THE BEHAVIOR OF FATTY ALCOHOL APPLIED TO SOILS

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ABSTRACT

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By Kenneth Gordon Brengle

X-ray diffraction, differential thermal analysis, infra-red absorption, and angle of wetting were used to investigate fatty alcohol adsorption by Wyoming bentonite. These materials are adsorbed by bentonite but the bonding energy could not be determined by DTA. The type of bonding could not be determined by the infra-red spectrophotometer, however, hydrogen bonding is assumed to be the primary attraction between fatty alcohol and bentonite. The angle of wetting of bentonite is decreased by sorbed fatty alcohol.

The effect of fatty alcohols on the soil water system was evaluated by soil moisture retention, infiltration and capillary rise studies. The effects which fatty alcohols exert at the solid-water and air-water interfaces have been demonstrated by these studies which indicate that fatty alcohols are most effective in reducing water movement in the soil when applied at rates sufficient to be active at the air-water interface. The success of these materials as evaporation suppressants depends on their reducing movement of liquid water and not on blocking vapor movement by the formation of an energy barrier.

Vertical and lateral movement of fatty alcohol in the soil is practically non-existent. The lack of lateral movement suggests that compressed monofilms are not formed at the air-water interface in soil.

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INTRODUCTION

The use of surfactants, particularly the fatty alcohols hexadecanol and octadecanol, has recently received considerable attention in the possible suppression of evaporation from soils. Recent studies have failed to clarify the usefulness of such products and the present investigation was initiated to further study the behavior of these fatty alcohols applied to soil and their effect on the soil-water system. This research is not concerned with the effectiveness of these materials in the control of evaporation from a soil system but rather with the behavior of fatty alcohols in the soil. Adsorption on solid particles, movement within the soil, effect on water movement and the mechanism by which water movement is affected are of primary concern.

REVIEW OF LITERATURE

Lemon (22) suggests that the potentialities for reducing evaporation from the soil lie in three areas: (a) decreasing the turbulent transfer above the ground surface; (b) decreasing the capillary conductance of water to the surface by decreasing capillary continuity; and (c) decreasing the capillary conductance of water to the surface by the application of surfactants.

The fatty alcohols have received considerable attention as evaporation suppressants on lakes and ponds (8) (38) (40) (41). They form monomolecular films on the free water surface which, according to Langmuir and Schaefer (21), reduce evaporation due to an energy barrier that opposes the penetration of water molecules into the film. The monomolecular films are formed only by hydrocarbon compounds having functional groups such as COOH, CO or OH. The functional groups are attached to the water and the hydrocarbon chains extend upward from the surface (20).

Monofilms exert a spreading pressure on the surface of water that is related to the surface tension of water according to the equation:

$$F = \gamma_o - \gamma$$

Where F is the surface pressure, γ_o the surface tension of water without a film and γ the surface tension of water with an oil film (24). Timblin (37) reports the equilibrium film pressure of hexadecanol to be over 40 dynes per cm.

Cruse and Harbeck (9) report studies of 152 compounds as evaporation retardants on open water surfaces. They list the following

criteria for a material being used for this purpose: (a) It must effectively reduce the rate of evaporation; (b) it must be nontoxic to animals and plants using the reservoir water; (c) it should be resistant to oxidation or degradation by microorganisms; (d) it should not affect oxygen and carbon dioxide transfer; (e) it should be effective in both hot and cold water; and (f) it must be economical. These criteria also apply to materials used in a soil-plant system. They found the homologous straight-chain fatty alcohols to be the best materials for retardants.

Magin and Randall (23) made a comprehensive review of the literature concerning the chemistry of surface films and their effectiveness as evaporation retardants on water surfaces.

Roberts (33) published one of the first papers on the effect of fatty alcohols on transpiration from plants. He reports reductions in transpiration of about one-third after adding a hexadecanol-octadecanol mixture to the soil. He considers that this reduction was due to two mechanisms; (a) film formation on the stomatal openings and (b) blockage in the root system, since radioautographs indicate the uptake and translocation of fatty alcohol molecules in the plant. Roberts did not report any detrimental effect on dry matter production.

Roberts also planted corn seeds in various concentrations of distilled water and hexadecanol and found no deleterious effects on germination.

Olsen et al. (27) found that fatty alcohols applied to corn grown in the greenhouse did not result in a saving of water. Using hexadecanol and octadecanol these workers found that both materials reduced

the yield of corn significantly when they were mixed in the soil at the rate of 25 grams per 3 kilograms of soil. They found a significant increase in the amount of water transpired per day per pound of dry weight produced.

Aubertin and Gorsline (2) report a decrease in evapotranspiration with the use of fatty alcohol in a soil-plant system. However, they found an increase in the total water required per gram of dry matter. Evaporation from the soil surface was reduced by the application of fatty alcohol but the transpiration requirement per gram of dry material remained unchanged. Where fatty alcohols were applied, the decrease in dry plant material was proportionately greater than the decrease in evaporation losses which resulted in greater total water use per gram of dry material.

Wooley (43) found reduced dry matter production due to the application of fatty alcohol but he reports that the amount of water used per square centimeter of leaf surface was unchanged.

Wooley used soil and sand in 3-oz. bottles with a water table at 4 cm. Under these conditions, he found that water loss from the sand decreased after the surface dried. Evaporation from clay or loam was not reduced with 0.5% and 2.0% fatty alcohol. He proposes that the difference between evaporation from the coarse and fine materials is due to water movement by vapor transfer in the sand and by capillarity in the finer material. This assumption is based on the fact that hexadecanol should be expected to interfere with vaporization within the coarse material more than with capillary movement in the soil. This assumption, based on the behavior of fatty alcohol on an open

water surface requires that a monofilm be formed on the curved surfaces of the water films within the sand.

Atsatt and Bliss (1) studied the effect of emulsified hexadecanol-octadecanol on germination, establishment, and growth of Kentucky bluegrass. They found that saturating the seed with emulsified TA 16-18 significantly reduced the rate and percent germination. However, germination was increased when the soil moisture was held at relatively high levels by applying fatty alcohols to the soil surface containing the seed. When large amounts of hexadecanol were added to the soil and the seed became partially coated, the effect was similar to direct seed treatment.

In greenhouse tests, 300 to 500 lbs. of fatty alcohol per acre gave the highest dry weight yields. In field trials, 450 lbs. per acre of the emulsion produced the most significant increase in seed germination, percent cover and subsequent dry weight yields. Powder and flake forms of TA 16-18 had little or a deleterious effect on germination, cover and dry weight yields. The increase in dry weight from the use of emulsion was due to greater stand densities.

Oertli (26) grew barley and red kidney beans in solutions containing 0.1, 1 and 10% fatty alcohol. Plant weight and water use were measured after 10 days; water use efficiency was not changed materially with up to 10% F.A. He interpreted reduced transpiration toward the end of the test period to be due to toxicity of the alcohol. Yields and water use were decreased with both crops. Although the bulk of the fatty alcohol floated on the surface of the solution he considered the solution to be saturated even at low concentration due to the very low solubility of the materials.

Timblin (39) reports that the contact angle of water and the monofilm forming material is important in film formation. The rate of release of molecules is a function of several factors; one of which is the length of the wetted perimeter. Since a monomolecular layer of hexadecanol is generated at the air-water-solid interface of a particle floating on the surface, this factor assumes some importance. The author concludes that the flake form of hexadecanol outperforms the beaded form in establishment of a monolayer because surface tension causes the beads to become nearly submerged, thereby decreasing the length of the wetted perimeter. This study would suggest that the alcohols in Oertli's solutions, although in great excess would have very little dissociation. It seems more likely that plant uptake under these conditions would depend primarily on root contact with the solid alcohol.

Bourget and Parups (5) found that soil treatments with hexadecanol and docosanol ($CH_3(CH_2)_{21}OH$) reduced all growth measurements when applied at rates of 0.02 percent or greater. Treatments at 0.002 percent did not affect either plant growth or water use. Tobacco was the test plant. The total amount of water used decreased significantly as the rates of application of both alcohols increased from 0.002 percent to either 0.02 or 0.2 percent. However, the water use efficiency increased with hexadecanol at 0.2 percent only.

These workers also found water evaporation losses from the surface layers of Rubicon sand, Castor silt loam and Rideau clay loam to be significantly reduced when the soils were treated with fatty alcohols.

Olsen *et al*. (28) report an elaborate study of the effect of hexa-octadecanol on evaporation. They found that both rate of application and placement affected evaporation. Fatty alcohol mixed with

the surface one-fourth inch of soil was more effective than that mixed with the entire soil mass or placed in layers 1 and 3 inches below the surface. Over a 14-month period, hexadecanol in surface placement reduced evaporation 17 percent at the low rate (0.033%) and 43 percent at the high rate of 0.833 percent.

Near the beginning of the experiment, the hexadecanol uniformly mixed with the entire soil mass caused a reduction in evaporation equal to that of the surface placement, but six months later and thereafter, the mixed placement was less effective.

The treatments where fatty alcohol was mixed with the soil reduced evaporation at all rates of application, while the two layered treatments reduced evaporation significantly at the highest rate.

They found that hexadecanol increased the rate of drying of the surface one-fourth inch of soil. They conclude that this "self mulch" is instrumental in reducing evaporation and propose that hexadecanol possibly has an effect on aggregation. They found an increased infiltration rate with hexadecanol treated soils which they considered to support this assumption. A reduced water content at several tensions between one-third and fifteen bars was also found. These reductions were generally greater at low tensions.

Hexadecanol could be recovered from soils at the higher rate 14 months after treatment. At the lower rates, identification of the material was not possible but the effect on evaporation was still evident. Roberts (33) also reported that hexadecanol remained undecomposed during the growing season of corn.

Oertli (26) found the bulk of the fatty alcohol in the solutions he used still in the flake form after five months.

Apparently, fatty alcohols do not have the waterproofing effect on soil that some other materials have (28). Bowers and Hanks (7) found that dimethyloctadecylammonium chloride (DDAC) caused waterproofing of the soil by increasing the contact angle at the solid-water interface. This resulted in decreases in both infiltration and evaporation.

Various types of organic molecules have been shown to be adsorbed by clay minerals (3), (14), (19), (30). Gieseking (14) found that the d(001) spacing of montmorillonite treated with various amines was not always dependent on the dimension of the cation in the free state. Since the cations were strongly adsorbed and the effect of adsorbed water on the d(001) spacing of the treated clay minerals was negligible, he concluded that the variation in the d(001) spacing resulting from a given cation was due to the orientation of the adsorbed cation or its tendency toward packing, deformation or polarization.

