THE EFFECT OF VARIOUS ORGANIC AMENDMENTS ON THE PHYSICAL AND CHEMICAL PROPERTIES OF SEVERAL SOILS AND CLAY MINERALS

Ву

John Arthur Archibald

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

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ABSTRACT

The effect of a number of organic amendments on the physical and chemical properties of a typical Ontario grape soil was measured. Although several of the materials markedly improved aggregation, porosity, and other physical properties, there was no significant difference in grape yields between treated and untreated plots.

Following the field experiment, a laboratory study was made of the effect of soil conditioners on the ion-exchange properties of four Ontario soils, Wyoming bentonite, and kaolinite. Preliminary experiments indicated a marked effect of small amounts of conditioner on cation-exchange capacities of soils and clays.

A detailed study was made of the effect of various concentrations of the acid form of VAMA, a vinyl acetate-maleic acid copolymer, on the cation-exchange properties of a hydrogen-saturated bentonite. It was found that at very low concentrations of VAMA, the cation-exchange capacity of the clay-conditioner mixture dropped rapidly. Slight increases in conditioner concentration resulted in a large increase in exchange capacity. As conditioner concentration was further increased, the cation-exchange capacity again decreased, and remained below theoretical value for the clay-conditioner mixture at all higher concentrations used.

This evidence shows conclusively that there is an ionic exchange reaction between a VAMA-type conditioner, and a montmorillonite-type clay.

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I. INTRODUCTION

The recent introduction of soil-conditioning materials has resulted in an upsurge of interest in the value of organic soil amendments. Perhaps the greatest value of these new conditioners is that they have created more interest in the whole field of clay-organic complexes. Even if they do not become widely used, the knowledge obtained from their study will add greatly to the field of Soil Science.

In the Niagara Peninsula of Ontario, an area favored by the moderating influences of Lake Ontario and the Niagara Escarpment, there are grown about 20,000 acres of grapes. Because of a relatively low acre-return of this crop compared to peaches and other tree fruits, grapes are invariably put on soil unsuited to other fruits. The average grape soil is fine-textured, compact, and low in organic matter. On such soils, naturally fertile but unproductive, additions of fertilizer materials have not increased yields. Organic matter additions have increased yields consistently.

With this fact in mind, it was felt desirable to compare the effects of soil conditioners presently available with conventional organic supplements, to evaluate their effects on soil properties. The first part of this thesis then deals with the effect of these organic amendments on a typical Ontario grape soil.

In the short time that conditioners have been available for experimental work, much has been learned of their effect on physical properties of soils. Little is yet known of the nature of the clayorganic union which is assumed to form the basis of their action.

A series of laboratory experiments were made in an attempt to elucidate the nature of the clay-organic linkage, or at least to accumulate information on the effect of various conditioner materials on the properties of several representative soils and clay minerals.

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II. REVIEW OF LITERATURE

Part A - The Effect of Organic Soil Amendments on Grape Production

There is considerable evidence to indicate the value of organic matter additions, and of high organic content of soil, in grape production. This evidence has accumulated from work done under widely varied conditions of climate and soil.

Partridge and Veatch (21) working in southwestern Michigan on Plainfield, Fox, and Oshtemo soils, pointed out that variations in the thickness of the humus layer of the surface soil had more influence on vine growth and production than did any other soil factor. Fruit production on humus layers three to six inches in depth was double that where the humus layer was less than three inches.

Gourley (9) in Ohio, reported yield increases from applications of manure, Cooper and Vaile (4), in Arkansas, also found that moderate manure applications increased the yield of Concord grapes.

Faurot (6), working in Missouri, has shown that manure appears to be of greatest value for use on older, established vineyards. He further found that the use of commercial fertilizer, of various analyses, and at varied rates, did not produce yield increases sufficient to pay for the cost of the materials used.

Upshall et al (31), carried out a long-term experiment with the Concord grape in the Niagara Peninsula of Ontario, on a Vineland clay-loam soil. This soil is poorly drained, with a heavy clay subsoil. The experiment was begun in 1929 and concluded in 1948. Various rates of application of nitrogen, phosphorus, and potassium fertilizers were used alone, and in combination. In addition hay and straw treatments were included, alone, and in combination with the above fertilizer materials.

The hay and straw treatments were the only ones that produced continuous and statistically significant yield increases. Greenmanure crops tended to produce higher yields. A complete fertilizer did increase growth and total dry matter content of green-manure crops and in this way fertilizers may have indirectly influenced crop returns.

The above evidence, particularly that from Ontario, indicated that organic soil amendments are of great value in grape production. There is little evidence presented, however, on the actual effects of such amendments on soil properties. It was confined in most cases to the effect of treatment on crop yield.

Part B - Development of Soil Conditioners

The nature of the clay-organic complexes involved in soil aggregation and stabilization is a problem which has received considerable attention in the past several years. Following the introduction of the new "soil-conditioners," interest was intensified.

Gieseking (7) in 1939 was able to spread the c-axis spacing of montmorillonite by the addition of organic bases.

Ensminger and Gieseking (5), in 1942, showed that adsorption of proteins on the base-exchange complex interferes with normal enzymatic hydrolysis. This interference was dependent on the base-exchange capacity of the clay, and was greatest at lower pH values.

Norman and Bartholomew (19), in 1943, found evidence of combination of uronides with clay particles. Uronides are constituents of hemicelluloses, pectins, mucilages and gums. The higher the number of uronic groups, the greater the resistance of these compounds to decomposition. These materials have been shown to be of value in soil aggregation.

Martin (15), was able to show in 1946, that becterial polysaccharides were definitely responsible for increased aggregation and stability.

Quastel and Webley (26), found that methyl cellulose and carboxymethyl cellulose had good aggregating effects, but decomposed readily.

Van Bavel (32), in 1950, found that the use of dimethyl dichloro silane stabilized structure and produced a waterproofing effect. This

increased stability may have been due to the slower rate of wetting when placed in the wet-seiving apparatus. A serious disadvantage of this gaseous material lies in its toxicity to animal life.

Hedrick and Mowry (10) point out that polyuronic acid salts, and related polysaccharides have not proven successful because: (a) the large quantities needed release toxic quantities of cations (b) the large amounts of rapidly decomposable organic matter upset the microbiological balance of the soil (c) the rapid microbiological decomposition of added polysaccharide derivatives makes the use of such materials uneconomical. These authors found that the sodium salt of a hydrolyzed polyacrilonitrile (released as Formulation 9 by the Monsanto Co.) of general formula

> н н - С - - С -= О Н С - О - Na X

and the calcium salt of a modified vinyl acetate-maleic acid compound (Formulation 6)

-
$$CH - CH_2 - CH - CH -$$

O COOR COOR
C = O
CH₃ X

were effective in stabilizing structure. Further, these water-soluble polymeric electrolytes of high molecular weight were effective in extremely low concentrations. These authors also showed by the Warburg technique that these two materials were non-toxic to yeasts and other soil organisms. Also, trace-element availability was not affected, and the materials were not toxic to higher animals. The leaching losses of the polyelectrolytes from a treated soil were negligible. Although they found that abietic acid, silicates, and volatile silicones also stabilized structure, the water-proofing effect lowered the water holding capacity.

