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Conditioning of Agricultural Soils with Fatty Acid Still Pitch[1]

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VEGETABLE PITCH is the residue obtained from the commercial distillation of fatty acids. This material is very soluble in ethyl ether but only slightly soluble in acetone, low boiling aliphatic hydrocarbons, and acetic acid. It may be concluded that this material, like soil humus, is of high molecular weight and is highly polar. This paper reports successful preliminary experiments on the use of vegetable pitch as an agricultural soil conditioner. Since this laboratory contemplates no further studies at this time, it is hoped others may wish to extend the work, especially to field trials.

In this paper a "soil conditioner" is considered to be an agent which improves the tilth and water-holding capacity of agricultural soils. It is measured in the laboratory by the resistance to disintegration of standardized pellets of the soil by means of agitation with water. The term "soil stabilizer" is reserved for agents which tend to water-proof soils and implies load-bearing characteristics such as necessary for roads, runways, levees, etc. Although pitch can act as a stabilizer when used in larger amounts than necessary for agricultural purposes, this use is not considered in this report.

Experimental

Materials. Boston blue clay was used as obtained from T. W. Lambe, Massachusetts Institute of Technology.

Princeton clay was obtained near Glendorado, Minn., at a location recommended by C. O. Rost of the University of Minnesota. It was screened (¼-mesh) to remove stones, pebbles, twigs, and roots.

Solvents and chemicals were reagent grade.

The Krilium (CRD-186) used was a commercial product of the Monsanto Chemical Company.

Vegetable Pitch 250[2] was a product of General Mills Inc. It is the still residue remaining after distillation of monomeric fatty acids. It is dark brown and highly viscous. It contains thermally and oxidatively polymerized fatty acids esterified in part with glycerine. No doubt the unsaponifiable fraction contains some hydrocarbons. Possibly polyketones are also present. The original source is cottonseed and soybean oil soap stock. Figure 1 shows the infrared scan of the sample used and indicates the presence of hydroxyl, acid, and ester groups and about three times as many methyl groups as is normal for C_{18} fatty acids. The excess methyl groups may be caused by sterols, which are known to be present.

Procedure for Testing. Krilium was applied to the soil merely by mixing the dry powder with the dry clay.

Still pitch was applied by dissolving it in ethyl ether, slurrying this solution with the dry clay, and evaporating the solvent on the steam bath. The samples were tested by a modification of the method of Yoder (1) as recommended by Professor Rost (2). Then 100 g. of the dry soil sample were mixed with sufficient distilled water to form a plastic mud. The amounts of water required are shown in Table I and are rough measures of the water-holding capacity of the sample. A more accurate method is that of Bouyoucos (4). The plastic mud was then extruded through a 5.0-mm. sieve, and the "crumbs" were allowed to air-dry about 10 days although two days are said to be sufficient. Next 100 g. of the dried crumbs were added to 1,000 ml. of water in a 1,000-ml. graduated cylinder. The stoppered cylinder was inverted 30 times in 60 seconds. The slurry was poured through a set of sieves (0.5 mm. to 0.1 mm.) and washed with a gentle stream of water until no more soil passed through. The aggregates were dried and weighed. The total weight of these aggregates is called the percentage of aggregation.

TABLE I

Conditioner	H_2O needed [a] to form plastic mud	Aggregate on 0.5-mm. screen	Aggregate on 0.1-mm. screen	Total aggregates
		%	%	%
None	....	0	0	0
1% pitch	40	3.9	6.9	10.8
2% pitch	45	34.6	23.0	57.6
4% pitch	60	97.8	0.3	98.1
0.1% Krilium	48	5.4	3.1	8.5

[a] Grams H_2O per 100 g. treated soil.

Emulsification of Vegetable Pitch. Both 180 ml. of warm distilled water and 20 ml. of concentrated ammonium hydroxide (57%) were agitated in a Waring blendor. To this were added 40 g. of fluid (hot) pitch. After one minute of agitation an emulsion stable for several days was obtained.

Discussion

Vegetable pitch as examined in this brief study shows considerable promise as a soil conditioner.

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[2] Iodine value 93, acid number 15, saponification number 120, unsaponifiables 25%, nitrogen 0.4%, ash 0.6%.