Hendricks (17) reported that organic cations were held to the surface of the silicate layers by van der Waals forces as well as by Coulomb forces between the ions. The value of the d(001) spacing depends upon the structure of the organic cation and the manner in which it is adsorbed upon the silicate surface.

Kohl and Taylor (19) report hydrogen bonding between the carbonyl group of several compounds and Wyoming bentonite. They conclude that a shift in the adsorbed spectra of 0.05 μ or more to longer wave lengths indicates hydrogen bonding. For VAMA they found a shift from 5.82 to 5.89 microns for the C-0 groups when adsorbed on bentonite. With the addition of larger amounts of VAMA they found the adsorbed

spectra of the free carbonyl groups of 5.82. They interpreted this to indicate the presence of C=0 groups which were not bonded to the clay.

Bellamy (4) states that the OH band length is increased and the absorption band shifts to a lower frequency with hydrogen bonding of such compounds as alcohols. The magnitude of the shift of the OH band, due to hydrogen bonding could be used as a measure of the strength of the hydrogen bond formed. Absorption occurs between the upper limit of 3760 cm^{-1} and the lower limit of about 3500 cm^{-1}.

carbonyl groups of 5.82. They interpreted this to

which were not bonded to the clay.

MATERIALS AND METHODS

This study was based on the assumptions that hexadecanol forms a monomolecular film on soil water in the same manner that it does on a free water surface and that the amount of hexadecanol adsorbed on solid particles will be in relation to the surface area of the particles.

In order to apply rates of fatty alcohol in relation to the surface area of the solid particles in the media, the surface area of kaolinite, Wyoming bentonite, and Hillsdale sandy loam was determined by ethylene glycol retention. Duplicate samples of the clays and soil were used. The procedure was essentially that of Bower and Gschwend (6). The samples were dried under a vacuum using P_2O_5 until a constant weight was obtained. Fifteen drops of ethylene glycol was distributed over each sample. After sitting overnight the samples were again evacuated using $CaCl_2$ as the desiccant. After the samples attained a dry appearance, they were weighed at hourly intervals until a constant weight was reached. The surface area was then calculated by the equation:

$$\text{Total surface area } (M^2/g) = \frac{\text{Wt. ethylene glycol retained}}{\text{Wt. dried sample} \times 3.1 \times 10^{-4}}$$

The average surface areas obtained by this procedure were 12.61 M^2/g for kaolinite, 765.1 M^2/g for bentonite, and 43.1 M^2/g for the Hillsdale soil. Once the surface areas of the materials were established the rates of fatty alcohol were measured in symmetry concentrations where one symmetry equaled the amount of material capable of forming a monofilm over the surface of the solid medium used.

X-ray Diffraction

X-ray diffraction patterns were taken of the clay materials. The clays were sodium saturated and hexadecanol was added as an emulsion at one and one-half symmetry concentrations. The treated suspensions were shaken overnight, centrifuged, and the supernatant liquid discarded. Each sample was resuspended and placed on ceramic plates by suction. They were then dried over $CaCl_2$, x-rayed, oven dried and x-rayed again. Since the only peak desired was the d(001) spacing a complete diffraction pattern was not determined.

Differential Thermal Analysis

Differential thermal analysis was used to study the heat of desorption from bentonite treated by shaking granular fatty alcohol with bentonite suspension and by treating the clay with solid fatty alcohol dissolved in ethanol. The suspensions were dried under infrared lamps and ground to a fine powder. The differential thermal apparatus used was described by Ellis and Mortland (10) (11). The variable pressure apparatus had a nickel alloy sample holder and the differential thermocouple was Pt-Pt (90%), Rh (10%). The heating rate was $13 \pm 0.5^\circ$ C. per minute. The samples treated with granular fatty alcohol were run in a normal atmosphere and in nitrogen gas with pretreatment described by Ellis and Mortland (11). The nitrogen pretreatment consisted of adding nitrogen gas that was purified by passing it through a pyrogallic acid trap and a H_2SO_4 trap. This procedure was repeated three times, then the sample was allowed to pretreat with nitrogen passing through it at slightly greater than atmospheric pressure for one hour. The flowing gas was stopped and the pressure reduced to atmospheric prior to making the analysis.

Infra-red Spectrograph

Films of treated and untreated bentonite and of pure fatty alcohol were studied by a Beckman Model 7 infra-red spectrophotometer to determine the type of bonding between the alcohol and clay.

The films of bentonite were prepared by drying suspensions on microscope slides, then removing them from the slides with a razor blade. The best method found to obtain films of pure fatty alcohol thin enough for IR determinations was to melt the granular material and re-solidify it rapidly by dropping it on glass in water at about 25° C. Even with this method several trials were necessary to obtain films large enough to use.

Angle of Wetting

The effect of fatty alcohol on the angle of wetting of bentonite was studied by the use of an instrument similar to the one described by Bowers and Hanks (7). This instrument was constructed by attaching a plastic protractor to a 4.5 by 6-inch sheet of plexiglass. A 10x magnifying glass with crosshairs and a pointer attached was inserted in the plexiglass. The magnifying glass was centered with one crosshair on the base line of the protractor and the other one in line with the 90° mark. A platform was attached to the back side of the plexiglass sheet to hold the slides.

The treated and untreated bentonite suspensions were dried on microscope slides under infra-red lamps. The clay-coated slides were mounted on the platform and the contact angle between a drop of distilled water and the slide was measured by rotating the lens until the crosshair was aligned with the water surface. The pointer then indicated

the contact angle directly from the protractor scale. It was found that the contact angle varied with the distance which the drop fell. Therefore, the instrument was modified to hold a medicine dropper one inch above the slide so that all measurements were made under identical conditions.

Soil Moisture Retention

Desorption curves for the Hillsdale sandy loam and a Fort Collins clay loam were determined in the pressure membrane apparatus. The points determined on these curves were 0.3, 0.6, 5, 9, and 15 bars. The soils were treated at rates equivalent to 100 lbs. per acre, 200 lbs. per acre, and 0.1 symmetry concentration of fatty alcohol by adding the required amount of hexadecanol to soil which had sufficient water added to make a saturated paste. For treatment with granular hexadecanol, the soil was then placed in a water bath at 60° C. to melt the fatty alcohol. The mixture was stirred several times while being heated. Half of the samples were dried under infra-red lamps after mixing and the remaining samples were kept wet. The dried samples were made into a paste again before the pressure determinations were made. Soil that had not been treated with fatty alcohol was subjected to the heating, mixing, and drying also. The same soils were also treated at the same rates of application with 10% TA 16-18 emulsion.

Infiltration

Undisturbed cores 7.62 cm in diameter by 7.62 cm deep of Hillsdale sandy loam were saturated with water by placing the cores in a tray containing water to a depth sufficient to allow movement upward through the cores until a free water surface covered the soil. Hexadecanol

dissolved in hexane was added at rates sufficient to cover the surface of the core and half the amount needed to cover the surface. The cores were allowed to stand for fifteen minutes so the hexane could evaporate and a monofilm could form on the water surface. One set of cores was then dried at room temperature and another set was drained of excess moisture and infiltration rate determined. The dried cores were saturated with water before infiltration was measured.

The infiltration rate was measured by hourly determination of the amount of water that leached through the cores under a constant head of 8.72 cm.

Vertical Movement of Fatty Alcohol

The downward movement of hexadecanol was studied by applying 1/8, 1/4, 1/2 and 1 symmetry concentrations of fatty alcohol to undisturbed cores of Hillsdale sandy loam. These concentrations were based on the average weight of soil in five cores. The cores were treated with granular fatty alcohol after being saturated with water. The soil cores were then leached for ten hours in the same manner as the cores used in the infiltration study. After being leached, the soil from each core was sampled at 0.5 cm. depths. The fatty alcohol was extracted with hexane in a Soxhlet extraction unit and the content measured with a Beckman GC-2A Gas Chromatograph with a hydrogen flame detector. The column used was 10% SE-30 on Gas-Chrom P.

Lateral Movement

Metal trays about 35.6 x 35.6 x 3.8 cm. were divided so that each tray would hold two treatments. The trays were lined with Saran wrap dissolved in [illegible] sufficient to cover the surface of the cure [illegible] cata [illegible] and Hillsdale sandy loam soil was added to a depth of 2 cm. except for a strip 5.1 cm. wide in the center of each side. The soil from this area was treated with hexadecanol and placed in the trays. The treatments consisted of 1/2 and 1 symmetry concentrations of fatty alcohol using both granular material and emulsion. The emulsion was mixed with wet soil before being put in the tray and the granular material was mixed with the dry soil for some treatments and banded in the center of the treated strip for others.

Wetting and drying cycles were imposed on the treated soils. Some trays were kept wet during the entire time while others were subjected to one, two, or three drying cycles. On wetting the soils care was taken to saturate the soils without forming a free water surface for the movement of fatty alcohol.

At the end of five days the soils were sampled in 2 cm. strips on both sides of the treated area. Hexadecanol was extracted with hexane and measured with the gas chromatograph.

Capillary Rise in a Column of Soil

Eight hundred gram samples of soil that had been passed through a 20-mesh sieve were treated with fatty alcohols at rates of 0, 100 lbs. per acre, 200 lbs. per acre, and 0.05 symmetry (approximately 12,000 and 9,000 lbs. per acre by weight for the Fort Collins clay loam and the Hillsdale sandy loam, respectively).

The soils were treated with solid fatty alcohol in the same manner as those for moisture retention. Equivalent rates of 10% emulsion with the exception of the 0.05 symmetry concentration, were also used. After treatment the soils were ground and put through a 20-mesh sieve. Seven hundred and fifty grams were measured into and [illegible] added to a depth of 2 cm. except for [illegible] plastic tubes 91.4 cm. long and 3.2 cm. in inside diameter. The Fort Collins soil was packed in the tubes at a bulk density of 1.30 g/cm^3 and the Hillsdale at 1.42 g/cm^3. The packing was done by tapping the tubes until the soil reached the desired height within the tube.

