usage in high unit cost materials such as paints, lubricants, and asphaltic materials.

with a percentage ratio of 70 to 30, about half of the aniline would be free to be used as a large organic cation for exchange reaction with the soil exchange complex.

On the other hand, Winterkorn's work was concerned mostly with naturally acid or acidified soils and beach sands. Winterkorn states that according to literature and to his own experiments it is probable that using the 2-to-1-aniline-furfural ratio, the following molecule results:



The structure of this molecule indicates, on one hand, the cationic nature of the substance which fills Geiseking's demand for large organic cations that are able to replace natural exchange cations in the soil. On the other hand, it is also obvious that a polar compound of this type tends to polymerize due to its large number of double bonds, since double bonds are always a sign of great chemical activity because of their unsaturated character.

It may be of interest that this compound contains even a vinyl-alcohol group - $\text{C}(\text{H}) = \text{O}$ - which is known as one of the most reactive groups for modern plastics.

From the point of view of the very-strong trend of aniline-furfural towards condensation and polymerization it seems to be more likely that in a mixture of 70 to 30 (aniline to furfural) the 2-to-1 compound is actually formed instead of the 1-to-1 furfuraldehyde-aniline compound. The 2-to-1 compound is, of course, a large organic cation and acts in accordance with Geiseking's explanation of the effect of large organic cations on the water affinity of soils. Consequently, a compound of the above-mentioned character is able to accomplish two principle purposes: (1) giving the soil particles water repellent properties by base exchange and (2) cementing the particles together and giving to the system strength by polymerization.

It must be mentioned that the 70-to-30 combination in amounts from 2 to 6 percent by weight of the soil had given good results with respect to compressive strength and weathering resistance, of soils treated with it (2).

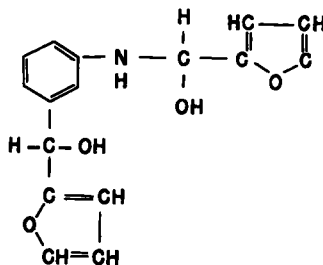
As aniline is higher in price than furfural and will probably always be more im-

portant as a valuable material in other chemical branches, it must be considered as desirable to reduce its proportion to the lowest possible limit. Of special interest in this connection is the work of A. Tager (3), who extended the use of the aniline-furfural method to alkaline-reacting soils. He obtained good results in stabilizing soils with a combination of 1 percent of 3-to-2 aniline-furfural and 1 percent of hydrated lime. This shows the ability of furfural to react in various proportions with aniline and other aromatic amines at different hydrogen-ion concentrations.

Furthermore, Winterkorn had already reported (2) that besides the maximum strength reached with an aniline-furfural ratio of 70 to 30, reasonable compressive strength is obtained already with an aniline-furfural ratio of 30 to 70, and that there probably exists another strength maximum in the range of about 30 to 50 percent of aniline, provided that a proper amount of catalyst is used. This catalyst should influence first of all the pH value of the system.

As results of Winterkorn's work show, addition of a certain amount of acid increases enormously the compressive strength of soils mixed with two percent of a 35-to-65 (aniline-to-furfural) combination. Though this catalytic effect is not uniformly observed for all the different ratios of aniline to furfural, it may be of special importance within the range of 35 percent to 65 percent of aniline.

A ratio of 35 to 65 of aniline and furfural in weight percent approximately equals a molecular ratio of 1 to 2. The structure of a chemical compound with such a molecular ratio of the two constituents is probably the following:



This compound must also be considered as an intermediate product, tending to form spontaneously resins of higher molecular weight. The analogy with phenol-formaldehyde condensation is obvious.

first part of this letter would be expected to form in Tager's process.

Furfural enters into many different types of reactions. One wonders if anyone is able to comprehend all of the possibilities

and all of the conditions that might tend to alter the courses of the reactions. We can be sure, however, that some of the products of the reaction between furfural and aniline will be large organic cations.

Microbiological Factors in Soil Stabilization

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Introductory Remarks by the Chairman: It is a maxim in the carbon economy of the biosphere that all carbon compounds formed must be destructible in order to avoid carbon starvation and to maintain life as we know it. A great role in this destruction is played by bacteria and fungi. During the last 20 years the probable contribution by microorganisms to destruction under certain conditions of stabilized soils and of other construction materials containing organic matter has been mentioned a number of times in the engineering literature. But this awakened little interest and less reaction among highway engineers.

The problem became acute, however, during World War II, when airfields successfully waterproofed by means of small amounts of natural resin derivatives returned to their previous unstabilized condition within relatively short periods of time. It was on that occasion that the Road Research Laboratory in Great Britain sponsored a thorough study of this problem at the famous Rothamstead Agricultural Experiment Station. The man entrusted with this investigation was Jones, who did a beautiful job in identifying and isolating the microbial culprits and in exposing their working methods.

Jones, who has long since left the field of soil stabilization research, has taken time out from pressing and important medical research to give us an account of the important role microbiology plays in certain types of soil stabilization.

● IN recent years, interest in the problem of soil stabilization has arisen in two separate contexts: (1) on account of the intimate relation between soil structure and the important problem of erosion (and in relation to the water and nutrient supply to the living plant) and (2) on account of its relationship to civil-engineering problems of road construction.

In both these cases, variations in the microflora (and microfauna) of the soil will occur and will be of particular importance when foreign readily decomposable materials (such as the resins currently used) are added. The use of cohesive soil materials for construction purposes is of considerable antiquity. Adobe construction is still widely used in the world, even at the present, and (as archaeological find-

ings disclose) was of yet greater importance in times past.

One important feature of the soil and mud materials used was soon established: under wet conditions, mechanical strength is soon lost. Cohesive soils will carry a heavy load as long as they are dry, but when they become wet, the individual soil particles become surrounded by a water film which acts as a lubricant between the platy surfaces of the soil clays and so renders them susceptible to shearing motion, and the soil degenerates into mud.

If the pressure applied to such a soil by a heavy load is spread over a large area, as with the concrete mattress frequently used in road construction, sufficient support is present. Otherwise, depression of that area will occur on account of the plas-