Characterization of Clays and Clay-organic Complexes

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INTRODUCTION

Clay-minerals investigations have produced strong evidence of some sort of reaction between the component parts of clays and organic matter. Fundamental changes in the nature of the reactants like, for instance, decolorization of oils when in contact with clays, and variation in the optical properties of the clays, have inspired scientists to carry out further studies in an attempt to determine possible bond mechanisms responsible for such changes.

In the present study an effort was made to determine the nature of linkages, if any, between blackstrap molasses, distillery slops, and slops active residue and soil colloids extracted from Evesboro, Whippany, Fe, and Guánica soils. (Fe is not an iron soil; this word means "Faith" in English.)

REVIEW OF THE LITERATURE

Hunt (9)[2] examined 15 different clay minerals using infrared rays and found that each had absorption bands characteristic of the individual clay mineral. In all clays a common strong band was found in the 1,100 to 900-cm.$^{-1}$ range. He suggested the use of this tool as an aid in identifying clay minerals.

In 1957 Holmes and Toth (8) postulated the existence of a Si-O-C link occurring with kaolin at extremely high concentrations of S-17. They considered this bond to be of special significance since the carbon of this linkage is not carbonyl carbon.

Michaels and Martin (10), working with montmorillonite and illite, noted a marked increase in bonded OH and a corresponding decrease in free OH bonds. Considering the relatively small number of OH groups in montmorillonite, it is believed that the detection of linkages of this type is rather difficult to observe.

Brydon and Sowden (3) have shown that amino groups are in many instances involved in the reaction between organic matter and soil mineral constituents. Others (7) have shown that organic cations, such as those containing the amino group, will be adsorbed at cation-exchange sites by montmorillonite. Soil-conditioning chemicals being anionic in nature, have

been shown to protect soil aggregates against dispersive forces. X-ray work has definitely shown that organic anions do not enter the interlamellar spaces of expanding lattice clays, and this has led to the suggestion that organic anions are adsorbed on, and form bridges between the edges of clay crystals.

Hoffmann and coworkers (7) showed that the C-axis dimension of montmorillonite varied following treatment with alcohol, acetone, and ether. Ensminger and Geiseking (4) showed that organic ions could be sorbed on the basal plane surfaces of montmorillonite. This suggested that organic compounds with polar-active groups could be adsorbed by clay minerals.

Several organic cations are known to contain basic amino groups. It is the reaction between these compounds and the clay minerals that has been studied in greatest detail. Hendricks (6) found that some of the organic ions studied were oriented between the montmorillonite layers in such a way as to cause minimum expansion of the layers. This adsorption between the layers is known to render the organic compounds quite resistant to microbial degradation. The adsorption of organic ions also changes the properties of the clay mineral and, for example, swelling is greatly reduced.

MATERIALS AND METHODS

Infrared absorption analyses were made of selected samples using a double beam Perkin-Elmer, self-recording infrared instrument. Sodium chloride prisms were generally used, but Irtran was used when the samples were dispersed or dissolved in water.

The clays used in these determinations were those isolated from Guánica clay, Fe clay, Whippany clay, and Evesboro loamy sand, all poorly drained soils. Two micron-sized clays were separated by sedimentation.

Complexes were prepared by reacting 9 parts of clay to 1 part of slops, or with molasses, or with clay-slops active residue. Spectra of the clays and those of the slops, molasses, and slops active residue complexes were all examined. Nujol[3] was the material used to mull the clays and clay-organic material complexes. Correction for the peaks due to Nujol were made on most spectra.

Since montmorillonite was the dominant clay mineral in the clay fraction of both Guánica and Fe soils (figs. 1 and 2), and since both molasses and slops are known to contain amino groups, an effort was made to determine whether a shift in the 001-spacings could result from the adsorption of these materials. X-ray diffraction spectroscopy studies using an RCA-Leiments crystalloflex IV X-ray diffractometer were made on samples