The samples were placed in beakers with the water maintained at a constant height of 3.5 cm. above the bottom of the tubes. Each sample had an individual water source that maintained the water head at the desired level. The determinations were made in a constant temperature room at 24° C. The water flasks were filled and allowed to sit overnight in the constant temperature laboratory so that all samples would have water at the same temperature. Duplicate samples were used for the 0.05 symmetry concentrations with the Fort Collins clay loam. Five replications were used for all other rates.

Microbial Decomposition

Twenty five ml. samples of bentonite suspension were treated with fatty alcohol at 0, 0.5, 1.0, and 2.0 symmetry concentrations. Ten mls. of solution containing 2 g. of Bond's modified Crone's stock salt per liter were added to each suspension. The suspensions were inoculated by adding 0.5 ml. of inoculant prepared by shaking 0.1 g. of soil in 1 l. of distilled water. The samples were then placed on a reciprocating shaker and shaken continuously except for periods when CO_2 was measured. The air from the sample was passed through a $CaCl_2$ trap to remove the water before the CO_2 was collected on Ascarite. Suction was applied to the Ascarite tower to force the air from the sample through it. After the air from the flask had passed through the Ascarite, the tower was closed off to prevent air movement and weighed. The gain in weight was due to sorbed CO_2.

plastic [illegible] inside diameter. The [illegible]

[illegible]

A second group was run by continuously passing air through the samples instead of shaking them. The air was passed through traps containing Ascarite and KOH to remove CO_2 from the air entering the samples. The samples were kept in a water bath at 30° C. The Ascarite tower was weighed every 24 hours.

At 10, 20, and 28 days clay was removed from the flasks and x-rayed to study the extent of removal of absorbed fatty alcohol.

Surface Tension of Water

The surface tension of water was measured at different concentrations of solid and emulsified fatty alcohol using a Cenco-DuNouy tensiometer number 70535.

The measurements were made from a petri dish 14 cm. in diameter. The dish was washed in benzene, methyl-ethyl ketone and sulfuric acid-potassium dichromate cleaning solution before each measurement. The platinum ring was also thoroughly cleaned and heated in the oxidizing flame of a bunsen burner before each measurement.

The rates of fatty alcohol, 0.00006 g and 0.0169 g, were in excess of the amount calculated to be necessary for the formation of a monofilm on the surface of the petri dish.

RESULTS

Symmetry concentrations as used in this study are analogous to symmetry concentrations in cation exchange studies, except they are used in regard to the relationship of monofilm formation to the surface area of the media. One symmetry is defined as the concentration of fatty alcohol necessary to cover the surface of the clay or soil with a monomolecular layer. For a bentonite system, a one symmetry concentration is equal to 0.62 moles per 100 grams of clay.

These concentrations were used primarily in the studies with bentonite. In the experiments where soils were used, most concentrations of fatty alcohol are expressed as percentage by weight.

X-ray Diffraction

X-ray analysis showed that the d(001) spacing of Wyoming bentonite was increased about 1.2 - 2.2 angstroms with various rates of treatment (Table 1). The samples were dried in a desiccator over $CaCl_2$ at room temperature, x-rayed, dried in an oven at 105° C. and x-rayed again. The only material change in the d(001) spacing upon oven drying occurred with the untreated bentonite and that treated at the rate of 0.025 symmetry. With both of these treatments the spacing was decreased by about one angstrom. Since the treated bentonite decreased to 12.82 Å as compared to 11.63 Å for the untreated it is evident that some material remains to prevent the lattice from collapsing. The decrease

in lattice spacing of the treated bentonite could be due to rearrangement of the molecules within the lattice or loss of trapped water upon heating. With the samples having an excess of fatty alcohol present either of these could be prevented. For the most part, the x-ray patterns showed rather narrow, sharp peaks indicating a narrow range for spacings. In all cases the width at the peak for the untreated bentonite samples were comparable to those treated with fatty alcohol.

The variation in the basal spacing of bentonite treated with large organic molecules has been reported by several workers (14) (17) (18). Jackson and Hellman (18) found the d(001) spacing of montmorillonite treated with amines to vary from 13 to 15 Å depending on the temperature and drying media. They considered the failure of large organic compounds to give complete and consistent expansion of the crystal lattice to be due to their inability to hold water and the slight positive influence on adsorption of water by the clay.

Hexane Extraction

Hexane has been used to extract fatty alcohol from soil. However, due to adsorption by the clay lattice, the possibility of incomplete extraction existed which could lead to a lowered efficiency of recovery. It was felt that it could be this decreased recovery that had led to speculation that fatty alcohol was decomposed rapidly in the soil

To study the recovery of adsorbed fatty alcohol, treated samples of bentonite were subjected to two different hexane treatments (Table 2). One set of samples was shaken in hexane for 30 minutes, and washed

Table 1. Interplanar spacing of Wyoming bentonite treated with hexa-octadecanol.

Treatment*	$CaCl_2$ dried - 30° C.	Oven dried - 105° C.
	Å	Å
B - 0	12.63	11.63
B - 0.025	13.81	12.82
B - 0.1	--	13.70
B - 0.5	13.81	13.60
B - 1.0	13.81	13.81
B - 2.0	13.92	13.70

* Treatments are in symmetry concentrations where one symmetry is the amount of fatty alcohol required to cover the surface of the clay with a monomolecular film.

with water after the hexane was decanted. The clay lattice of the bentonite treated with 0.5 symmetry concentration collapsed upon drying to 10.78 Å. This spacing was less than any obtained with untreated bentonite and indicated that not only was the fatty alcohol removed but the lattice itself was altered. The d(001) spacing of the clay treated at the higher rates remained expanded on drying. This could be due to the high concentration of fatty alcohol and the limited quantity of hexane used which resulted in a saturated solution.

Rather than shake the samples repeatedly in hexane it was decided to place them in a Soxhlet extraction apparatus and extract them with hexane for 6.5 hours, since this is the procedure called for in extracting hexadecanol from soils. The fatty alcohol content of the resultant extract was not measured but x-ray diffraction patterns of the clay showed the existence of fatty alcohol within the crystal lattice. This indicates that the adsorbed alcohol, at least after the treated sample has been dried, is not easily soluble in liquid hexane under normal extraction procedures. Two explanations exist as to why fatty alcohol was removed from the clay lattice when the samples were shaken in hexane but not when they were put in a Soxhlet extraction unit. The samples that were shaken were not dried prior to the removal of fatty alcohol. It is possible that bringing the material into intimate contact with the clay by drying, as in the case of the samples extracted in the Soxhlet unit, is necessary to provide the maximum bonding energy. Secondly, the mechanical action of the agitated

Table 2. Interplanar spacing of Wyoming bentonite extracted with hexane after treatment with hexa-octadecanol.

Treatment	$CaCl_2$ dried - 30° C.	Oven dried - 105° C.
	Å	Å
	Samples shaken in hexane for 30 minutes	
B - 0	12.62	11.79
B - 0.5	13.39	10.78
B - 1.0	13.60	12.82
B - 2.0	13.81	13.81
	Samples extracted 6.5 hours in a Soxhlet extraction unit	
B - 0.1	--	14.03
B - 0.5	--	13.39
B - 1.0	--	14.26

suspension and an increase in temperature due to the mechanical action could increase the solubility of the sorbed fatty alcohol.

Microbial Decomposition

Microbial decomposition of adsorbed fatty alcohol was also studied. Bentonite treated with fatty alcohol was inoculated from a soil suspension and Bond's Modified Crone's solution was added to provide a medium favorable for microbial growth. Samples were x-rayed after 10, 20, and 28 days of incubation (Table 3). The adsorbed fatty alcohol had not been decomposed after ten days. The d(001) spacing was still above 13.60Å for the clays treated with fatty alcohol. By the end of 20 days, the fatty alcohol was removed from the lattice of the bentonite treated at 0.5 symmetry. The higher treatments still had spacings of greater than 12 Å after oven drying, but the decrease of about 1 to 1.5 Å may indicate the presence of some decomposition products rather than fatty alcohol. After 28 days the spacing of all clays was approaching that of the untreated samples. Only the sample treated at one symmetry concentration exhibited a lattice spacing of greater than 12 Å while the lattice of the clay treated at 0.5 symmetry collapsed to less than 11 Å.

This study indicates that the effect of fatty alcohol adsorbed in the clay lattice will remain for a period of at least three weeks under nutrition and aeration conditions favorable for microbial growth.

Table 3. The effect of microbial decomposition on fatty alcohol adsorbed by Wyoming bentonite.

Treatment	$CaCl_2$ dried - 30° C.	Oven dried - 105° C.
	Å	Å
	Incubated 10 days	
B - 0	13.81	11.63
B - 0.5	14.26	13.60
B - 1.0	14.26	13.81
	Incubated 20 days	
B - 0	13.01	11.63
B - 0.5	12.45	11.79
B - 1.0	13.20	12.62
B - 2.0	13.00	12.11
	Incubated 28 days	
B - 0	11.79	11.48
B - 0.5	12.28	10.78
B - 1.0	12.82	12.28
B - 2.0	12.62	11.59

It is evident from the various x-ray patterns that the hypothesis that fatty alcohols remain in a monofilm as the molecules come closer to the soil particles with a discontinuous water film is not true. Visual observation of treated samples also substantiated this. In all treatments above 0.1 symmetry excess fatty alcohol was easily distinguished in washing the samples.

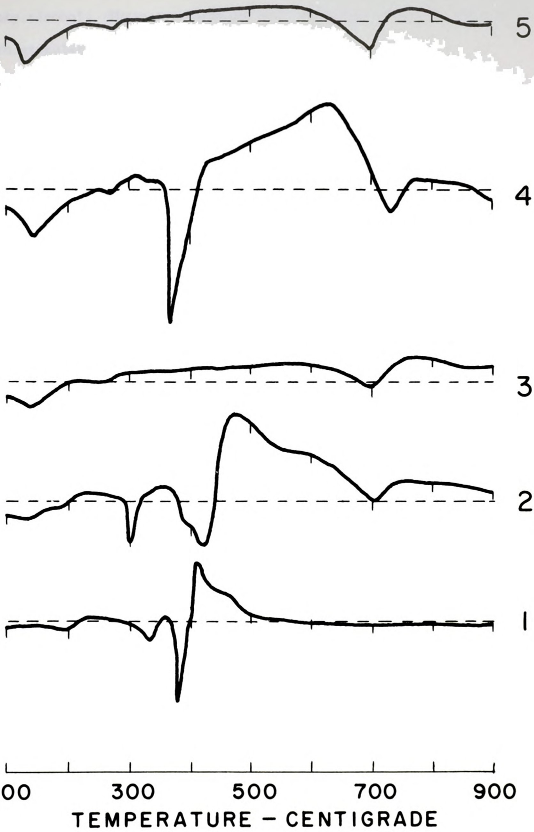
Adsorption of these materials occurs as a single molecular layer. The CH_2 or CH_3 groups have a slightly greater bond distance than water and the OH group of the alcohols will have a slightly smaller bond distance (29). Using the bond distance as a criterion for expansion of the clay lattice, a comparison can be made with the work of Hendricks _et al_. (16). These workers interpret a 12 Å spacing of the clay lattice to correspond with a single layer of water molecules whereas a 16 Å spacing is equivalent to a double layer. Since under the conditions of this study the interplane spacing was within the limits of a single layer of water molecules it appears that the fatty alcohol was adsorbed in a single layer also. They were also within the limits found by Jackson and Hellman (18) for organic molecules.