Ruchrwein and Ward (29) used sodium polymethacrylate, a poly-anion, and poly B-dimethylaminoethylmethacrylate hydroacetate, a polycation, to study the mechanism of clay aggregation by polyelectrolytes. Using Wyoming bentonite, they found by X-ray diffraction measurements that the c-axis spacing of the montmorillonite was increased by the polycation but not by the polyanion, thus indicating that polycations but not polyanions are adsorbed in the interplanar spacing of montmorillonite. They also found the polycation to be an effective flocculating agent. The polyanion did not act as a flocculating agent, but was effective in stabilizing flocculated clay. They state that it is possible for sodium polymethacrylate to bridge between two clay particles, since the length of the molecules is comparable to that of the clay particles. For a given heat of adsorptiono the adsorption of the polyanion on clay is more likely than that of simple ions, due to the smaller entropy of adsorption of the polyelectrolyte.

Martin et al (17) used HPAN (Krilium 9) and VAMA (Krilium 6) on Miami, Crosby, Brookston and Paulding soils. They found a marked

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stabilization of aggregates, with the major portion of the particles stabilized in the two to five mm., and greater than five mm., size ranges. Of a variety of crops grown, corn, oats, and carrots were most responsive. These authors also showed that soil crumbs treated with either of these materials remained stable for 32 months at 76 F.

Allison (1) showed the value of the two Krilium conditioners on saline soils. They reduced crusting and resulted in a much higher rate of seedling emergence. Weeks and Coulter (33) studied the effect of HPAN on erosion control. They found that the material was of value in temporarily controlling erosion until vegetation became established. This material, however, was not superior to straw mulch for reducing runoff and erosion.

W. P. Martin (16) in a recent article summarizes the early results with VAMA and HPAN on Ohio soils. He points out the value of these materials for increasing water infiltration rate and early spring drainage. This may explain the fact that he found earlier maturity dates for a variety of crops on treated soils. He also found that conditioner applications may result in greater crop response to fertilizer materials.

Sherwood and Engibous (30) in a similar paper state that ionexchange capacities may be affected by treatment with conditioners. They indicated that an application of 0.15 percent conditioner decreased cation-exchange capacity in treated soils.

To summarize, the interaction between clay, and organic cations and anions, has received considerable attention in recent years. Recent interest has centered mainly around two materials, the sodium salt of a hydrolyzed polyacrilonitrile and the calcium salt of a modified vinyl acetate-maleic acid compound. These materials are effective at low concentrations in stabilizing soil structure, and are less readily decomposed than the naturally-occurring polyuronides which have been shown to be of value in improving soil structure and stability.

An ideal synthetic soil conditioner then, should be effective for long periods in stabilizing soil structure without reducing water holding capacity. It should have a low rate of destruction, and should not adversely affect biological activity, either by toxic effects on plants or animals, or by disturbing microbial activity. Also, it should not remove trace elements necessary for plant nutrition. Once a material meets these conditions, it must then be determined whether it can be produced in large quantities economically enough to make its widespread use as a soil conditioner practicable.

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III. EXPERIMENTAL

Part A. Field Experiment

Experimental Methods

The field experiment was carried on in the grapery of T. G. Bright and Co. Ltd., in Niagara Township, Lincoln County, Ontario near the hamlet of Virgil. The experimental plots are part of a 1000 acre tract of land owned by the above Company and used solely for grape production. The soil is typical of Niagara Peninsula grape soils, and has been temtatively classified as a Jeddo clay loam, by the Ontario Soil Survey staff. Since the Soil Survey Report for Lincoln County has not yet been written, the following description was taken from notes of the Survey staff.

<u>Description of soil</u>. The Jeddo soils are developed on heavy subaqueous till from calcareous materials. The weathered profile is more acid than the Brookston and lacks distinct color and textural horizons. The Jeddo is the poorly drained member of the Haldimand catena, the Caistor being the imperfectly drained member. It exhibits characteristics in accord with those of the Gray Hydromorphic Soils.

Profile.

- Al Four inches; dark gray clay to silty clay; sticky; some grit; pH 5.8.
- A2 Six inches; very dark gray clay with yellowish brown mottlings; some grit; pH 5.8.

- G Twenty inches; gray clay with light yellowish brown mottlings; structure large to massive; sticky; some grit; pH 6.2.
- C Fine gray till with some light yellowish brown mottlings; some grit, stones, and dark colored shale fragments; massive; sticky; pH 7.4.

The topography is level to gently undulating, with small depressional areas. Both external and internal drainage are poor. The native vegetation was elm, soft maple, hickory, swamp and bur oak.

The major difference between the Jeddo and Brookston series is the lower pH and the larger proportion of shale found in the Jeddo. The Brookston has a higher organic matter content, a darker surface, and the profile contains a slightly greater concentration of rusty-colored mottles.

<u>Plot design</u>. A randomized block experimental design was used, with ten treatments, and four replicates. The plot size was eleven by thirty feet, with buffer rows between series. The six grape vines bordering the plots were used for record purposes. The grapes were the Agawam variety, a red grape widely grown for wine production in that area of Ontario.

Treatments. The following treatments were used in the experiment:

- 1. VAMA (Krilium 6)
- 2. HPAN (Krilium 9)
- 3. Sugar
- 4. Lical
- 5. Sawdust

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- 6. Grape pomace
- 7. Alfalfa meal
- 8. Straw
- 9. Lionex
- 10. Check

The straw, alfalfa meal, sawdust, sugar, and grape pomace were applied at the rate of five tons per acre on a dry matter basis. The two Krilium formulations, the VAMA and HPAN previously described, were applied at the rate of 1000 lbs. per acre. The Lionex material, a cation-exchange resin produced as a by-product of the paper milling industry, and the Lical, a paper mill waste largely composed of lignin and lime, were applied at the rate of one ton per acre. The Lionex material had given evidence of promise as a soil conditioner. All materials were applied on August 1, 1952, and immediately incorporated in the soil to a depth of six inches with a large self-driven rotary tillage implement. Nitrogen as ammonium nitrate was applied to the sawdust, sugar, straw and grape pomace plots to maintain a C/N ratio of approximately 20:1. This nitrogen was applied as a split application, half at time of treatment and half the following spring, except in the case of the sugar plots, where the total amount was applied at the time of treatment. A cover crop of wheat was sown August 15, 1952. and was worked down the following May.

Soil samples for organic carbon and aggregate analyses were taken in late September, 1952, at the zero to six inch depth. Organic content on these samples was determined by the wet combustion method of Walkley (33). The wet seiving technique of Yoder (36) was used for the aggregate analyses. Duplicate determinations were made on all samples. Undisturbed three inch soil cores were taken in April, 1953. Six cores were taken from each plot. These cores were used to determine pore size distribution, permeability, and volume weights (27).