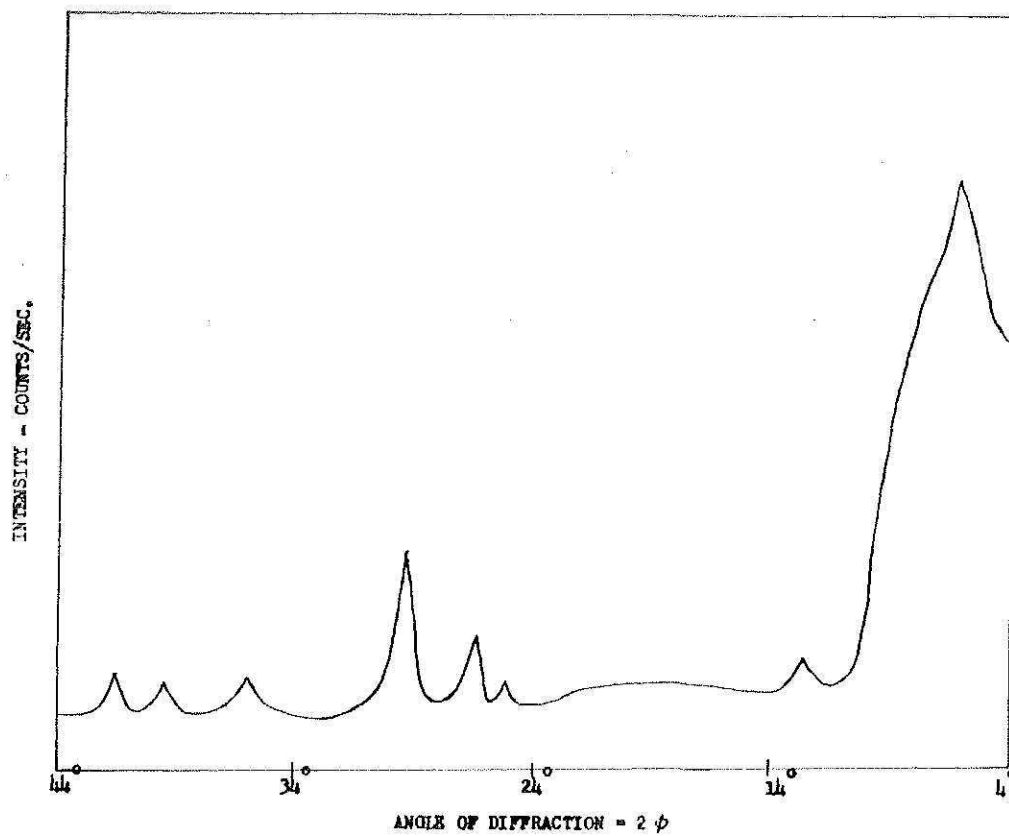[3] Trade name used to provide specific information; this does not imply endorsement or recommendation.

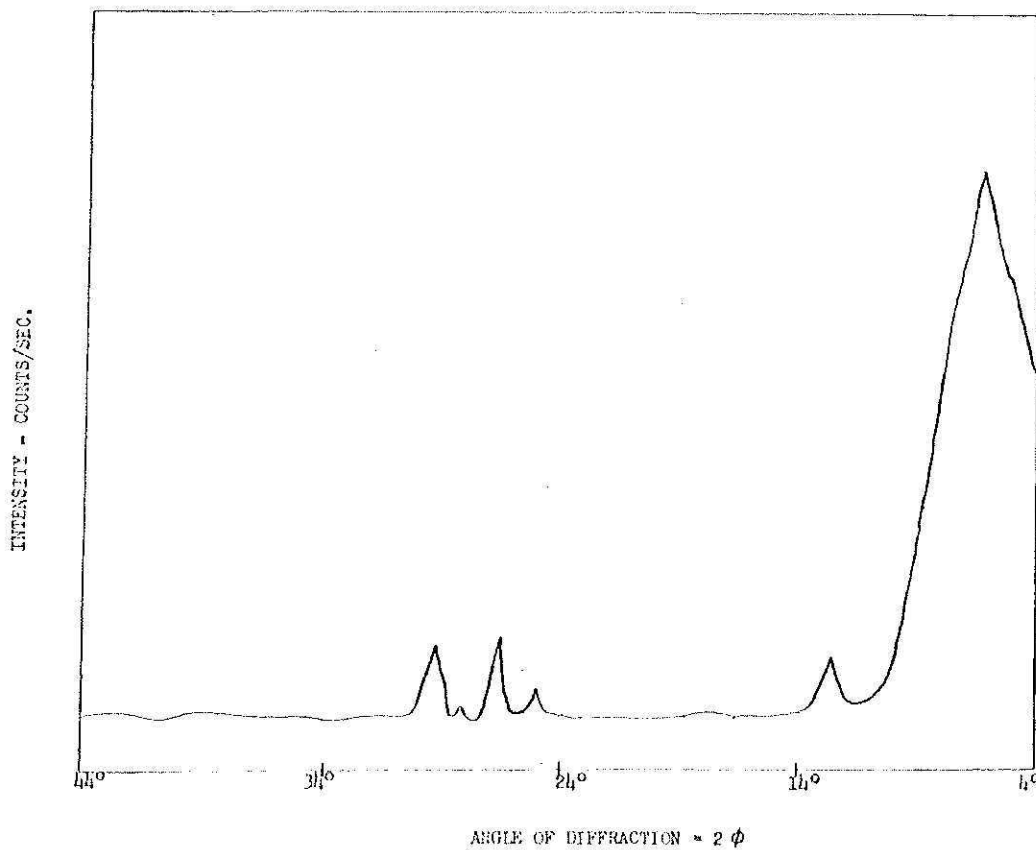FIG. 1.—X-ray diffractogram of clay fraction of Guánica soil.

FIG. 2.—X-ray diffractogram of clay fraction of Fe soil.