Barshad (3) states that the expansion equivalent to a molecular layer, with the molecules lying parallel to the oxygen sheets, would be equivalent to the largest diameter of the molecule. In hydrocarbon derivatives such as alcohols, ethers, and ketones, it would be equivalent to the diameter of the CH_3 or CH_2 groups.

Differential Thermal Analysis

Differential thermal measurements were made on samples treated with solid fatty alcohol. Curves 2, 3, 4, and 5 in figure 1 are from

Figure 1. Differential thermal analysis of granular fatty alcohol and fatty alcohol treated bentonite.
Curve 1, granular fatty alcohol mixed with Al_2O_3; Curve 2, bentonite treated with 1 symmetry granular fatty alcohol; Curve 3, bentonite treated with 1 symmetry fatty alcohol run in a nitrogen atmosphere; Curve 4, bentonite treated with 2 symmetry concentration of fatty alcohol; Curve 5, bentonite treated with 2 symmetry concentration of fatty alcohol run in a nitrogen atmosphere.


5
4
3
2
1
100
300
500
700
900
TEMPERATURE — CENTIGRADE

bentonite shaken in suspension with different amounts of granular fatty alcohol. These are compared with anhydrous aluminum oxide mixed with granular material (curve 1).

The curve for fatty alcohol mixed with Al_2O_3 and those with bentonite which have oxygen in the system exhibit endothermic peaks between 300 and 400 degrees centigrade (curves 1, 2, and 4, fig. 1). However, the peaks with the bentonite samples differ from the Al_2O_3 check and from each other.

These endothermic reactions are probably associated with the breakdown of the carbon chain. According to Muldoon (25), dehydration of primary alcohols results in intermediate products and side reactions with the net result of the hydroxyl and hydrogen from adjacent carbons uniting to form water. The free bonds then form a multiple bond to form an alkene. Temperature is an important factor in these reactions.

By controlling the oxidation of primary alcohols, aldehydes and acids containing the same number of carbons are obtained. However, the higher alcohols cannot be distilled without decomposition, therefore, energy should be required to break the carbon chain. It is quite likely that the first endothermic peak is associated with dehydration, or alkene formation, and the second, larger peak is associated with the breaking of the carbon chain.

Although these reactions are evident with the treated clay it is apparent that they are altered. This alteration is due to adsorption by the bentonite.

The large exothermic peaks of curves 1, 2, and 4, beginning at about 400 degrees are due to complete oxidation to CO_2 and H_2O and are bentonite shaken

fatty alcoho

with

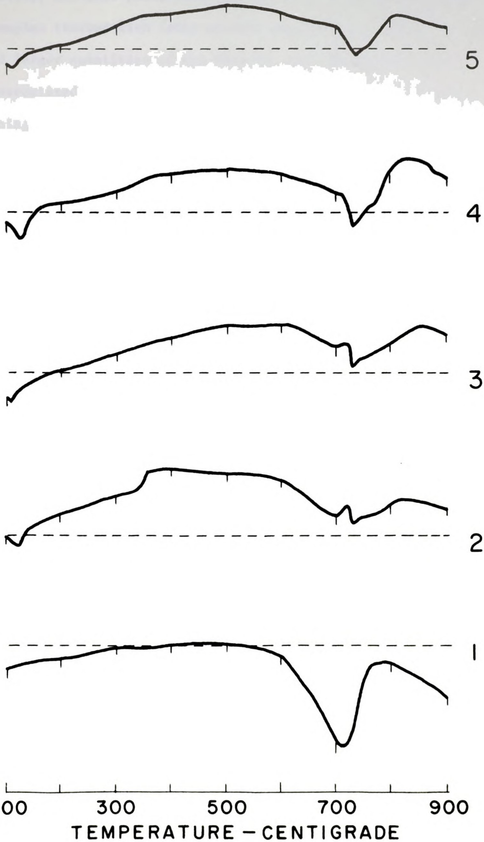
also altered by the adsorption of fatty alcohol. With the samples treated with fatty alcohol the exothermic peaks are broadened to partially mask the area of dehydroxylation at about 700° C. This broadening of the range of temperatures required for oxidation is due to an increase in energy required for the decomposition of adsorbed fatty alcohol.

The replacement of oxygen in the system by nitrogen eliminates the endothermic peaks as well as the exothermic peak as seen in curves 3 and 5, fig. 1. The complete oxidation of organic material is eliminated by the removal of oxygen from the system. It is evident that the intermediate steps of alcohol combustion require oxygen also.

Curves 3 and 5 of figure 1 did not exhibit any energy requirement for the desorption of fatty alcohol from bentonite. Ellis and Mortland (11) used this procedure to determine the change in enthalpy due to desorption of NH_4, methylamine and ethylamine. However, they found little evidence of bonding energy between bentonite and lower alcohols. The fatty alcohol-bentonite curves for the nitrogen system did not differ greatly from the untreated bentonite curve of figure 2, indicating that all reactions are associated with oxidation of the fatty alcohol.

Curves 2, 3, 4, and 5 of figure 2 are for samples of bentonite treated at different rates of fatty alcohol dissolved in ethanol. These curves are quite similar to each other but differ greatly from those of figure 1. The difference in oxidation between the two fatty alcohol-bentonite systems is likely due to difference in the degree of absorption. The clay samples shaken with granular fatty alcohol contain relatively small amounts of absorbed material due to its low

Figure 2. Differential thermal analysis of bentonite treated with solid fatty alcohol dissolved in ethyl alcohol. Curve 1, untreated bentonite; Curve 2, bentonite treated at 0.0001 symmetry concentration of fatty alcohol; Curve 3, bentonite treated at 0.01 symmetry concentration of fatty alcohol; Curve 4, bentonite treated at 0.1 symmetry concentration of fatty alcohol; Curve 5, bentonite treated at 1 symmetry concentration of fatty alcohol. All samples were run in an air atmosphere.


5
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TEMPERATURE — CENTIGRADE

solubility, and show peaks characteristic of the original material. The samples treated with fatty alcohol dissolved in ethanol have adsorbed larger quantities of the material and exhibit an exothermic peak associated with complete oxidation. The low energy oxidation beginning at about 150° C. is probably due to ethanol in the system.

The oxidation of the adsorbed fatty alcohol has a more pronounced carry-over into the area of dehydroxylation of the clay. These samples were not run in a nitrogen atmosphere to study the heat of desorption.

Differential thermal analysis of dialyzed bentonite treated with solid fatty alcohol dissolved in ethanol and with TA 16-18 emulsion show essentially the same picture. However, the raw bentonite exhibited peaks characteristic of aluminum or hydrogen bentonite and water dialysis with NaCl accentuated these characteristics.

The bentonite treated with solid material did not exhibit as prominent exothermic peaks as those discussed previously but the samples treated with emulsion had large exothermic peaks at all concentrations. One of the characteristics of the dialyzed clay was an endothermic, low energy dehydroxylation at 400 to 450° C. Apparently this opposite reaction reduced the effect of the oxidation peaks observed in the treated samples of figure 2.

Differential thermal analysis of these samples in a nitrogen atmosphere did not show any measurable heat of desorption.

Due to the chemical nature of alcohols, it is logical to assume that bond formation will be due to hydrogen bonding. Likewise, the logical place for such bonds to be formed between alcohols and clays is at the exposed reactive groups on the clay surfaces. Apparently,

the bonding energy of these compounds is quite low. Pauling (29) states that the energy of hydrogen bonds in methyl and ethyl alcohol is about 6.2 Kcal/mole, and there is no evidence that the bonding energy of higher alcohols would be greater. Since Ellis and Mortland (11) could not determine the bonding energy for the lower alcohols in a bentonite system it appears that this method is not suitable for the determination of low bond energies.

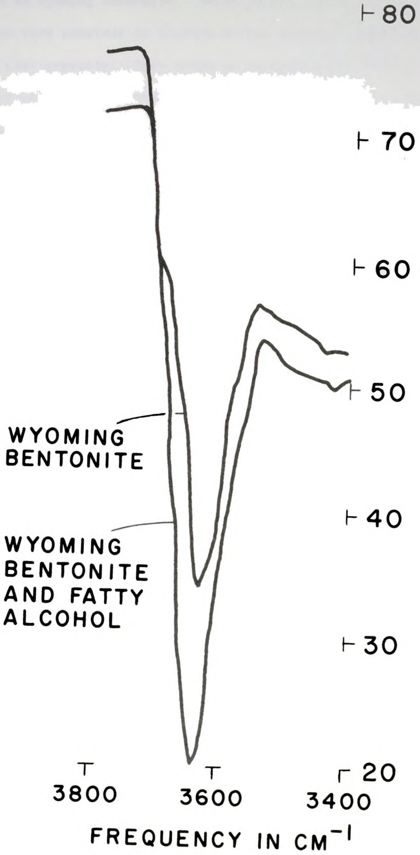
Infra-red Spectra

Infra-red spectrophotometry was used to study the type of bonding which exists between the clay and the adsorbed fatty alcohol.

With hydrogen bonding the OH bond length should be increased and the absorption band should shift to a lower frequency (4). Absorption arising from O-H stretching occurs in the region of 3760 - 3500 cm^{-1} and intramolecular hydrogen bonds in which no resonance structures are involved give rise to broad absorption bands in the range 3450 - 3200 cm^{-1}. The O-H bending frequency in the region of 1420 - 1000 cm^{-1} is also sensitive to hydrogen bonding (35).