In July of 1953, soil samples were taken again for aggregate analyses, and organic carbon determinations. In addition, cation-exchange capacity was determined by the ammonium acetate method. Exchangeable potassium, calcium, and sodium contents were determined on all samples by the methods outlined by Peech, Alexander, Dean, and Reed (22). Oxygen diffusion readings (13) were taken during the summer of 1953. In September 1953, samplings for aggregate analyses were again made.

Individual vine yields were recorded for both 1952 and 1953. Cover-crop yields were taken in May of 1953, just before the green cover was worked into the soil.

Results

At the time of application of the organic materials mentioned earlier, it was noted that the HPAN material was very hygroscopic, and stuck readily to anything with which it came in contact. This is a serious disadvantage of this material, in that if the soil is not rather dry at the time of incorporation, it will form large rubbery masses.

Several weeks after application, following a rather heavy rain, a large amount of brownish viscous exudate appeared on the soil surface of the HPAN-treated plots. This material apparently had picked up large amounts of colloidal organic matter from the soil. This exudate remained on the surface for at least a month. The cumulative percent porosities are shown in Table I for all treatments. Since the values for all treatments except the VAMA, HPAN, Lical and Check were very close together, only these four are shown in Figure 1. The difference due to the VAMA treatment is great, and is noticeable even in the very large pore sizes. The HPAN-treated soil showed porosities greater than were found in any other soil except that treated with VAMA, although in the case of the smaller pores, the Lical treatment was more effective. All other treatments produced results which fell between those obtained for the check and the Lical material, and to avoid confusion were not included in Figure 1.

The distribution of stable aggregates in the surfaces of the plots, as determined by wet-seiving are shown in Tables II, III, and IV for the sampling dates September 1952, July 1953, and September 1953. Figures 2, 3, and 4 show the cumulative percent aggregation for the VAMA, HPAN and check plots for these dates. There again, all treatments were not shown on the graph to avoid confusion.

It can be seen that in September 1952, about eight weeks after treatment, there was a large response to the Krilium formulations. The response was not nearly as evident in July of 1953, but was again noted in September of that year.

The water permeabilities and volume weights are shown in Table V. It will be noted that all treatments except the Lical and grape pomace greatly increased the permeabilities. The VAMA treatment was far superior to all others.

Only the two Krilium materials produced significantly lower soil volume weights, although all treatments resulted in somewhat lower values than were found for the untreated soil. In Table VI are shown the exchange capacities and amounts of some exchangeable cations. It will be noted that the HPAN and Lical treatments were the only ones which caused significant increases in cation exchange capacity. These materials were also the only ones which gave significant increases in exchangeable calcium. The HPAN material approximately doubled the exchangeable sodium content of the soil. No treatment significantly changed the exchangeable potassium level.

Organic carbon content, Table VII, was not changed significantly by treatments, due to replicate variability. There was a trend towards higher organic carbon contents in the soils treated with large amounts of organic material. There was also a consistent seasonal variation between September of 1952 and July 1953.

Grape yields for the two years 1952 and 1953 are shown in Table VIII. It will be noted that all yields were much higher in 1953 than in 1952. This was general in this grape-growing area, and was not due to treatment. The cover-crop yields are shown in Table IX. Here, the plots which received nitrogen, or an organic material high in nitrogen such as alfalfa produced the highest yields. There were no significant differences between the yields from the Krilium plots and those from check plots.

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Figure 1. Cumulative Percent Porosity of a Jeddo clay loam soil held at various moisture tensions, after treatment with several organic amendments.

TABLE I

THE EFFECT OF ORGANIC AMENDMENTS ON CUMULATIVE PERCENT POROSITY OF A JEDDO CLAY LOAM SOIL HELD AT VARIOUS MOISTURE TENSIONS

		Tension	(atmosphere:	.				
Treatment	10*01	0•02	0•03	0-04	0•06	0•33	0.50	1.00
Check	1.8	1.9	2.4	2.8	3.5	4.9	7.2	7.9
уама	4•0	ۍ وې	7.2	7.9	9•6	12.4	14.5	17.2
EPAN	2.9	4°2	4°2	ي. د م	7.6	8 • 5	10.3	11.7
Sugar	1.7	2.3	2•5	3.0	L•4	5. 8	6•9	10.1
Lical	2.7	3.4		t•3	4 . 8	7•3	11.7	12.7
Sawdust	1.8	2.4	3•0	3.2	3•9	6.2	7.8	10.7
Grape pomace	2.4	2.9	3•5	4 • 1	4 . 8	6.3	8.1	10.4
Alfelfa meel	1.9	2.9	3.4	3.9	4•3	6•5	8.1	10.0
Straw	2.6	3•0	3.5	3.9	4°6	6.2	8.1	10.4
Lioner	2.1	2.9	3.2	3.7	4.7	6•11	7.9	10.2



Figure 2. Cumulative percent aggregation of a Jeddo clay loam soil treated with organic amendments, six weeks after treatment.

TABLE II

PERCENT AGGREGATION OF A JEDDO CLAY LOAM SOIL TREATED WITH VARIOUS ORGANIC AMENDMENTS SIX WEEKS AFTER TREATMENT

		Aggre	gate size mm				Total	
Treatment	× د د	2-5	1-2	ŗ.	.255	•1-•25	1. <	י. <
Check	0•6	9.8	8.2	12.0	15.0	18.6	72.6	27.4
тама	21.6	21.6	13.8	11.8	9.8	8•8	87.4	12.6
HPAN	18.6	18.0	9 • 8	10.8	10.4	11.2	78.6	21.4
Sugar	4•6	10.0	7.6	10.4	12,8	19.0	69.2	30.8
Lical	6 . 4	10.0	6. 8	11.8	15.8	20.4	71.2	28.8
Sawdust	8 • †	9.8	5•6	10.2	14.8	20.6	65.8	34.2
Grape pomace	5•2	7.8	6 . 4	11.8	15.6	22.2	69•0	31.0
Alfalfa meal	11.8	12.8	4 • 8	12.0	14•6	16.6	76.2	23.8
Straw	6.2	0 - 4I	ti 8• Ìi	12.6	18.0	16.6	75.8	24.2
Lionex	0°†	9•2	6 . 4	4°6	15.2	22.0	66.2	33.8

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Aggregate size - mm

Figure 3. Cumulative percent aggregation of a Jeddo clay loam soil treated with organic amendments, eleven months after treatment