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mounted as thin films on glass slide. The slides were mounted in a sample-holder and scanned on the diffractometer through an angle of 3° to 9°, since it was intended to determine whether a shift occurred in the 001-spacing. In order to check the X-ray diffraction studies, different levels of
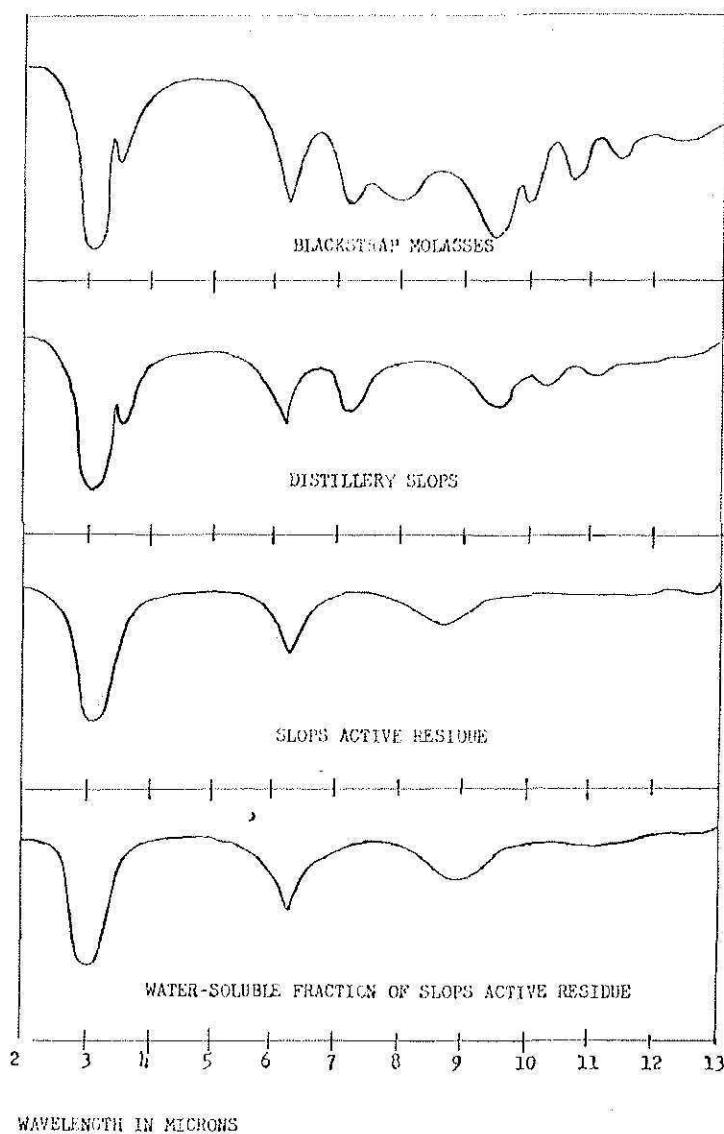

FIG. 3.—Infrared spectra of the organic materials.

slops were brought to equilibrium with a known amount of soil of both Guánica and Fe clay. Cation-exchange capacity was determined in them by the sodium-acetate method (1).

RESULTS AND DISCUSSION

The spectra of the clay fractions of these soils are presented at the top of figures 3 through 7. All clays except the fraction isolated from the Evesboro

soil showed the presence of unbonded OH groups. These bands appeared in the region of 2.75μ. The bonded hydroxyls caused a marked absorption in the 3μ-region of all four clays studied. The somewhat pronounced peak at 6.1μ has already been assigned to adsorbed water. The peaks at 6.90
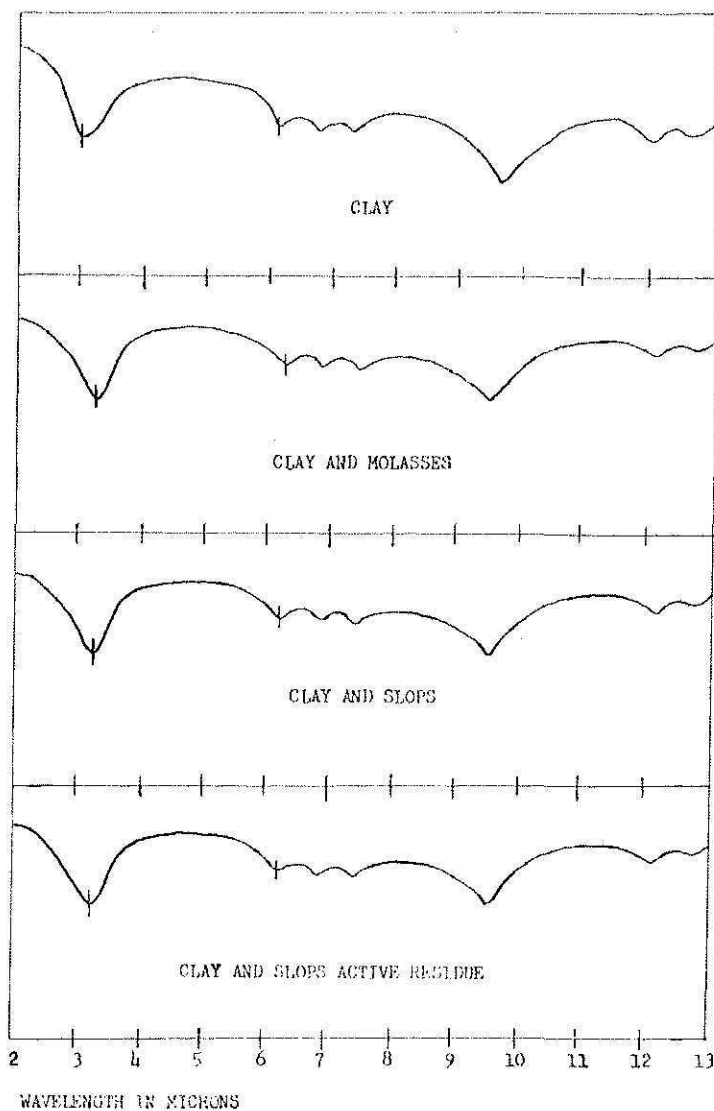