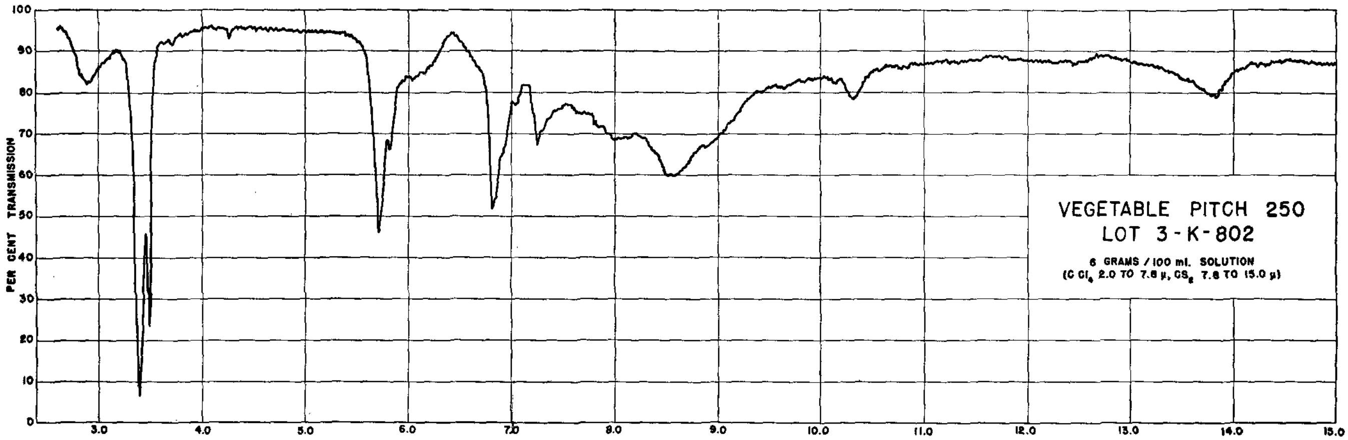

FIG. 1.

Table I shows the results of the addition of 1, 2, and 4% to Boston blue clay.

One per cent of vegetable pitch is more effective than 0.1% of Krilium on this Boston blue clay. The present price of Krilium to distributors is $1.47 per lb. while the price of pitch is only $0.02 per lb. Thus if the cost per acre is $200, using Krilium, the same or greater degree of aggregation can be obtained for less than $28 by using vegetable pitch.

No pre-treatment of the pitch was attempted. Undoubtedly its efficiency could be increased by increasing its molecular weight or by altering its ratio of polar to non-polar groups. Its low price in comparison to that of the synthetics would certainly justify some effort being spent to upgrade it.

The Boston blue clay appears to require an extremely large amount of conditioner. Most agricultural soils would probably contain more natural polyelectrolytes and particles of larger size. When 1% of pitch was applied to "Princeton Clay," waterproofing occurred. A quarter percent also gave this effect temporarily. However with 0.05% the soil wetted well. The percentage of aggregation was not determined.

It is obvious that economical commercial large-scale application could not be done by the laboratory solvent methods. One emulsion in dilute ammonium hydroxide was prepared and was relatively stable. Twenty parts of hot pitch were dispersed in 100 parts of 6% NH_4OH, using a Waring blendor. With commercial equipment perhaps even higher concentrations of pitch could be used. Such emulsions or preferably the hot, fluid pitch itself could be sprayed on the soil as it was being rigorously tilled. It may not be necessary uniformly to coat each soil particle with a film of pitch. Indeed, to minimize waterproofing and to increase the effective life of the material, it may be desirable to have much of the pitch present as discrete particles which slowly disperse throughout the soil. Thus as thin films were being destroyed by natural forces, they would be replaced by material migrating from the larger particles of pitch. This may in part simulate that which occurs when large pieces of organic material decay in the soil.

Another method of applying the pitch would be to spray it on crop residues, which are then plowed under. Also it should be possible to use conventional farm equipment if the pitch is converted to a granular form with fillers such as lime, sawdust, or ground corn cobs.

Trace elements required by growing plants are rapidly complexed by the inorganic components of many soils and hence become unavailable. Organic chelating agents and even glass powder has been used to release these elements slowly to the soil. Pitch, especially in the form of discrete particles, should be an excellent vehicle for this purpose with the elements in solution or perhaps even chemically bound to organic radicals.

No studies were made of the length of time that vegetable pitch would remain effective as a soil conditioner. Natural agents such as occur in manure and decaying crop residues are rapidly broken down by soil organisms. The synthetics, on the other hand, are relatively resistant and many last several years. Since the chemical nature of the polymers comprising pitch are somewhat natural but largely synthetic as the result of processing conditions, it would be expected that its useful life in agricultural soils would approach that of the true synthetics.

Little is known about any possible toxicity to growing plants. Quack grass was not killed when treated with 1 gal. of a solution of 2 lbs. of pitch in equal parts of ethyl ether and hexane per 100 sq. ft. The area was immediately mulched with straw, but within a few days fresh vigorous sprouts appeared and flourished. It is quite possible however that less vigorous plants would be affected.

Erosion in the United States is a serious problem as evidenced by loss of useful farm lands, the burying of towns under as much as 14 ft. of washed-in mud (3) as well as floods resulting from reduced water-holding capacity of the soil. The importance of soil conservation is shown by the probability that our population increase will wipe out present farm surpluses and make us a food-importing nation within 20 years.

The annual production of vegetable pitch is many millions of pounds, increasing with increased use of distilled fatty acid. If practical applications confirm the present laboratory indications, vegetable pitch as a soil conditioner may help conserve agricultural soil for posterity.