TABLE III

PERCENT AGGREGATION OF A JEDDO CLAY LOAM SOIL TREATED WITH VARIOUS ORGANIC AMENDMENTS ELEVEN MONTHS AFTER TREATMENT

		Aggreg	ete size, mm				Total	
Treatment	> 5	2-5	1-2	• 5-1	•25-•5	• 1- •25	>.1	ז. א
Check	13.8	12.6	6.0	8•8	10.4	15.8	67.4	32.6
VAMA	0°41	12.2	10.6	11.2	9.8	12.4	70.2	29 . 8
HPAN	6•2	11.6	7.8	14.2	13.2	17.4	70-4	29.6
Sugar	10.6	12.2	7•0	10.4	11.6	14.2	66.0	34•0
Lical	12.4	10.6	5 •0	8.0	11.2	18.2	65.4	34.6
Sewdust	9•6	14.4	6 . 2	4•2	10.0	3•µ1	62.4	37.6
Grape pomace	10.4	9•6	5.6	8.6	10.0	16.4	60.6	39.4
Alfalfa meal	12.6	13.2	6 . 8	9 • 8	10.6	14.2	67.2	32.8
Straw	14.6	15.2	7.0	7.6	0•6	15.0	68 . 4	31.6
Lionex	10.6	10.0	5.6	8•0	10.6	16.2	61.2	38.8



Aggregate size - mm

Figure 4. Cumulative percent aggregation of a Jeddo clay loam soil treated with organic amendments, thirteen months after treatment

TABLE IV

PERCENT AGGREGATION OF A JEDDO CLAY LOAM SOIL TREATED WITH VARIOUS ORGANIC AMENDMENTS THIRTEEN MONTHS AFTER TREATMENT

		Acoreco	te cire mm.				Total	
Treatment	× ت	2-5	1-2	5-1	•25-•5	•1-•25	, , ,	۲. 1
Check	4.2	15.6	9•6	11.8	7.8	17.0	66.0	34.0
VAVA	6.6	20•2	14.2	17.0	15.6	10.2	83.8	16.2
HPAN	5•0	17.8	10.6	13.4	14.4	16.8	78.0	22.0
Sugar	2.6	15.0	8 . 8	0.11	15.2	16.2	68. 8	31.2
Lical	5•2	13.8	10.6	10.8	14.8	15.8	0.17	29.0
Sawdust	3•2	16.0	12.0	12.4	12,8	14.0	70.1	29.9
Grape pomace	1.4	13•4	4•2	0•0	14.0	18.4	63 . 6	36.4
Alfalfa meal	2 . 8	16.2	0.11	12.4	14°0	13.4	69.8	30.2
St rag	3•0	15.0	0 •6	11.8	15.6	18.2	72.6	27.4
Lionex	1.2	0.11	9.2	8.0	12.2	15.4	57.0	43.0

TABLE V

MEAN VOLUME WEIGHTS AND PERMEABILITIES OF UNDISTURBED SOIL CORES FROM A JEDDO CLAY LOAM SOIL TREATED WITH A NUMBER OF ORGANIC AMENDMENTS

Treatment	Volume Weights	Permeabilities Inches/hour
Check	1.39	0.52
VAMA	1.24	5.87
HPAN	1.29	2.91
Sugar	1.35	1.99
Lical	1.35	1.18
Sawdust	1.37	1.40
Grape Pomace	1.35	0.63
Alfalfa meal	1.36	2.07
Straw	1.34	2.32
Lionex	1.38	2.16
L.S.D. 5	percent 0.08	1.02

TABLE VI

CATION-EXCHANGE CAPACITIES AND EXCHANGEABLE SODIUM, CALCIUM AND POTASSIUM CONTENT OF A JEDDO CLAY LOAM SOIL TREATED WITH VARIOUS ORGANIC AMENDMENTS

	Milliequivalents per	100 grams soil		
Treatment	Cation-Exchange Capacity	Sodium	Calcium	Potassium
Check	17.6	•194	10.43	• 504
VAMA	18•4	•198	10.46	•456
HPAN	22.1	• 408	11.96	• 420
Sugar	19.9	6hI.	10.48	• 504
Lical	21.6	•177	12.53	• 628
Sewàust	17.8	•230	10.74	• 548
Grape pomace	17.4	.172	11.00	• 520
Alfalfa meal	18.6	•193	10.55	•758
Straw	20.1	•207	06•0t	• 564
Lionex	18.5	•192	10.62	• 604
L.S.D. 5 perce	at 3.05	•076	1.54	• 280

TABLE VII

ORGANIC MATTER CONTENT IN PERCENT OF A JEDDO CLAY LOAM SOIL TREATED WITH VARIOUS ORGANIC AMENDMENTS AT TWO DIFFERENT SAMPLING DATES

.13
•17
.20
.18
•22
.17
.10
.13
.12
.07
TABLE VIII

YIELDS OF AGAWAM GRAPES FOR 1952 AND 1953 IN POUNDS OF FRUIT PER VINE GROWN ON A JEDDO CLAY LOAM SOIL TREATED WITH VARIOUS ORGANIC AMENDMENTS

Treatment	1952	1953	Mean
Chaola	ור 9	25.2	20 5
Uneck	-0-C		20.5
VAMA	18.3	25.8	21.8
HPAN	16.5	27.8	22.1
Sugar	15.8	24.8	20.3
Lical	17.3	26.3	21.8
Sawdust	18.3	25.8	22.0
Grape pomace	14.5	25.0	19.8
Alfalfa meal	17.5	25.3	21.4
Straw	18.3	28.3	23•3
Lionex	15.3	24.3	19.8

TABLE IX

YIELD OF WHEAT COVER-CROP IN POUNDS PER ACRE GROWN ON A JEDDO CLAY LOAM SOIL TREATED WITH VARIOUS ORGANIC AMENDMENTS

Treatment	Green Weight	Dry Weight
Check	4,250	1,360
VAMA	3,940	1,110
HPAN	4,440	1,200
Sugar	12,500	3,071
Lical	4, 520	1,320
Sawdust	9, 980	2,490
Grape pomace	4,020	1,090
Alfalfa meal	8,080	2,220
Straw	8,910	2,400
Lionex	3,970	1,120
L.S.D. 5 percent	1,700	430

Discussion

Some of the most striking differences obtained from the treatments used were in the distribution of pore size in the soils treated with VAMA, HPAN, and Lical. The Vama increased the percentage of non-capillary pores from less than three in the check to eight percent in the treated soils. It should be kept in mind that although this material almost trebled the percentage of non-capillary pores, the level was still considerably below the optimum for such crops as sugar beets, according to Baver and Farnsworth (2). This soil, then, even at best, has a very small percentage of large pores. It should also be noted that the experimental grapery has received heavier applications of manure over the past years than has the average grapery in the area, thus its initial physical condition was at least average for this soil, and perhaps better than average. The VAMA was superior to the HPAN under all tension conditions used in the experiment. The increased porosity with the Lical may be due to the high lime content, resulting in microbial stimulation. The other physical measurements made did not indicate any superiority of this material.

With regard to aggregation, it is interesting to note that the highest percentage aggregates greater than 0.1 mm occurred shortly after epplication, about six weeks after the materials were applied. This was probably a seasonal effect. The greatest response to conditioner treatment was also evident at this early date. During the following July, both the total percentage of large aggregates, and the differences caused by treatments were less. In the September 1953 samples, the effect of the Krilium treatments again stood out, and the differences were much greater than in July. Again the VAMA had proved to be superior to the HPAN material. However, as reported by Martin, the greatest difference was in the higher percentage of aggregates in the larger size ranges.