Fig. 4.—Infrared spectra of the clay fraction of Evesboro soil and clay-organic complexes.

and 7.25μ resulted from CH vibrations of the mulling material used, namely, Nujol. Since the silica tetrahedra and aluminum octahedra are common to all clays, vibrations attributable to these structural entities were found in the four clays examined. These appeared in the region of 9.70μ. Only the clay fractions of the Whippany and Evesboro showed octahedral OH stretching vibrations at 10.95μ whereas the clay fractions

of the Fe and Guánica soils showed them in the region of 11.45μ. The clay fractions of Whippany and Evesboro soils showed rather weak absorption peaks at 12.55 and 12.85μ. These have not yet been identified.

The spectra of blackstrap molasses, distillery slops, and slops active

CLAY

CLAY AND MOLASSES

CLAY AND SLOPS
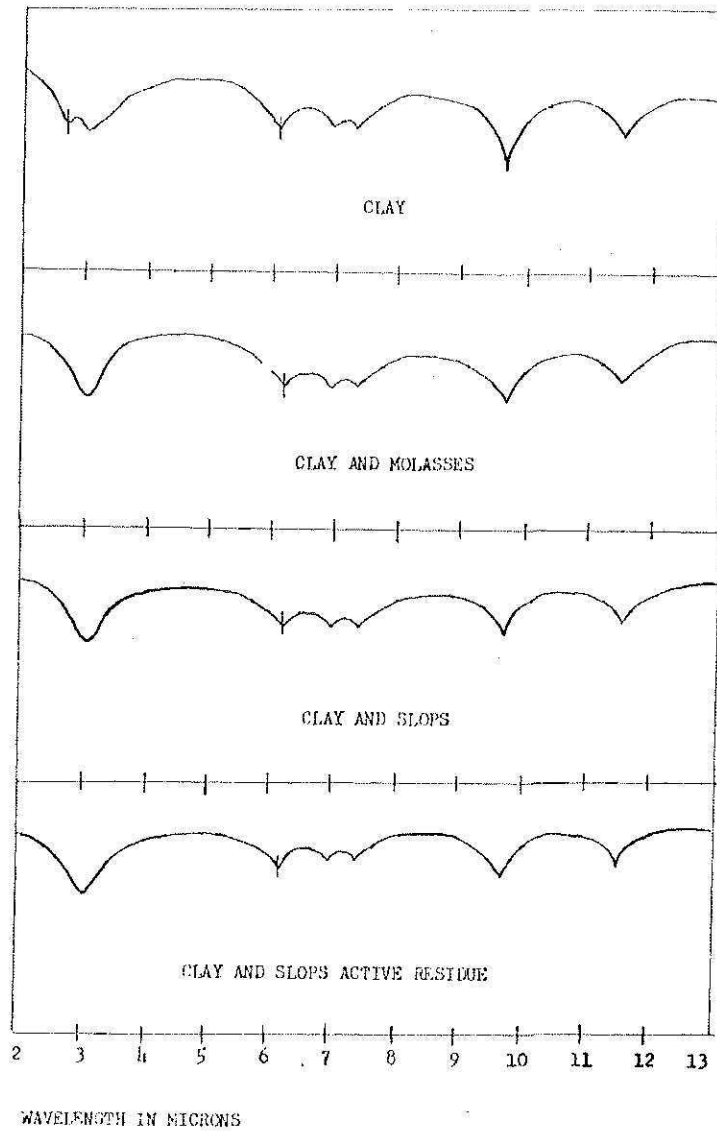
CLAY AND SLOPS ACTIVE RESIDUE

WAVELENGTH IN MICRONS

FIG. 5.—Infrared spectra of the clay fraction of Whippany soil and clay-organic complexes.