The IR spectra for the O-H stretching frequency of bentonite and bentonite treated with fatty alcohol are compared in Figure 3. There is no shifting of the absorption band to a lower frequency in this range. There was also no shift in the other regions sensitive to hydrogen bonds. This is not conclusive evidence that the assumptions about hydrogen bonding are incorrect. It suggests that either hydrogen bonding has not occurred or that it is masked. Kohl and Taylor (19) showed that the C = O stretching frequency shifts toward a longer wave length when several organic compounds with these functional groups are

Figure 3. Infrared spectra of Wyoming bentonite, and of Wyoming bentonite treated with fatty alcohol.



adsorbed on Wyoming bentonite. These shifts are due to hydrogen bonding which they conclude is located at the hydroxyl groups on the broken edge of clay crystals. They found no evidence that the O-H stretching frequency is reduced or the O-H bending frequency is increased. They conclude that the frequency shifts were not observed due to the masking of these regions of the spectra by the many internal hydroxyl groups of the clay mineral that are not in a position to take part in the proposed mechanism and by the adsorbed water on the clay mineral. The organic anions which they used are not adsorbed within the clay lattice as the fatty alcohols are but this should not alter the conclusion that hydrogen bonds are primarily concerned in the absorption of fatty alcohol.

Considering the alternative that hydrogen bonding does not take place, the attraction between fatty alcohols and bentonite would depend on van der Waals forces. Hendricks (17) has reported that organic cations are held to the surface of the silicate layers of the mineral by van der Waals forces between the molecule and the surface as well as by Coulomb forces between ions. The adsorption on the surfaces of the crystal plates by van der Waals forces also affects the interplanar spacing. Although van der Waals forces are undoubtedly active in the fatty alcohol-bentonite system, they are probably not the primary bonding forces. Since alcohols are active in hydrogen bond formation and clays have been shown to enter into hydrogen bonding with compounds having reactive groups other than hydroxyl groups, it is likely that this is the principal type of attraction between bentonite and fatty alcohol.

Angle of Wetting

Using an instrument similar to that used by Bowers and Hanks (7) the wetting angle of bentonite treated with various concentrations of fatty alcohol was determined (Table 4).

Table 4. Angle of wetting of Wyoming bentonite treated with fatty alcohol.[1]

Rate F.A.[2]	0	0.0001	0.001	0.01	0.1	1.0
Degrees	28.2^a	27.2^a	25.4^b	23.9^b	17.9	20.3

[1] Average of 40 measurements.
[2] Rates in symmetry concentrations.
[3] The values having the same letter designations are not statistically different according to the Duncan multiple range test.

The angle of wetting was decreased as the rate of fatty alcohol increased to 0.1 symmetry. The increase in wetting angle with the 1.0 symmetry concentration is difficult to explain. An average of nine measurements made on solid fatty alcohol melted onto a microscope slide was 19.7°. This few number of measurements is unsatisfactory for a test that has so much variation between individual measurements. However, the extreme values for the nine measurements were 17.5° and 21.5° and this could be an indication that at excessively high rates the wetting angle approaches that of the fatty alcohol. The value of the untreated clay is higher than those reported by other workers, but this discrepancy is probably due to the fact that the bentonite used was not separated into the less than 2 micron fraction although the very coarse material that settled out of suspension rapidly was removed.

The question of how fatty alcohol suppresses evaporation in the soil has led to speculations by several investigators (27) (43). These materials are known to affect the surface tension of water. In fact, the surface pressure is defined as the difference between the surface tension of pure water and the surface tension of water with a monofilm formed on it (24).

The formation of a compressed monomolecular layer on the water surface is required to obtain the maximum depression of the surface tension. At 25° C. this will be approximately 31.97 dynes per centimeter since the surface tension of pure water at this temperature is 71.97 and the equilibrium surface pressure is about 40 dynes per centimeter (37). Considering the small air-water interface and the curved surface of the water films in soil pores it is logical to assume that film formation does not obtain equilibrium conditions and the resulting decrease in surface tension of the water is somewhat less than 40 dynes per centimeter.

Olsen *et al*. (28) suggest that alteration of the wetting angle has some effect on the suppression of evaporation from soil by hexadecanol. However, they assumed this alteration of the wetting angle to be an increase as reported by Bowers and Hanks (7) for DDAC applied to soils. Grim (15) states that "the water absorbing properties of montmorillonite are gradually reduced as the basal surfaces of the mineral are coated with organic ions." This also suggests that all organic compounds impart a hydrophobic property to the soil. Robinson and Page (34) also concluded that organic matter decreased the wettability of the soil by increasing the wetting angle of the extracted clay fraction.

Surface Tension of Water

The surface tension of water at different concentrations of solid and emulsified fatty alcohols was measured using a Cenco-DuNouy tensiometer number 70535. The surface tension of water against air is 71.97 dynes per centimeter at 25^{o} C. However, the average measurement with the tensiometer used in this study was 74.60 dynes per centimeter although the calibration of the instrument was accurate.

The results in Table 5 indicate that there is little difference in the surface tension of water due to equivalent rates of solid and emulsified fatty alcohol until a large excess of material is present. The values reported are the averages of five individual determinations.

Table 5. The effect of solid and emulsified fatty alcohol on the surface tension of water.

	Average surface tension (dynes/cm)	
	0.00006 g.F.A.	0.0169 g.F.A.
Solid	36.5	52.3
Emulsion	40.9	28.7

The differences between the lowest rates can be partially attributed to differences in temperature since the test was not conducted under conditions of constant temperature. However, the difference of as much as 5^{o} C. in temperature should account for only about one dyne per centimeter difference in the surface tension.

The 0.00006 g. rate of solid material was attained by dissolving 0.003 g. of fatty alcohol in 10 ml. of hexane and applying a 0.2 ml. aliquot to the water surface. The required amount of emulsion was not

completely soluble in 10 ml. of hexane so it was weighed on an automatic balance accurate to four places and applied directly to the water. This was possible since the emulsion contains only 10 percent fatty alcohol. The 0.0169 g. rate was selected by weighing one granule of solid material which was then applied to the surface of the water. An equivalent amount of fatty alcohol from TA 16-18 emulsion was also weighed and applied directly to the water surface. Solid fatty alcohol at the 0.0169 g. rate, dissolved in hexane resulted in a re-solidification of the excess alcohol as thin flakes on the water surface but the surface tension was decreased to an average of 34.5 dynes per centimeter.

The decrease in surface tension due to fatty alcohol did not reach 40 dynes per centimeter for any of the measurements except for the high rate of emulsion. This was probably due to impurities in the organic material and the technique used in spreading the films, which according to Weissberger (42) are the sources of the largest errors in pressure-area relationships. Differences in surface tension due to the method of application are demonstrated with the 0.0169 g. rate of solid material. However, the high value obtained with solid material added directly to the water is difficult to explain. It is undoubtedly related to the method of spreading although sufficient time was allowed to permit monofilm formation. Talc applied to the treated surface indicated that a film was present. This value was used in Table 6 instead of the value for fatty alcohol dissolved in hexane, because it more closely represents the method used to apply fatty alcohol to the soils being studied.

completely soluble [illegible]

matic ba [illegible]

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Table 6. The effect of fatty alcohol on moisture retention by soils.

	Samples kept wet				Samples dried - rewetted			
	Rates of F.A.1/				Rates of F.A.			
Bars suction	0	0.005%	0.01%	0.90-1.24%	0	0.005%	0.01%	0.90-1.24%
	Fort Collins clay loam - solid fatty alcohol							
0.3	27.3	27.8	27.5	26.0	25.0	25.2	25.1	24.7
0.6	22.7	24.1	23.4	22.7	22.3	23.4	23.3	22.9
5.0	13.7	13.9	14.6	14.4	14.0	14.6	14.8	14.3
9.0	12.3	12.3	12.0	12.5	12.3	12.6	12.7	11.5
15.0	10.7	10.4	10.9	10.2	11.0	11.3	11.1	10.5
	Fort Collins clay loam - TA 16-18 emulsion							
0.3	27.3	25.2	24.7	23.7	25.0	24.6	24.6	24.1
0.6	22.7	23.2	23.6	20.9	22.3	23.5	23.1	23.0
5.0	13.7	13.0	13.1	14.1	14.0	14.2	14.0	12.3
9.0	12.3	12.0	12.0	12.1	12.3	12.3	13.0	12.2
15.0	10.7	10.3	10.4	10.8	11.0	10.6	10.7	12.1
	Hillsdale sandy loam - solid alcohol							
0.3	11.7	11.6	11.3	8.1	11.0	10.8	11.0	8.1
0.6	9.3	9.4	9.3	7.8	9.0	9.6	9.8	6.6
5.0	4.6	4.6	4.6	4.6	4.3	4.3	4.2	3.6
9.0	3.4	3.1	3.4	3.6	3.4	3.4	3.2	3.5
15.0	2.9	3.0	3.2	3.5	2.7	2.8	2.9	3.3
	Hillsdale sandy loam - TA 16-18 emulsion							
0.3	11.7	11.3	10.0	8.5	11.0	11.0	11.0	8.8
0.6	9.3	8.9	8.8	7.0	9.0	9.2	9.3	7.5
5.0	4.6	4.5	4.3	5.7	4.3	4.3	4.3	6.0
9.0	3.4	3.2	3.1	5.2	3.4	3.7	3.5	5.4
15.0	2.9	3.0	3.0	4.3	2.7	2.9	3.0	3.9

1/ The heaviest rate is 0.90% for the Hillsdale sandy loam and 1.24% for the Fort Collins clay loam.

This study indicates that at high rates of application, such as would be expected to occur at the air-water interfaces of small surface area in soil pores, the emulsion does cause a greater decrease in surface tension which is not entirely dependent on a monomolecular film. The difference between the surface tensions resulting from solid and emulsified materials in the soil should be even greater due to the formation of a less compressed film with the solid material on the curved surfaces of the soil water.