The lack of differences resulting from treatments at the time of the July sampling is probably due to the fact that the soil was worked several times prior to ceasing cultivation about August 1. The cultivation tended to destroy the aggregates or at least reduce their size. Once the soil was left undisturbed for a month or more, the effect of treatment was again more noticeable, with more large stable aggregates in all soils.

It is also interesting to note that the Lionex and grape pomace treated soils contained a smaller percentage of aggregates greater than 0.1 mm. than did any of the soils treated with the other materials or those which were not treated. The Lionex contained a large amount of sulphur, which may have suppressed normal microbial activity. The acid state of the grape pomace may have resulted in the same effect.

The permeability measurements showed that the VAMA had been very effective. The water permeability rate was increased more than tenfold. However, all materials, except the Lionex and grape pomace at least doubled the infiltration rates as compared with the untreated soil. This would be more important if some economical means could be devised for incorporating these organic materials to a greater depth, so the increased permeability would reach the lower horizon.

The volume weight results also indicate the superiority of the VAMA material. A smaller decrease in volume weight was caused by the HPAN material. Here again, even the lowest volume weight indicates a very compact soil.

The failure of the oxygen diffusion results to show significant differences as a result of treatment is probably due to the fact that the soil had been recently cultivated. It was difficult to get uniform readings in the disturbed soil, and after cultivation had ceased, the soil was too dry for readings to be taken satisfactorily.

With regard to cation exchange capacity and the exchangeable cations measured, explanation is difficult. In the case of sodium, the HPAN material, a sodium salt, would be expected to add considerable sodium to the soil. The sodium content was approximately doubled by the HPAN treatment. The difficult fact to explain is that the exchangeable calcium and total exchange capacity were also higher where HPAN was applied. The VAMA material, although it was the calcium salt, did not increase the exchangeable calcium or total exchange capacity significantly despite its greater effect in altering the physical properties of the soil. The explanation may be that the VAMA material was combined more completely with the clay than was the HPAN material, thus reducing some of the exchange positions that would exist were the materials not combined. The failure of the quantity of exchangeable calcium to increase may be explained by the fact that the calcium acts as the cation bond between the negativelycharged clay particles and the conditioner anion. In the plots treated with HPAN, since there apparently was less clay-organic interaction, the exchange sites of the two materials were somewhat cumulative. There were no significant differences between exchangeable potassium levels in the variously-treated soils.

The treatments did not significantly affect the organic carbon content of the soils. Some of the organic materials applied in large quantities tended to raise the organic level slightly.

That the grape yields were not significantly changed by the treatments is not surprising, in view of the fact that the grape is a long-lived plant, and responds slowly to treatment. However, it was shown that the physical properties of the soil were altered, in what is believed to be a desirable direction. If the reported responses of grapes to organic-matter additions were real, a definite yield increase should be eventually expected.

With regard to the cover-crop yields, the only significant yield increase was produced on plots where nitrogen had been applied separately, or in the case of the alfalfa meal, where the material itself contained large amounts of nitrogen.

Summary

This work was undertaken to study the effects of different types of organic soil amendments on a typical fine-textured Niagara Peninsula grape soil. Treatments included two new Krilium soil-conditioners, VAMA and HPAN, and a number of more commonly-used soil amendments.

The two Krilium materials were outstanding in that they increased the percentage of large pores, and large aggregates. They also were the only two materials which produced significantly lower volume weights. The VAMA material appeared superior to the HPAN formulation.

All treatments except the grape pomace, Lical and sawdust resulted in water permeability rates significantly higher than was found for the untreated soils. Exchangeable sodium content of the HPAN-treated soil was approximately double that treated with any other material. This was due to the fact that the material used was the sodium salt of a hydrolyzed polyacrilonitrile. The exchangeable calcium and total cation exchange capacity was also significantly higher where this material was used. It is believed that there was less chamical union between this material and the clay particles than was the case with the vinyl acetate-maleic acid polymer.

Neither grape nor cover-crop yields showed significant differences due to treatment, except that nitrogen-treated plots produced higher cover-crop yields. It is difficult in such an experiment to get consistent results, due to replacement of vines, frost injury, disease, etc. Such an experiment should be run for at least five years to arrive at concrete results.

Part B Laboratory Experiment

1. The effect of a number of different conditioner materials on aggregation and ion-exchange properties of four Ontario soils.

From the time the field experiment was initiated in 1952 until the fall of 1953, a considerable number of new conditioner materials were released for experimental purposes. In order to evaluate these materials, four Ontario soil samples, and eight conditioner materials were used. <u>Description of Soils used</u>. The Jeddo clay loam, previously described, was used as one of the four soils. The others were a Brookston clay, a Burford loam, and a Guelph loam (28). The surface soil was used for this experiment.

Brookston Clay. The Brookston series, as used in Canada, is the poorly drained member of the Huron catena. This series has a fairly

high organic matter content in the surface soil and it exhibits the characteristics of the Dark Gray Gleisolic soils.

Profile

- Ac 6-8 inches of dark gray brown clay; medium granular structure; sticky when wet; almost stone-free; pH 6.8 - 7.0.
- GA2- 6 inches of gray drab clay with yellow brown mottlings; fine to medium nuciform structure; sticky when wet; pH 6.8.
- G1 18 inches of gray clay with yellow brown mottling; coarse blocky structure; tough and plastic; pH 7.0.
- G2 6-8 inches of gray to light gray clay; mottling less intense than in G1; very coarse blocky to massive structure; tough and plastic; pH 7.2.
- C Heavy calcareous clay till; gray to light gray in color; gritty; containing shale and limestone fragments; tough and plastic; pH 7.8.

Burford loam. The Burford series is developed on well sorted gravelly materials derived largely from dolomitic limestone and containing smaller proportions of shaley and siliceous materials. The Burford is the well drained member of the catena of the same name. The profile exhibits well developed Gray-Brown Podsolic characteristics.

Profile

Ac - 6 inches of dark brown loam; medium crumb structure; friable consistency; medium organic matter content (under cultivation some areas have become moderately gravelly, particularly where the upper layers have been eroded); pH 6.5.

A2 - 12-18 inches of light yellow-brown loam or sandy loam; medium

nuciform structure; friable consistency; moderately stony or gravelly; pH 6.5 - 6.8.

- B 6-18 inches of light brown gravelly clay loam; wavy horizon; medium nuciform structure; hard consistency when dry, sticky when wet; pH 7.0.
- C Gray, gravelly outwash; well sorted; largely of dolomitic limestone origin, with smaller proportions of shale and siliceous material; calcareous; pH 7.8.

Guelph loam. Guelph loam exhibits the characteristics of the Gray-Brown Podzolic Great Soil Group. Its characteristics are illustrated in the following profile description.