residue are shown in figure 3. The very strong absorption peak in the 3.05-μ region is due to free OH. The sources of this functional group are water and sugars. The rather sharp peak at 3.45μ is believed to be characteristic of the CH₃ group of organic acids present in the molasses. The

absorption in the region of 6.2μ is related to the presence of amino groups characteristic of amino acids, polypeptides, and proteins. The broad and strong peak shown in the region of 7.10μ is also characteristic of ionized carboxyl groups. Several investigators (5) have attributed this peak to the
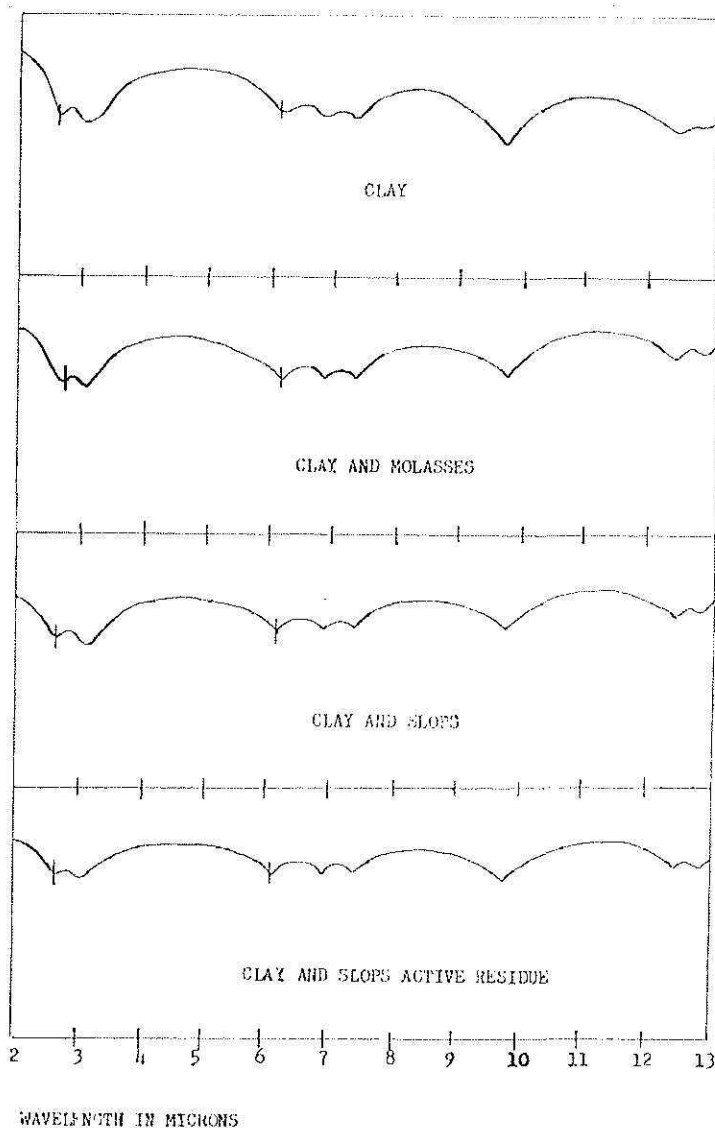

CLAY

CLAY AND MOLASSES

CLAY AND SLOPS

CLAY AND SLOPS ACTIVE RESIDUE

WAVELENGTH IN MICRONS

FIG. 6.—Infrared spectra of the clay fraction of Fe soil and clay-organic complexes.

presence of methoxy groups (—O—CH₃). Browne and Phillips (2) reported the presence of these groups in sugarcane juices and the blackstrap molasses. The broad bands between 9 to 10μ, with a peak at 9.5μ, are probably caused by CH, COOH, and C=O ketoaldehyde groups. The peaks

arising in the regions of 10.05 and 10.80μ are probably produced by CH₂=CH₂ and COOH groups.