Soil Moisture Retention

The effect of fatty alcohol on moisture retention was studied using Hillsdale sandy loam and Fort Collins clay loam soils. Two sources of fatty alcohol and five suctions were used (Tables 6, 7, and 8). The rates of fatty alcohol used were 100 lbs. per acre, 200 lbs. per acre, and 0.1 symmetry but are reported as percentage by weight, being 0.005% and 0.01% for the first two rates. The 0.1 symmetry concentration is 0.90% for the Hillsdale sandy loam and 1.24% for the Fort Collins clay loam. One series of samples was kept wet after treatment with fatty alcohol and another set was dried and rewetted before being subjected to suctions of 0.3, 0.6, 5.0, 9.0, and 15.0 bars.

The data was analyzed in a split-plot design with two subdivisions. This permitted a statistical comparison of the effect of drying and rates of fatty alcohol for each material with each soil. The effect of solid fatty alcohol versus emulsion is not compared statistically although both materials are compared with the same untreated samples.

This [illegible] high rates of application, such as

Table 7. The effect of drying on water retention by soils treated with fatty alcohols.

Soil	Material	Wet	Dried	LSD 5%	LSD 1%
F.C. cl.	Solid	17.46	17.13**	0.23	0.33
F.C. cl.	Emulsion	16.77	16.96*	0.16	N.S.
Hd. s.l.	Solid	6.14	5.87**	0.12	0.17
Hd. s.l.	Emulsion	6.14	6.21	N.S.	

* Significant at the 5% level.
** Significant at the 1% level.

Table 8. The effect of rate of fatty alcohol on average moisture retention by soils.

		Rate of fatty alcohol - LSD					
Soil	Material	0	0.005%	0.01%	0.90-1.24%	5%	1%
F.C. cl.	Solid	17.12	17.55**	17.54**	16.97	0.32	0.36
F.C. cl.	Emulsion	17.12	16.90*	16.91	16.52**	0.22	0.30
Hd. s.l.	Solid	6.22	6.25	6.28	5.27**	0.19	0.25
Hd. s.l.	Emulsion	6.22	6.20	6.04	6.23	N.S.	

* Significant at the 5% level.
** Significant at the 1% level.

The effect of drying the samples was significant at the 1% level for those treated with solid fatty alcohols and at the 5% level for the samples treated with emulsion (Table 7). All other variables and interactions, rates of fatty alcohol, rates x tension, drying x tension, rates x drying, and rates x tension x drying were significant at the 1% level, with the exception of rates x drying for the samples with solid fatty alcohol.

Mean soil moisture values for rates of fatty alcohol are given in Table 8. The lighter rates of application of the solid material increased the average water content of the Fort Collins soil but resulted in a significant decrease with the same soil treated with emulsion. The higher rate resulted in a lower average water content when either material was used.

With this soil the effect of rates of application and drying were not consistent at all tensions used. With the solid material the 0.005% and 0.01% rates tended to increase the average water content at tensions less than 5 bars but at the higher tensions the water content of the treated samples was about equal or slightly less than that of the checks.

The water content of the samples treated with emulsion at the 0.005% and 0.01% rates tended to decrease at all tensions except 0.6 bar. With the high rate of emulsion, the water content was decreased at the lower tensions and increased at the higher tensions.

The trends with the Hillsdale sandy loam treated with both solid and emulsion form of fatty alcohol are quite similar to those of the Fort Collins soil treated with emulsion. The differences are greater

with the soil treated at high rates but there appears to be little difference due to the form of fatty alcohol.

The effects of drying and rate of fatty alcohol were not statistically significant with the Hillsdale soil treated with emulsion, however, all interactions were significant.

The differences between rates and tensions due to treatment with fatty alcohol appear to depend on whether the influence exerted on the soil-water system is active at the soil-water interface or the air-water interface. Where an excess of fatty alcohol is present the effect is at the air-water interface due to a decrease in surface tension and less water is held at the lower tensions. The presence of an emulsifying agent acts in the same manner as excess fatty alcohol. Apparently, the water films in the soil become discontinuous at lower tension than is normally required due to the lower surface tension. The result is an increase in water content at high tensions.

At the lower rates of application the emulsified material has a greater effect on the surface tension than the solid material applied at the same rates. The fatty alcohol in both materials is adsorbed by the soil particles and the decreased surface tension is probably the effect of the emulsifying agent which remains in the soil solution.

Infiltration

The effect of fatty alcohols on infiltration of water into undisturbed cores of the Hillsdale soil was studied. The cores were treated by adding sufficient solid fatty alcohol to the surface of the cores to have concentrations of 0.125, 0.25, 0.50, and 1.0 symmetry. The fatty alcohol added at these rates remained in great excess on the

surface of the soil. Only three replications were run. All samples were saturated with water before treatment with fatty alcohol.

The results show that infiltration was increased under the conditions of the test (Figure 4). Due to the low solubility and the excess of material even at the lowest concentration, the effect due to rates of fatty alcohol should not be great. In fact, infiltration into the soil cores treated at 0.125 and 1.0 symmetry concentrations parallel each other rather closely while the results from the two intermediate rates are quite similar. This indicates that averaging all treated samples to give one curve for excess, fatty alcohol might give the most accurate picture.

The increased infiltration rate in the treated samples is due to the decreased angle of wetting at the surface of the soil which was in contact with the fatty alcohol. The excess of fatty alcohol on the surface of the cores was so great that little free water was present for monofilm formation.

Two other sets of soil cores were placed in a tray of water deep enough to permit a free water surface above the soil. Some cores were treated with sufficient fatty alcohol to form a monomolecular film on the water surface. Other cores were treated with one half this amount of fatty alcohol, while the remainder were left as untreated checks.

Infiltration was determined on one set of cores while they were wet. The other set of cores was dried for 24 hours at room temperature and then saturated again. Ten replications of each set were run.

Infiltration was decreased in the cores that were kept wet (Figure 5). The average amount of water infiltrated per hour was quite

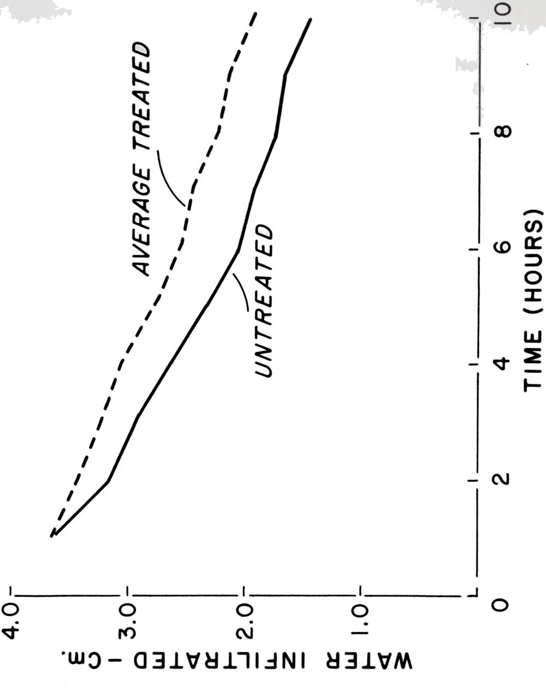

Figure 4. The effect of high rates of fatty alcohol on infiltration of water into undisturbed cores of Hillsdale sandy loam.

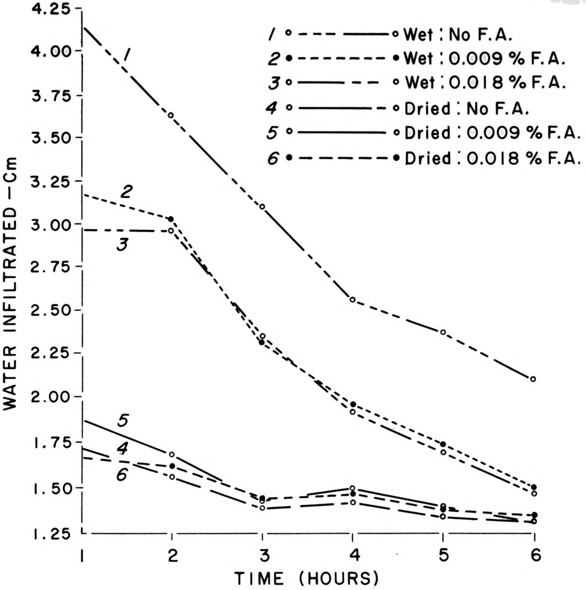

Figure 5. The effect of fatty alcohol applied at low rates on infiltration of water into undisturbed cores of Hillsdale sandy loam.

similar for the cores treated with the two rates of fatty alcohol. After one hour they reached essentially the same infiltration rate and remained together for the remainder of the test period. The rate of infiltration into the untreated soil was about 0.56 cm. greater per hour than those of the treated soils. Under these conditions, the fatty alcohol did not come in contact with the soil and did not show any influence at the solid-water interface.

When the samples were dried the infiltration rate was decreased considerably in both the treated and untreated soils. By drying the samples, the fatty alcohol was brought into contact with the soil where its adsorption prevented the formation of a monofilm on the water surface during the period in which infiltration was studied. The adsorbed fatty alcohol decreases the angle of wetting and results in a slight increase in infiltration rate. The infiltration rate was slightly higher at the higher rate of fatty alcohol and it is likely that the increase in infiltration rate would become considerably greater as the amount of the soil surface covered increased.

Vertical Movement

The excess fatty alcohol was removed from the cores used in the first infiltration study and the soils were sampled at 0.5 cm. depths to measure the vertical movement of fatty alcohol. The samples were extracted with hexane in a Soxhlet unit. The extracts were concentrated and a 5 microliter aliquot was run through a Beckman gas chromatograph to determine the fatty alcohol content.

Fatty alcohol was recovered from the 0 - 0.5 cm. depth only. The amounts recovered were variable, indicating incomplete removal of excess

material from the soil surface. Also, the amount recovered was not related to the original rate applied. Since there was adequate material present, it is apparent that fatty alcohol does not move downward in the soil with percolating waters to any great extent. This is undoubtedly due to the low concentration of fatty alcohol and the large amount of surface area in the soil. The first increments of applied fatty alcohol are adsorbed by the soil and even with an excess of material present, only small quantities remain free on the diminishing water surfaces in a drying soil. Therefore, it is possible that with repeated wetting and drying the depth of penetration would become progressively greater after the surfaces of the soil in one region became covered with sorbed material.