Profile

- AO Accumulated layer of partially decomposed litter from deciduous trees.
- Al 0-4 inches dark grayish brown loam; fine granular structure; friable consistency; slightly stony; pH 6.9.
- A21- 4-12 inches pale brown loam; fine platy structure; very friable consistency; slightly stony; pH 6.8.
- A22-12-14 inches gray loam; fine platy structure; friable consistency; stonefree; pH 6.6
- B 14-24 inches brown clay loam; hard consistency; few to frequent stones; pH 7.0.
- C Light gray loam till; medium nuciform structure; hard consistency; moderately stony; boulders vary from few to frequent; calcareous; pH 7.8.

The relief consists of smooth slopes, and erosion is moderate. External drainage is good, and internal drainage is moderate.

Conditioner Materials.

The eight conditioners used were designated as follows:

- 1. VAMA (Krilium 6)
- 2. HPAN (Krilium 9)
- 3. IBMA (Krilium 212-100D)
- 4. BRQ 12582
- 5. BRQ 12583
- 6. Conditioner B
- 7. Conditioner X
- 8. WVA (Wettable)

The VAMA and HPAN, as already described, are the calcium salt of a vinyl acetate-maleic acid polymer, and the sodium salt of a hydrolyzed polyacrylonitrile. The IBMA is the copolymer of isobutylene and the half ammonium salt-half amid of maleic acid. Its structural formula is probably:

сн ₃	H	H	H	
C	C	C	C	
CH3	Ħ	C=0	C==0	
		NH2	ONH	x

The BRQ 12582 and 12583 materials are both phenolformaldehyde capolymers. The conditioner B is similar to the IBMA material. Conditioner X is the sodium salt of abietic acid in an unpurified form. The WVA wettable material is the sodium salt of tall oil. Method of treatment. The various conditioner materials were incorporated at a concentration of .02 percent, with 1000 gm. samples of soil which had been passed through a 1 mm. selve. After thorough mixing, the moisture content of the soil was raised to approximately field capacity. The soil samples were then sealed in two-quart containers and allowed to incubate at room temperature for one month. Following this, the samples were dried, and the percentage of water-stable aggregates was determined by the wet-seiving technique. Cation-exchange capacities were determined by the conventional ammonium acetate method and also by the conductance method proposed by Mortland and Mellor (18). In this method the soil is saturated with barium chloride solution, then washed to remove excess chloride ion, and the barium soil is titrated with magnesium sulphate solution. There is a marked change in conductance once the end point is reached, all the barium having been precipitated as the sulphate.

Since it was felt that these conditioners might be involved in anion exchange, a similar conductance method was used to determine the anionexchange capacity of the soils for the sulphate and chloride anions. The samples for sulphate anion measurement were saturated with magnesium sulphate and titrated with barium chloride solution to precipitate the sulphate as barium sulphate. To determine the exchange capacity for chloride, the sample was treated with barium chloride solution and titrated with a solution of silver nitrate.

Results and Discussion

The results of mechanical analysis by the pipette method (11) are shown in Table X. According to these results, the Brookston, Jeddo,

Burford and Guelph soils would be classed respectively as a clay, clay loam, loam, and loam.

In Table XI are shown the values obtained for cation-exchange capacities with the four soils. While differences between untreated samples and the various treatments used are not consistent between the different soils, there do appear to be some differences that may be important in interpreting the value of these various conditioner materials. Conditioner X, for all four soils, produced an increase in exchange capacity. This was also true for the WVA material except in the Guelph loam. The Krilium 9 increased exchange capacity in every soil but the Burford. While there certainly is no evidence here to explain the nature of the soilconditioner effect, it would appear that cation-exchange studies over a range of concentrations of these materials on soils and clays might cast some light on this problem.

The results of aggregate stability measurements are shown in Table XII, and in Figures 5, 6, 7, and 8. Since the soils had been passed through a 1 mm. sieve prior to treatment, only the 0.5 mm, 0.25 mm. and 0.1 mm. sieves were used. In cases where treatments did not change the aggregate size distribution, or where the results were similar to those obtained for other treatments the data were not included on the graphs, to avoid confusion.

The Brookston clay soil, a naturally well aggregated soil, was not appreciably changed by the conditioners. However, the IBMA material and the VAMA had the greatest effect.

The Jeddo soil is naturally very poorly aggregated. Its stable aggregate percentage greater than 0.1 mm. was only slightly more than half that of the Brookston clay. With the Jeddo, the IBMA was far superior to any other material. VAMA was in second place, with Conditioner B also quite effective. EPAN and Conditioner X produced slight increases in stable aggregates. The other materials, WVA, and the two BRQ preparations gave little or no effect.

On the Burford loam, the response was not so great. The IBMA and VAMA were again in first and second place. HPAN, WVA, Conditioner B, and Conditioner X gave smaller responses.

In the Guelph loam there was marked response to the conditioner applications. All treatments except the two BRQ materials resulted in a marked increase in stable aggregate size. The IEMA and VAMA were again far superior to any of the other materials.

To summarize, the maleic acid polymers were far superior, under the conditions of this experiment, to any other material used in increasing the percentage of water-stable aggregates. The polyacrylonitrile formulation, the salt of abietic acid, and the tall cil preparation produced some effect, the magnitude of their effectiveness depending on the soil. The phenol-formaldehyde copolymers were of little or no value in increasing the percentage of water-stable aggregates.

With regard to the anion-exchange measurements for the chloride and sulphate anions, none of the soils used were able to adsorb these anions whether treated with conditioner or not.

TABLE X

MECHANICAL COMPOSITION OF THE FOUR SOILS USED AS DETERMINED BY THE PIPETTE METHOD OF ANALYSIS EXPRESSED AS PERCENTAGE

-

	Part	icle Size,	microns				
Soil	20	20	10	5	2	1	
Brookston Clay	29•7	70.3	62.2	52.1	40.3	34•7	
Jeddo Clay Loam	45.3	54.7	54.3	48.7	35.6	34•5	
Burford Loam	66.9	33.1	29.9	23.1	19.9	19.9	
Guelph Loam	65.4	34.6	32.3	26.2	19.2	15.6	

1

TABLE XI

THE EFFECT OF EIGHT CONDITIONER MATERIALS ON THE CATION-EXCHANGE CAPACITY, EXPRESSED IN MILLIEQUIVALENTS PER 100 GRAMS SOIL, OF FOUR SOILS USED

Treatment				
	Brookston	Jeddo	Guelph	Burford
Check	34.8	26.9	14.0	15.5
Conditioner X	35.6	27.3	14.0	18.9
BRQ 12582	34.6	28.3	14.2	16.4
BRQ 12583	34•9	25.4	14.2	18.6
WVA wettable	34•9	25.7	14.1	18.2
IBMA	34.8	24.6	14.4	14.4
VAMA	34•7	27.9	15.2	14.0
Conditioner B	34.6	27.5	14.5	15.5
HPAN	34•8	29.0	14.1	14.1

TABLE XII

PERCENT WATER STABLE AGGREGATES GREATER THAN 0.1 mm. IN FOUR SOILS TREATED WITH EIGHT CONDITIONER MATERIALS

Treatment	Soil Samples			
	Brookston	Jeddo	Guelph	Burford
Check	68,8	39.6	74.8	62.8
Conditioner X	82.8	47.6	76.0	68.8
BRQ 12582	82.4	46.0	74.4	64.4
BRQ 12583	81.0	40.4	70. 0	68.0
WVA wettable	82.8	41.2	78.8	70.4
IBMA	92.0	79.6	92.4	83.6
VAMA	85.2	61.2	90.0	77.2
Conditioner B	83.6	57.2	80.8	73.2
HPAN	84.8	41.2	82.0	74.0



Figure 5. Cumulative percent aggregation of a Brookston clay soil treated with a number of organic amendments



Figure 6. Cumulative percent aggregation of a Jeddo clay loam soil treated with a number of organic amendments



Figure 7. Cumulative percent aggregation of a Burford loam soil treated with a number of organic amendments.