The spectrum of the slops shows essentially the same pattern as that of

CLAY

CLAY AND MOLASSES

CLAY AND SLOPS

CLAY AND SLOPS ACTIVE RESIDUE
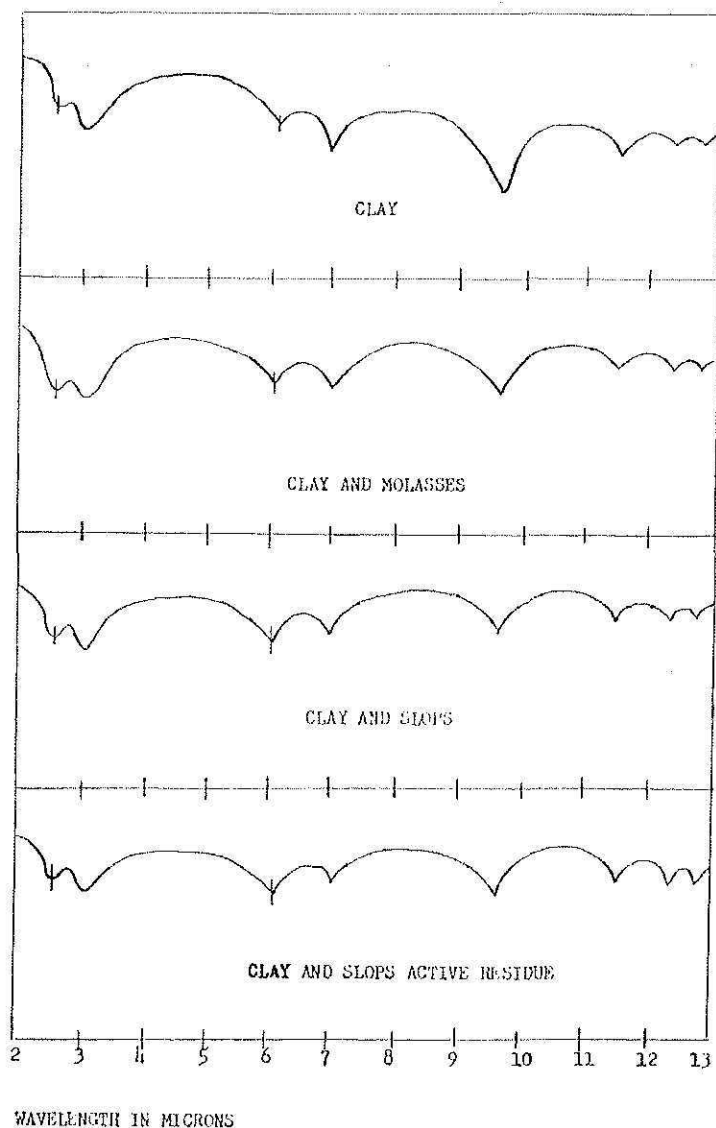
WAVELENGTH IN MICRONS

FIG. 7.—Infrared spectra of the clay fraction of Guánica soil and clay-organic complexes.

the blackstrap molasses, except that the peaks in the region of 10.05 and 10.80μ noted in molasses are absent in the slops spectrum.

The spectrum of the slops active residue (*12*) is somewhat different from the spectrum of the slops. The peak characteristic occurring at the 3.45-μ region can hardly be detected. The absorption peak at 7.1μ has virtually

disappeared. It is speculative whether some of the groups associated with it were left behind in supernatant liquid after precipitation with ethyl alcohol, or whether hydrogen-bonding occurred to the extent that only a small absorption band could be detected.

The clay fraction of the Evesboro soil, figure 1, showed a shift in the OH position from the 3.00 to 3.05μ, indicating that the exposed OH of the crystal edge was bonded to the blackstrap molasses by way of a hydrogen bond. Another linkage of the same type was observed when the 6.1 vibration of the clay shifted 0.05μ toward a region of longer wavelength. There was no difference between the linkages occurring in this clay fraction complexed with molasses, slops, and slops active residue.

When the clay fraction of the Whippany soil (fig. 5) was complexed with the three organic materials, only hydrogen bonding by means of the free hydroxyls was found in the 2.80μ regions. Surprisingly no linkage could be detected for adsorbed water.

Figure 6 shows the same type of bonding occurring when the clay fraction of the Fe soil was complexed with the various organic materials. When the clay fraction of the Guánica clay was complexed with molasses, slops, or the slops active residue, no bonding occurred, as shown by the spectrum in figure 7. It is worthwhile to point out that the pH of this soil was 9.0 which should not have favored the formation of a linkage. As pointed out elsewhere (*11*), neither blackstrap molasses nor distillery slops were effective in stimulating aggregate stability in this soil unless acid conditions were created by means of sulfur applications.

To summarize, it is apparent that only H-bonding, through the exposed OH of the clay crystal, is operative between the organic materials tested and clays isolated from the Evesboro, Whippany, and Fe soils. The linkage is probably via the carbonyl groups in the organic materials. A shift, however, in the peaks of the COOH groups was not observed, since the organic materials could not be properly mulled with Nujol. The complexes could not be run in Irtran because the scattering of the infrared rays was such that practically all the energy was lost.

Whether hydrogen bonding is of any significance is primarily dependent on the number of hydrogen bonds formed. These bonds are known to be relatively weak in nature, but, if sufficient numbers are present, their sums will be large.

In a heterogeneous system, such as exists in soil colloids, blocking of exchange sites because of the presence of primary formation will reduce the number of potential linkage sites available for reaction. This means that the adsorption of potentially reactive organic substances will be reduced, and may therefore be subjected to breakdown by micro-organisms.