Lateral Movement

Lateral movement of fatty alcohol was studied by mixing solid material and emulsion with Hillsdale sandy loam which was placed in a 5.1 cm. strip in the middle of a tray. Additional soil was placed on each side of the treated strip and movement was measured in the same manner as in the vertical movement study. Solid material was also banded down the center of the 5.1 cm. strip. Some samples were kept wet for the five-day period of the study. Others were allowed to dry one, two, or three times. The soil was sampled at 2 cm. intervals on each side of the treated strip. The fatty alcohol was applied at 1 and 2 symmetry concentrations based on the surface area of the soil in the entire tray.

The mg. of fatty alcohol recovered per gram of soil are given in Table 9 for the mixed treatments. The figures are for hexadecanol

Table 9. Lateral movement of fatty alcohol in a Hillsdale sandy loam.[1/]

Times	Flake				Emulsion			
	1 sym.		2 sym.		1 sym.		2 sym.	
dried	C_{16}	C_{18}	C_{16}	C_{18}	C_{16}	C_{18}	C_{16}	C_{18}
				Mg. per g. soil				
0	0.07*	0.13*	0.50	0.93	0.10	0.25	0.39	0.73
1	--	--	0.05*	0.09*	0.45*	0.80*	0.26	0.49
2	1.33	2.43	0.10	0.18	0.15	0.32	0.86*	1.53*
3	--	--	1.70	3.27	0.43*	0.92*	0.17	0.43

[1/] All values are from the region 0 - 2 cm. from the treated soil. No fatty alcohol was recovered beyond this distance.

* Movement occurred only in one of the duplicate samples. Values reported are one-half the value measured from one sample.

(C_{16}) and octadecanol (C_{18}). Fatty alcohol was recovered from the 0 - 2 cm. distance only and the variation in the amounts recovered are erratic and show little relationship to the rate applied or the number of times the samples were dried. The results in table 9 marked with an asterisk indicate movement in only one of the duplicate samples and the blanks indicate no movement in either of the samples.

The results obtained from this test indicate that probably very little movement occurs as a monomolecular film. Rather, the erratic nature of the results suggests that most of the movement that occurred was probably due to currents set up in the system upon the addition of water. This could further be interpreted to mean that there is very little film formation on the curved surfaces of the water films in the soil.

There was no movement of fatty alcohol beyond the 5.1 cm. treated strip where band application was used.

Capillary Rise

The effects of fatty alcohol on the capillary rise of water in columns containing Hillsdale sandy loam and Fort Collins clay loam are given in figures 6 and 7.

The measurements were made over a 72-hour period. Five replications were used for all rates of fatty alcohol except for the 0.05 symmetry concentration. Two replications were used at this rate since the decrease in rise was consistently greater than the other rates and the rate of application was too high to have any practical significance. All rates are reported as percentage by weight and the 0.05 symmetry

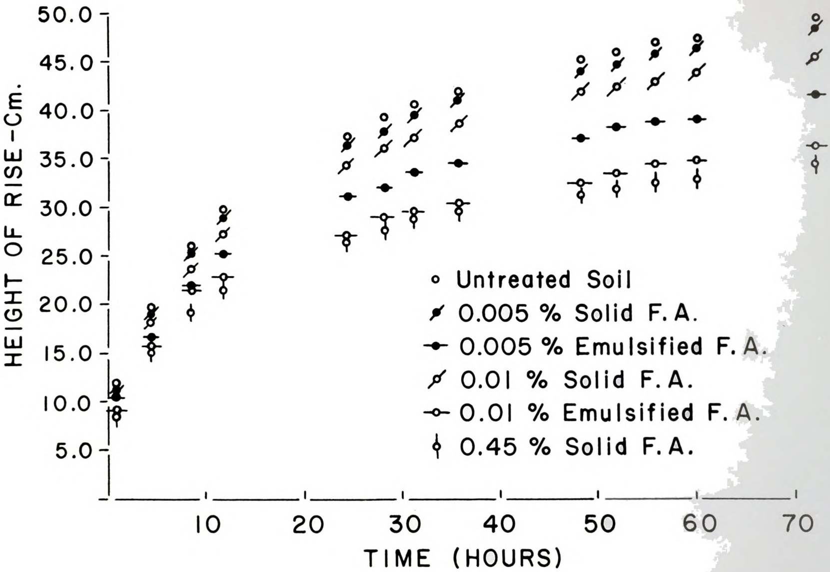

Figure 6. The effect of fatty alcohol on the rise of water in Hillsdale sandy loam.

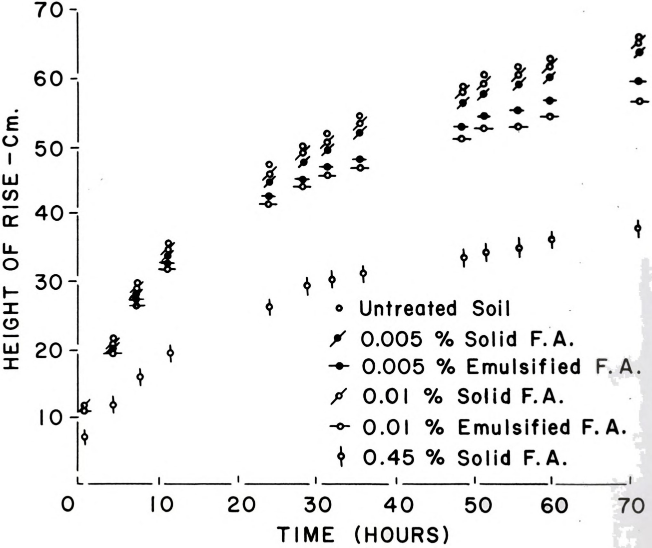

Figure 7. The effect of fatty alcohol on the rise of water in Fort Collins clay loam.

concentration is 0.45% and 0.62% for the Hillsdale and the Fort Collins soils, respectively.

The capillary rise was greater in the untreated soils than in the treated soils and with both soils, the height of rise was greater in the samples treated with solid material than it was in the samples treated with corresponding rates of emulsion after four hours. The 0.005% rate with emulsion caused a greater decrease in the height of rise than the 0.01% rate with solid fatty alcohol. This was probably due to the greater decrease in surface tension of the water because of the emulsifying agent added to the system.

The decrease in height of rise with the Hillsdale sandy loam (Figure 6) treated at the 0.005% rate with solid material was between 0.51 and 1.52 cm. less than the check at any sampling period but the rise in the samples treated at the 0.01% rate was 2.5 to 3.8 cm. less than the check after the first 4 hours. The samples treated with emulsion differed from the check by as much as 8.1 cm. for the 0.005% rate and 12.2 cm. for the 0.01% rate.

The effect of fatty alcohol on the capillary rise in the Fort Collins clay loam was quite different. The height of rise in the soil treated at the 0.01% rate with solid fatty alcohol was consistently greater than that of the soil treated at 0.005% with the same material.

The height of rise in the samples treated with emulsion was greater at the 0.01% rate through the first 12 hours but after this time it became greater with the 0.005% rate.

This experiment demonstrates the interaction between the decrease in the angle of wetting and the decrease in surface tension which occurs when fatty alcohols are put into the soil.

The equation:

$$h = \frac{2\,\gamma \cos\,\Theta}{\rho\;g\;r_p}$$

where h is the height of rise, γ the surface tension, Θ the angle of contact, ρ the density of water, g the acceleration due to gravity, and r_p the radius of the pores, shows the relationship of the contact angle and surface tension to capillary rise of a liquid. It is apparent that with a liquid of a given density in a system with the same average radius of pores, the height of rise due to capillarity will depend on the surface tension and the angle of contact between the solid and liquid phases. If the contact angle is decreased, Cos Θ will increase and h will increase if no other factors are altered. If the surface tension is decreased, with all other factors remaining constant, h will decrease.

The rate of fatty alcohol needed in a given material to effectively retard evaporation is related to the active surface in the system, but not in relation to monofilm formation. This can best be explained by figure 8 which demonstrates the relationship between the contact angle and surface tension. The line X' -- X" in figure 8 represents the height of rise of water in the untreated soil.

The data on the contact angle of treated bentonite systems shows a progressively greater decrease in the angle of wetting as the rate of hexadecanol increases to a concentration of about 0.1 symmetry. This is due to the increased surface covered by fatty alcohol as the concentration increases. This relationship plays a role in the rate of capillary rise by establishing a series of tension barriers between the normal soil particles and the coated surfaces of particles with

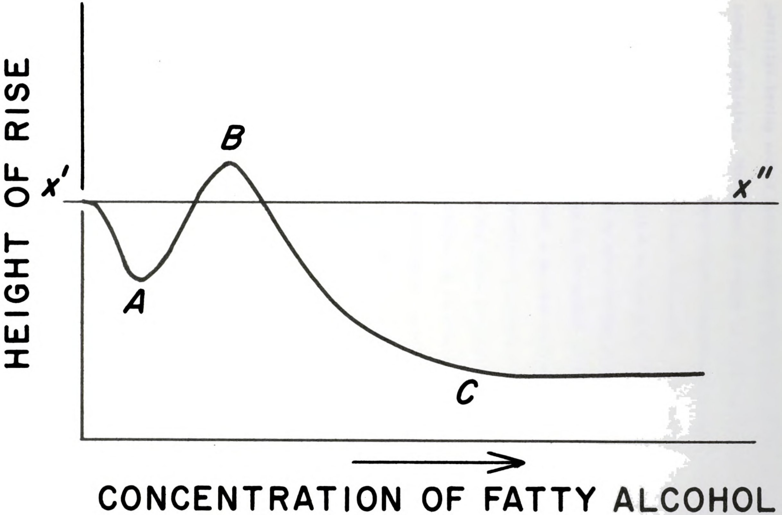

Figure 8. The proposed interaction between the contact angle and surface tension effects on capillary rise in soil treated with fatty alcohol.

adsorbed hexadecanol. These barriers are analogous to the tension barriers between fine and coarse layers in soil but are due to the particles having sorbed fatty alcohol being more easily wetted than normal particles. The effect of these barriers should become greater as the concentration of fatty alcohol increases to where about one-half of the surface of the soil is covered. This would correspond to the minimum reached at point A in figure 8. From this point the height of rise of water increases as more surface area is covered by fatty alcohol due to the decrease in the number of tension barriers. When the total surface is covered, a maximum in the height of rise is reached at point B. As the concentration increases above that necessary to reach the maximum at B for any given soil the effect of decreasing surface tension comes into effect. Up to this point the effect on capillary rise has been at the solid-water interface. At higher concentrations the effect is at the air-water interface due to the excess of unadsorbed fatty alcohol which decreases the surface tension of the water by the formation of at least a partial surface film.