Figure 8. Cumulative percent aggregation of a Guelph loam soil treated with a number of organic amendments

2. The effect of conditioner concentration on the ion-exchange properties of Wyoming Bentonite, keolinite, and a Jeddo Clay Loam Soil.

After establishing the value of the various conditioner materials available on the basis of their effect on stable soil aggregates, it appeared desirable to try the effect of the better materials on the cation-exchange capacities of typical clay minerals. Also, although there were none of the soils that exhibited a capacity to adsorb small anions, it was desired to measure the effect of conditioner treatment on the anion exchange capacities for phosphate ions, a relatively large anion. Accordingly, the IBMA material, the VAMA, and Conditioner X were applied at three concentrations to Wyoming Bentonite. Raclinite, and the Jeddo clay loam soil. The Conditioner X was used in addition to the other two, since other workers (10) have found it more effective than the work previously reported in this thesis would indicate. The concentrations used were 0.02 percent, 0.1 percent, and 1.0 percent. Water solutions of the first two materials and a water suspension of the Conditioner X were applied to the soil and clay suspensions. The resulting mixtures were allowed to stand for fortyeight hours before determinations were made.

Results and Discussion

It is interesting to note (Table XIII) the way in which the several concentrations influenced the cation-exchange capacity for the ammonium ion of the bentonite and kaolinite. With the montmorillonitic clay, very low concentrations of IBMA resulted in a tremendous increase in cationexchange capacity. With increasing concentration of the conditioner, the

exchange capacity decreased, although even at 1.0 percent concentration, it was slightly higher than in the bentonite alone. Were there no interactions, one would expect the exchange capacity of the clay-conditioner mixture to increase, the increase being greatest at the highest conditioner content.

With the IBMA, all concentrations decreased the cation-exchange capacity of the bentonite mixture, the decrease being greatest at the highest conditioner concentration. This might be explained by stating that the conditioner anion, through a cation linkage, occupies some of the exchange sites on the clay. Heavier applications would result in a further decrease until all exchange sites available were occupied; there were no more suitable cations to act as connectors; or until steric hindrance prevented the large conditioner anions from filling any further exchange positions.

The Conditioner X at low concentrations also increased the exchange capacity, but decreased it as concentrations were increased.

In the case of the kaolinite, all concentrations of all materials produced an increase in exchange capacity. It appears quite possible here then, that the effect of conditioner plus clay is additive, and that there is little if any interaction.

With regard to the Jeddo soil, low concentrations of VAMA produced disproportionate increases in exchange capacity. The IBMA, as in the case of the montmorillonite, caused a reduction in cation-exchange at low concentrations. At the 1.0 percent concentration, however, the exchange capacity was greater than that of the untreated soil. This is

not surprising, since the clay content of the soil is about 35 percent. Assuming that most of the clay is of the montmorillonitic type, the one percent concentration would be approximately equivalent to a three percent concentration with regard to the clay.

The results obtained for the Jeddo soil with Conditioner X show a consistent increase in exchange capacity with increasing concentration. This may indicate the absence of any appreciable interaction.

The anion-exchange capacities for the phosphate ion, as determined by the method of Piper (24), were not affected by the treatments either for the clays, or the soil.

This experimental evidence seems to indicate quite conclusively that the conditioner action in some way alters the cation-exchange capacity of the clay. 3. Cation-exchange properties of Wyoming bentonite and kaolinite treated with a wide range of conditioner concentrations.

Following the work outlined in 2, it seemed desirable to make further studies of conditioner materials at a wide range of concentrations in combination with bentonite, to determine the extent of the changes in base-exchange capacity. If possible, it appeared desirable to determine the exchange capacity by some method other than the conventional ammonium acetate method. There were two reasons in favor of a different method. The first is that it is very difficult to make a determination of exchange capacity of bentonite by the conventional ammonium acetate method, because of the physical nature of the bentonite. The second, and more important reason is that the results obtained with the ammonium ion might not be the same as would be obtained with other cations.

To eliminate the possibility that the associated conditioner cations and adsorbed clay cations might be responsible for any effect measured, the acid forms of the VAMA, IBMA and abietic acid were obtained, courtesy of the Carbide and Carbon Chemical Corp. A hydrogen-seturated clay was prepared by electrodialysis.

Once the conditioner acids and acid clay were available, a suitable method had to be devised to measure the extent of cation adsorption. A conductance method (35) seemed well-suited to this problem. Preliminary experiments indicated that this method would work very well, in titrating the acid clay with dilute NaOH and Ca(OH)₂ solutions.

Since the conditioner acids were not water-soluble, it was necessary to use an alcohol solution of the VAMA and abietic acid, and an acetone solution of the IBMA. One percent solutions of H-, Na-, and Ca- saturated clay and 0.1 percent solutions of the conditioners were prepared.

Since the VAMA material is the most widely known and used conditioner, most of the work was with this material. Clay suspensions containing VAMA at concentrations ranging from 0.002 percent to 25 percent were prepared, using the H-clay. These mixtures were titrated with .OlN NaOH and .O4N Ca(OH)₂. Similar titrations were carried out with the IEMA and Abietic acids using concentrations from 0.1 to 10.0 percent.

In addition to the above determinations, the clay acid was titrated with conditioner acid of the three conditioner materials. Also, the Naand Ca- clays were titrated with conditioner acids.

To establish whether the observed reactions were confined to 2:1 expanding-lattice type clay minerals, a H-saturated kaolinite was treated with VAMA and titrated with the NaOH solution.

Titration values were obtained for both conditioners, and for untreated clay. These values were used in arriving at the theoretical values that should exist were there no clay-conditioner interactions.

Ion-mobility measurements were also made on a number of H-bentonite-

Results and Discussion

In Figures 9 and 10 are shown the effect of conditioner concentration on the cation-exchange capacity of the clay systems used. It will be observed that at very low concentrations of VAMA (of the order of .002 percent) there was a marked decrease in exchange capacity. This was followed by a rather sharp increase at about .05 percent conditioner concentration. Following this abnormally high value, the exchange capacity dropped, and continued low with further increases in conditioner concentration, relative to the theoretical value. The theoretical value was obtained simply by adding the exchange capacity of the untreated H-clay to the titration value obtained for the various amounts of conditioner acid.