Summary

Still pitch remaining after the commercial distillation of soy and cottonseed oil fatty acids may be an effective agent for improving the tilth of certain agri-

cultural soils. It greatly increases the water-holding capacity. Up to 98% of Boston blue clay was converted to water-stable aggregates by 4% of pitch. One per cent of pitch ($0.02/lb.) gave 10.8% aggregation while 0.1% of Krilium ($1.47/lb.) gave 8.5%.

The cost of soil conditioning with pitch is estimated to be only 15% of the cost in using synthetic polyelectrolytes. Possible methods of application and the use of pitch as a vehicle for trace elements are discussed. Toxicity to plants and effective life in the soil are not known. Field evaluation is urged.

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Phase Behavior of Fatty Acids-Chlorinated Solvent Systems

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THE SOLUBILITY DATA of single fatty acids in a number of solvents and the separation of fatty acids by crystallization reported up to 1937 have been reviewed by Brown (3). Since then additional solubility data for the single acids in solvents for a number of temperatures have been reported by several investigators (4, 5, 6, 7, 8, 11). Melting point and eutectic composition data have been reported for binary systems of saturated and unsaturated acids (15, 16). The review of additional solubility and melting data has been brought up to date by Markley (9) and Bailey (1).

The effect of the presence of one acid on the solubility of another in solvents was first investigated by Waentig and Pescheck (17). Intersolubilization data have been reviewed (9), and more recent data have been presented for binary fatty acid systems in selected solvents (12, 13, 14). No general conclusions on intersolubility can be drawn from the small amount of data now available.

This work presents solubility isotherms for the binary mixtures of palmitic and oleic acids in ethylene dichloride and carbon tetrachloride and stearic and oleic acids in ethylene dichloride and trichloroethylene. These results permit predicting conditions for the separation of the pure saturated from the unsaturated acids and add to the knowledge of intersolubility effects. Solubilities of the three pure acids, palmitic, stearic, and oleic in each of ethylene dichloride, trichloroethylene, and carbon tetrachloride have been determined over a range of temperatures. Also the solubility of palmitic and stearic acids in oleic acid at 30° and 50°C. are included.

Experimental Part

Procedure

The solubility data for the ternary systems were obtained in the apparatus shown in Figure 1. This is a modification of one used by Bailey and coworkers (2). The well-agitated, constant temperature bath was controlled to within 0.1°C. by an interconnected heating and refrigeration system. This bath housed six equilibrium, filtration units mounted together for magnetic stirring of the contents. This arrangement of equilibrium units is shown at the extreme right of Figure 1.

Samples containing different proportions of the fatty acids and solvents were placed in tubes containing a tin-plated, iron stirring coil. The glass joints were lubricated with a starch-glycerol gel, and

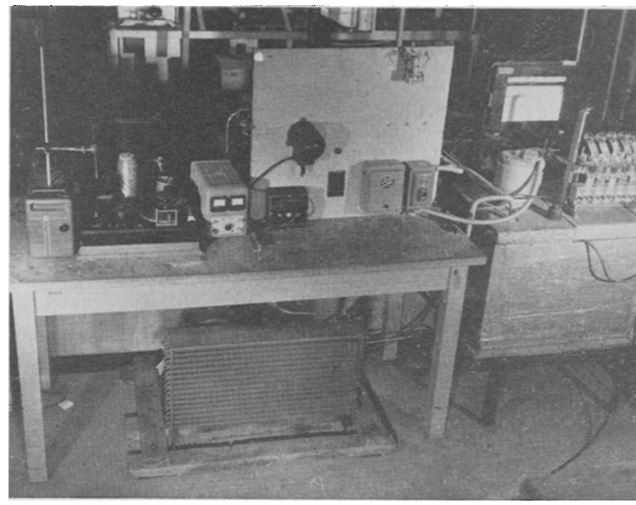

FIG. 1. Experimental apparatus.

the units were mounted on the electromagnet carrier. The samples were first heated to dissolve all solids, then cooled 5°C. below the initial crystallization temperature. This approach from the cold side has been discussed earlier (4, 13) and recommended (13) for reproducible results. An equilibrating period of 8 hrs. was used when it was found that no change in solubility occurred after 6 hrs. After this period the equilibrium cells were rotated in the bath, permitting the filtrate to pass through the coarse, fritted glass filter into a spherical flask collector. The filtrate was analyzed for solvent content, and the unsaturated and saturated fatty acids were determined by the method specified by the American Oil Chemists' Society. The composition of the solid was not determined and can be calculated from the composition of the original mixture and the filtrate composition by assuming closure of the material balance.

Materials

The fatty acids were obtained from the Hormel Foundation, which supplied the following analyses:

	I.N.	M.P., °C.	Purity %
Palmitic acid	none	63.5	99
Stearic acid	none	69.0	99
Oleic acid	89.8[a]	......	99

[a] Theoretical value is 89.87.

These were obtained in small tubes, sealed under an inert atmosphere to prevent oxidation. They were