At the concentration where the maximum decrease in surface tension is obtained, point C, the height of rise should remain constant with increased concentrations of fatty alcohol.

With the soils used in this study the Hillsdale has considerably less surface than the Fort Collins and the 0.005% rate with solid material would be on the portion of the curve from A - B or B - C near line X' - X", since this is evidently the concentration just above or below that at which the maximum height of rise would be obtained. The 0.01% rate with solid material is then farther down on line B - C. The

emulsified fatty alcohol affects the surface tension to a greater degree and both rates lie below the 0.01% rate of solid material on line B - C.

For this soil the 0.01% rate of emulsion is apparently approaching the minimum at C as evidenced by the small differences in capillary rise between this rate and the 0.45% concentration of solid fatty alcohol.

The 0.005% rate of solid fatty alcohol with the Fort Collins soil appears to be near the concentration needed to reach the minimum at A lying on the portion of the curve between X' - A or A - B. The 0.01% rate of solid material approached the maximum at B lying just below the line X' x X" on either the A - B or B - C portion of the curve.

Although the height of rise with both rates of emulsion was on the arc B - C below the 0.01% rate of solid material, the 0.01% rate of emulsion did not approach the minimum at C. The 0.62% rate reduced the rise of water considerably below that of the soil treated with emulsion.

DISCUSSION

The application of fatty alcohol to a free water surface results in the formation of a monomolecular film due to the attraction of the water for the hydroxyl group and repulsion of the hydrophobic carbon chain. The effectiveness of the film in suppressing evaporation depends on the density of the film. The equilibrium pressure reached by films formed from fatty acids rises to a constant value determined by the temperature of the water and the nature of the fatty acid (32). The determining factor concerned with the nature of the molecule is the straightness of the chain. Compounds with straight chains permit close packing of the molecules in the film and are more effective in retarding evaporation.

Since the formation of a monofilm is necessary for fatty alcohols to suppress evaporation from a free water surface their use in soils suggests that these materials form a monomolecular layer on the water surface in the soil pores. Due to the curved nature of the water surfaces in the soil, this assumption seems fallacious. However, in order to provide some basis for establishing rates of application this study was based on the hypothesis that monofilms were formed on the water surfaces in the porous media. The hypothesis was extended to consider that when the water films in the soil became discontinuous the fatty alcohol would be sorbed on the soil particles in relation to the surface area provided.

The behavior of fatty alcohols applied to soils is dependent on the sorption of the materials by the soil particles.

X-ray diffraction patterns show an increased d(001) spacing due to adsorbed fatty alcohol. The amount of adsorbing surface in the soil in relation to the amount of fatty alcohol applied will regulate the overall effect on the soil-water system.

Differential thermal analysis shows an increase in the energy requirement for oxidation of fatty alcohol adsorbed by Wyoming bentonite. However, the bonding energy is not great enough to be determined by this method. X-ray data in this study indicates some bonds between the clay and fatty alcohol are strong enough to withstand hexane extraction if the suspension is not agitated. When the samples are dried, the bond strength is apparently increased by bringing the clay and fatty alcohol into more intimate contact.

The type of bonding between the fatty alcohol and Wyoming bentonite cannot be identified with infra-red absorption. However, due to the nature of alcohols and the fact that shifts in the OH stretching and bending frequencies are masked by the large number of hydroxyl groups associated with the clay but not bonded, it is proposed that hydrogen bonding is the principal type of bond involved. It is also probable that secondary bonding occurs due to van der Waal's forces.

The angle of wetting of Wyoming bentonite is decreased by the sorption of fatty alcohol, resulting in increased wettability of the clay. This effect becomes dominant in the behavior of the soil-water

system at rates of fatty alcohol insufficient to satisfy the entire adsorbing surface of the soil. The behavior of the soil-water system is affected at the solid-water interface and is dependent on the degree of saturation of the adsorbing surface.

Fatty alcohols decrease the surface tension of water. At concentrations sufficient to permit excess material in the soil solution, above that required to cover the active soil surface, this effect becomes dominant and the behavior of the soil water system is affected at the air-water interface.

This effect of covering the surface at lower concentrations in coarse materials has caused hexadecanol to be satisfactory in suppressing evaporation in these materials while having little or no effect in fine material at the same concentration. As the amount of material is increased beyond that needed to cover the surface of the soil particles, the fatty alcohol becomes active at the air-water interface by decreasing the surface tension. The magnitude of the decrease is related to the amount of material present in the soil solution up to the point where the surface film obtains the maximum compression possible under the conditions of the system. Since the surface tension of water containing a surface film is related to the extent to which the film is compressed, it is not likely that the decrease in surface tension of the soil water will be as great as that of free water. Three factors which affect monofilm formation will be altered in the soil water system. Equilibrium monofilm conditions are obtained on the clean surface of pure water, the soil solution does not conform to this condition. The decreased wetted perimeter of the fatty alcohol due to complete or partial submersion of the material in the soil system will retard surface film

formation. If a monomolecular film is formed at the air-water interface of the soil-water system it would be less effective than that on a free water surface due to the poor fitting of the molecules on the curved water surfaces.

The effect which fatty alcohols exert at the solid-water and air-water interfaces in the soil-water system have been demonstrated by infiltration, capillary rise, and water retention studies. The results of these studies can be used to interpret the results of several studies involving the suppression of evaporation from soils with hexadecanol. Several investigators (12) (31) have found that the role of soil in evaporation is that of a reservoir, and the rate of evaporation is controlled by the ability of the soil to transfer water to the evaporating surface. Anything that will decrease the rate of capillary rise will also decrease the rate of evaporation from the soil, whether it is active at the solid-water interface or the air-water interface.

However, when the activity at the solid-water interface results in increased wettability of the soil it is possible, at least theoretically, to increase evaporation above that of the untreated soil. Thus, in soils treated with rates of fatty alcohol sufficient to cover the surface of the soil particles without providing excess material to be active at the air-water interface it should be possible to increase the rate of evaporation by increasing the rate of capillary rise.

Fatty alcohols are most successful at suppressing evaporation from soil when they are active at the air-water interface. The reduction of evaporation from the soil is dependent on retarding the movement of liquid-water by decreasing the surface tension rather than retarding vapor movement by the formation of an energy barrier.

Olsen et al. (28) found that the effectiveness of fatty alcohol in suppressing evaporation was increased by placement in the surface inch. This was undoubtedly due to the relative immobility of fatty alcohol in the soil which resulted in the concentration in the treated area remaining fairly constant. At the rates used, the effect was at the air-water interface and persisted over a long period of time. This study demonstrates the need to concentrate the fatty alcohol in order to effectively suppress evaporation.

The results of experiments such as Wooley's (43) can be interpreted on the basis of this study. Water movement in a medium of low capillary conductivity such as sand could be greatly retarded by a small decrease in surface tension of the water even with a high water table. Due to larger pores and more level water surface in a sand system, it is quite likely that the fatty alcohol molecules in a surface film are more compressed than they would be in a system containing heavy textured soil but the action retarding evaporation is more likely due to preventing liquid water from rising than from blocking vapor movement. The fact that he did not find any retardation of evaporation from loam or clay soils at the high rate of fatty alcohol used, was probably an artifact of the system. That is, a small volume of soil and a high water table.

Lemon (22) demonstrated a decrease in capillary rise in a sand-kaolinite mixture over the short period of 25 minutes using 0.1% by weight of hexadecanol. The soils and rates used in this present study showed little effect on capillarity until after about four hours except for the highest rate. However, the soils contained considerably greater surface area than a sand-kaolinite mixture and would therefore, require correspondingly higher rates in order for the fatty alcohol to become

active at the air-water interface. Lemon also assumed the cetyl alcohol to be active at the clay-water interface which is based on an assumed increased angle of wetting.

The amount of fatty alcohol needed to reduce the rate of capillary rise of water in soil is related to the specific surface of the soil but it is not associated with the formation of a monomolecular film since the molecules are adsorbed by clay particles with the carbon chains parallel to the oxygen sheets.

The rate needed to cover the effective surface is even less than can be calculated from the largest surface area presented by the fatty alcohol molecule. The length of the cetyl alcohol molecule is 22 Å and the cross-sectional area is 21 $Å^2$(13). The average increase in interplanar spacing due to adsorbed fatty alcohol is about 2.06 Å, therefore, the area covered by one molecule lying with its largest surface adjacent to the clay should be approximately 224.18 $Å^2$. This value is about 10 times greater than the cross-sectional area of 21 $Å^2$ used to calculate the symmetry concentrations. Thus 0.1 symmetry as used in this study should cover the surface area of the soil particles but actually, concentrations of at least one-half this amount provided ample fatty alcohol to affect the surface tension of the soil solution.

There are three factors which could prevent a linear relationship between the surfaces of the two materials: (a) The arrangement of the absorbed fatty alcohol molecules is not in close packing, that is, the bonding angles in the carbon chain are not arranged symmetrically upon absorption but rather the apices of the C - C bond angles are toward each other resulting in two molecules covering more surface than would occur if each of the molecules were oriented in the same direction;

(b) The adsorption of fatty alcohol is not complete in that partially adsorbed molecules block adsorption of other molecules which then remain free in the soil solution; (c) The strength of some bonds is not adequate to prevent the release of the molecules on wetting. All three of these factors may be active to some degree but it is likely that the arrangement of the molecules within the clay lattice will have the greatest effect on surface coverage and the tests conducted in this study indicate that (c) will likely be the least important.

CONCLUSIONS

Fatty alcohol added to soil is adsorbed by the soil particles. When the amount of material is less than that required to cover the entire surface, the movement of water in the soil is decreased due to tension barriers that are established between the normal soil particles and the more easily wetted particles with sorbed fatty alcohol. At the concentrations where the entire surface is covered by fatty alcohol, without an excess of material remaining in the soil solution, water movement within the soil is increased due to increased wettability of the soil. After the soil surface is covered, additional fatty alcohol becomes active at the air-water interface, decreasing the surface tension and water movement. The magnitude of the decrease is related to the amount of material present in the soil solution up to the point where the surface film obtains the maximum compression possible under the conditions of the system.

The attraction between fatty alcohol and clay is due primarily to hydrogen bonds, however, van der Waals forces are also active. These bonds are strong enough to resist solution by hexane extraction.

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