In Figure 11 are shown typical titration curves with NaOH for the clay conditioner systems. It was observed, that with no conditioner present and at low conditioner concentrations, the angle at the equivalence point was quite acute. As the concentration of VAMA was increased, the angle became less acute, until at concentrations of this material above 15 percent, it was not possible to establish a definite endpoint. In Figure 12 is shown a typical titration curve for the conditioner material alone.

Figures 13 and 14 show the effect of conditioner on a H-clay titrated with $Ca(OH)_2$. It is again apparent that at very low concentrations there was a rapid decrease in exchange capacity, followed by an increase, which again was followed by a decrease. Low values (below the theoretical) were obtained until about 20 percent conditioner concentration, at which point the actual and theoretical values practically coincided.

53•















Resistance - ohma x 1000



Cation-exchange capacity - meq. per 100 gm.

58,





The titration curves at low conditioner concentrations were similar with $Ca(OH)_2$ to those obtained with NaOH. However, with increasing concentration of conditioner, instead of the points becoming almost linear on the two sides of the equivalence point as they did with the sodium system, two distinct end points appeared. This is illustrated in Figure 15. It may be noted that the equivalence point on the pH curve approximates the second endpoint on the conductance curve.

While no data on the IBMA are presented here, it was observed that the material did behave similarly to VAMA. The slight dissociation of the IBMA and ABA materials, however, made it difficult to get consistent results. For this reason, data are not presented here on these two materials. Since both materials are maleic acid polymers, it was Notofelt necessary to conduct as detailed a study of clay-IBMA systems as was done with the VAMA. With regard to the ABA (abietic acid) there was no evidence of interaction, the results obtained approximating the theoretical values.

In Figure 16 are shown the values obtained by treating H-kaolinite with VAMA and titrating with NaOH. All values were practically identical to the theoretical values, indicating the lack of reaction with this material.

In Figure 17, the titration curve of H-clay titrated with VAMA is shown. It will be observed that there are two completely separate endpoints. This was also observed when the H-clay was titrated with the IBMA, (Figure 18). Titration curves of the Na-clay and Ca-clay with VAMA also show two separate endpoints, Figures 19 and 20, although these endpoints do not coincide between the three types of clay systems.







Cation-exchange capacity - meq. per 100 gm.

Figure 16. Effect of various concentrations of VAMA on the cation-exchange capacity of H-kaolinite for sodium ion
















It is very difficult to explain the effect of the vinyl acetatemaleic acid polymers in changing the cation-exchange properties of the bentonite. The following suggestions, however, are offered.

The reduction in exchange capacity may be due to the fact that the conditioner anion is linked through a cation to the cation-adsorption sites of the clay. These sites will not then receive the added cation, and are therefore not measured in determining the cation-exchange capacity. This explanation would seem more sound, however, were it not for the fact that a monovalent cation (Na) as well as a divalent one (Ca) produced this depression. It is difficult to explain why a resonating bond, which must exist if the sodium ion is the bridge between the clay and conditioner anion, produces a similar result to that obtained with the divalent calcium ion.

The only presently-conceived possibility that might explain the marked increase in exchange capacity following the initial decrease is as follows: as the first small amount of conditioner is added, it occupies, through a cation, the most available exchange sites, thus reducing the exchange capacity. As the concentration of conditioner is increased, conditioner anions become attached to internal exchange sites, and because of their large size, change the interplanar spacing. This may expose more exchange sites for which, at the conditioner concentration, there are not enough VAMA anions. As a result, the exchange capacity increases. As more conditioner is added, these new sites are conditioner-occupied, resulting in a second decrease in exchange capacity, compared to the theoretical value.

No account has been taken, in the above postulations, of such factors as steric hindrance, degree of dissociation of the VAMA, or the relative effects of the two acid groups on the conditioner. However, the experimental evidence obtained is given in the hope that at some future date, as more becomes known of clay-organic relations, it may help in the elucidation of the nature of this type of clay-organic system.

No attempt is made to justify the titration curves obtained on titrating acid clay with acid conditioner. Since one would not expect an endpoint in titrating a weak acid with a weak acid, it may be that some of the clay aluminum is forming a conditioner salt. It is doubtful if the points obtained in these curves bear any relation to the other evidence of clay-conditioner interaction presented.

Ion-mobility measurements were made of clay-conditioner mixtures at approximately the endpoints observed when the H-bentonite was titrated with VAMA. No differences in mobilities were caused by the conditioners. However, it was observed that at a conditioner concentration of thirty percent, there was definite flocculation at the positive electrode. This flocculation did not occur at lower or higher concentrations.

Part B Summary and Conclusions

Laboratory experiments were set up to study the effect of a number of conditioner materials on several soils and clay minerals, and to attempt to determine the nature of the mechanism involved in this clayconditioner interaction.

The surfaces of four Ontario soils, a Jeddo clay loam, Brookston clay, Guelph loam, and Burford loam were sampled and these samples were treated in the laboratory with .02 percent of eight different conditioner materials. Three of these materials were maleic acid polymer salts, one was a hydrolized polyacrilonitrile salt, two were phenol-formaldehyde copolymers, one was a sodium salt of abietic acid, and the remaining conditioner was the sodium salt of tall oil. The treated soils were allowed to incubate at a moisture content near field capacity for one month. Following this, aggregate stability was determined by the wet-sieving technique. Cation-exchange capacities were also determined.

The results of the wet sieving indicated that in all four soils, the vinyl acetate-maleic acid polymer, the copolymer of isobutylene and the half ammonium salt-half amid maleic acid were far superior to all other materials in increasing the percent water-stable aggregates greater than 0.1 mm. There did not appear to be any consistent change in cation-exchange capacity between soils as a result of any specific conditioner treatment.

The second part of this section of the thesis deals with the effect of three different concentrations of VAMA, IBMA, and Conditioner X on the cation-exchange capacities of Wyoming bentonite, kaolinite, and Jeddo clay loam soil as determined by the ammonium acetate method.

It was observed that at low concentrations of VAMA, there was a marked increase in the exchange capacity of the bentonite. This value decreased with a further increase in conditioner concentration. The IBMA decreased the exchange capacity of the bentonite at all three concentrations used.

The Conditioner X had little effect on the exchange capacity, compared to the other two materials. All three materials gave little indication of interaction with kaolinite. There did appear to be conditioner-soil interaction in the case of the IBMA and VAMA with the Jeddo soil.

It was shown by conductance methods that there was a definite interaction between conditioners and H-saturated bentonite clay. Initial small increments of conditioner resulted in a decrease in exchange capacity. Further increments caused a sharp and unexplainable increase in exchange capacity, followed by a further decrease. This was true whether sodium or calcium was the replacing cation.

Titration of clay acids with conditioner acids caused some type of two-step reaction to take place, when the conditioner acids were either VAMA or IEMA. These reactions are not believed to be related to the phenomena reported above.

Addition of conditioner acid to H-kaolinite resulted in no effect other than the expected increase in exchange capacity due to the cumulative effect of the clay plus conditioner.

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