Since it was shown earlier that montmorillonite was the dominant clay

mineral in the clay fraction of both Guánica and Fe soil and since both molasses and slops are known to contain amino groups, an effort was made to determine whether a shift in the 001 spacings could result from the adsorption of these materials.
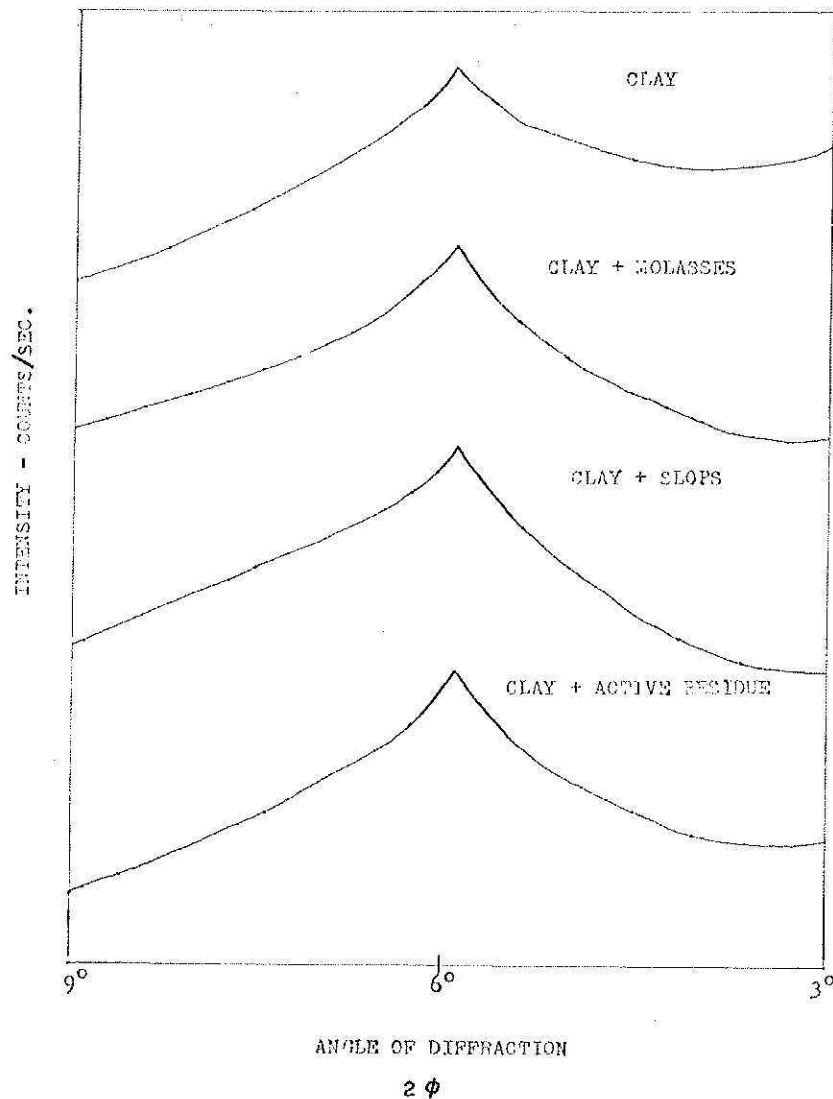

FIG. 8.—X-ray diffractograms of the clay fraction of Fe soil and clay-organic complexes.

X-ray studies showed that no changes resulted from adsorption of molasses or distillery slops between the basal planes of the clays, figures 8 and 9. It seems as if the size of the molecules found in the slops and molasses is such that they will not fit between the 001 planes. As shown by the infrared absorption-spectrum data, hydrogen-bonding is proposed for the

reaction between the exposed OH groups at the edges of the clay crystals and these materials. This implies that the active constituents of these two organic substances are not protected by the clays to a great extent, and their lasting effect in the soil depends entirely on their resistance. Microbial
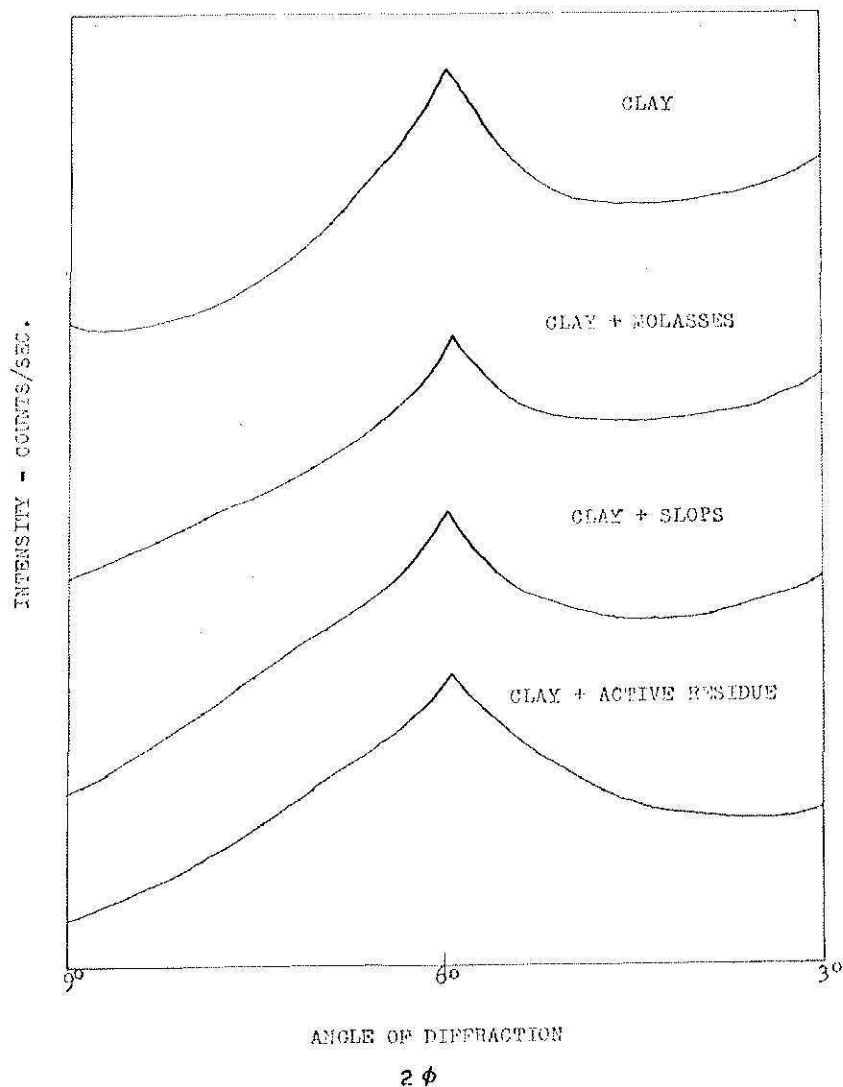

FIG. 9.—X-ray diffractograms of the clay fraction of Guánica soil and clay-organic complexes.

decomposition is preceded, however, by the production of enzymes which hydrolyze organic matter. These enzymes have specific isoelectric points and can be adsorbed by the clays with expanding lattices and rendered inactive. Under these conditions little decomposition of the organic clay aggregating material would occur.

A very slight increase in cation-exchange capacity was found to occur upon complexing the clays of Fe and Guánica soils with slops. This is shown in table 1. Reductions in cation-exchange capacity have been usually found to occur when some proteins are adsorbed by the expanding clay lattice minerals.

TABLE 1.—*Effect of distillery slops on cation-exchange capacity of the Guánica and Fe soils*

Treatment	Cation-exchange capacity (meq./100 gm.)	
	Guánica clay	Fe clay
Untreated	58.20	46.70
50 cc. slops	58.84	49.60
100 cc. slops	59.53	50.29
200 cc. slops	62.62	51.53
400 cc. slops	63.01	54.19

SUMMARY

Information is presented with reference to the infrared spectroscopy of blackstrap molasses, rum distillery slops, the active fraction of the slops, clays of four poorly drained soils, and of the complexes formed between organic materials and the clays of Fe, Guánica, Whippany, and Evesboro soils. The X-ray spectroscopy of two of the clays of montmorillonitic nature and of the complexes formed with the organic materials is also shown.

Characteristic peaks of the organic materials include those caused by hydroxyl, methyl, amino, methoxy, carbonyl, and ketonic groups.

The spectra of the clays showed peaks which are attributed to hydroxyl, bonded and unbonded, adsorbed water, silica tetrahedra, and aluminum octahedra.

Hydrogen-bonding occurred between the exposed hydroxyl groups of the clay crystals and the molasses, slops, and its active residue. There was no shift in the 2ϕ angle of diffraction of the expanding-lattice clays, indicating that there was no adsorption in the interlamellar spaces. The adsorption was possible at the edges of the crystal. This finding was strengthened by the fact that rather than undergoing a decrease in cation-exchange capacity there was a slight increase in the expanding lattice clays.

RESUMEN

En este trabajo se informa sobre la espectroscopía infraroja de la miel final, del mosto y su residuo activo, de las arcillas de cuatro suelos de mal

desagüe y de los complejos formados entre los materiales orgánicos y las arcillas de los suelos Fe, Guánica, Whippany y Evesboro. También, se incluye la espectroscopia, por medio de los rayos X, de dos de las arcillas de naturaleza montmorillonítica y de los complejos formados con los materiales orgánicos.

Los picos característicos de los materiales orgánicos incluyen los que corresponden a los grupos de los hidroxilos, los metílicos, amínicos, metóxicos (O—CH$_3$) y cetónicos.

El espectro de las arcillas reveló picos propios de los hidroxilos, sin enlazar y enlazados, del agua adsorbida, de los de tetrahedro de sílice y de los de octahedro de aluminio.

Se determinó la presencia de enlaces de hidrógeno entre los hidroxilos externos del cristal arcilloso y la miel, el mosto y su residuo activo. No hubo cambio en el ángulo 2 ϕ de difracción de las arcillas que se expanden, indicando que la adsorción de los materiales orgánicos tuvo lugar en el exterior del cristal arcilloso y no entre las lamelas.

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