of the improvements in the mechanical extraction of vegetable oils. Current and proposed developments will certainly lead to further improvements in the efficiency of the vegetable oil mill industry, which is constantly demanding finer machinery to meet the high standards established by the industry for a more profitable operation.

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Methods of Analysis for Functional Groups in Earth (Mineral) Waxes[1]

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Since J. Koettstorfer (1) utilized the saponification value as a controlling factor in determining the quality of butter, this and other methods of analyses such as acid, carbonyl, and hydroxyl values have been used generally to characterize and identify natural fatty products. However the reliability of these analyses when applied to mineral waxes is usually overestimated.

This investigation reports some available as well as some modified methods useful for characterizing earth waxes. These have been applied to crude peat wax and to known control chemicals. Crude peat wax in this report refers to that part of bitumen which is soluble in boiling ethanol (94 wt. %) but is precipitated at —7°C.

Experimental

Equipment and Materials. The Fisher Titrimeter, steam bath, and saponification reflux vessels[2] were used in a majority of the following experiments. Thiophene-free benzene and 94 wt. % ethanol were used as solvents; 94 wt. % ethanol was also used in standard and indicator solutions.

Acid Value. The first analytical procedure studied was the direct titration of the sample with 0.1 N potassium hydroxide, using an indicator (2). This method, although the most common one, is limited to solutions of materials where a color change can be easily discerned. The other color-indicator method studied is suitable for dark solutions because the high molecular weight acids found in such samples are converted into insoluble calcium salts by treating the solution with sodium acetate and then with calcium chloride. Simultaneously an equivalent quantity of acetic acid is liberated and therefore easily titrated (3).

In the potentiometric titration method the sample was weighed into a saponification vessel and dissolved in a solvent mixture of 30 ml. of benzene and 120 ml. of ethanol. The solution was refluxed for five minutes on a steam bath, cooled to 30–40°C., then titrated with 0.5 N alcoholic potassium hydroxide, using the titrimeter. Because the maximum rate of change in pH was difficult to observe, the end-point was taken at meter readings pH 9 and at pH 10. pH 9 gave results closer to the theoretical value.

In the above methods a 1.00 ± .01-g. sample was used. The results are compared in Table I.

Saponification Value. In the "Ordinary Method" a 1.00 ± .01-g. sample was weighed into a saponification vessel and then dissolved in a 20-ml. benzene-80-ml. ethanol solvent mixture. Exactly 20 ml. of 0.5 N alcoholic potassium hydroxide was pipetted into the solution. The sample was refluxed for 3 hrs. on a steam bath, cooled, then titrated with 0.5 N alcoholic acetic acid, using 1% alcoholic phenolphthalein as an indicator. This procedure can be used only for clear or faintly colored solutions.

TABLE I
Acid Value

Material analyzed	Method	Mean value	Number of determinations	Range	Standard deviation[c]
Salicylic Acid[a]	Fischer (2)	409.8	10	408.2–411.4	1.4
	Pschorr *et al.* (3)	410.4	10	405.8–419.7	4.8
	Potentiometric				
	(a) pH 9	407.6	6	406.3–408.5	0.9
	(b) pH 10	408.2	6	407.4–409.2	1.3
Crude wax[b]	Pschorr *et al.* (3)	50.8	9	43.3– 56.9	4.3
	Potentiometric				
	(a) pH 9	51.9	10	48.8– 56.1	2.1
	(b) pH 10	59.3	10	54.2– 61.2	2.1

[a] Theoretical acid value for Salicylic Acid, 406.3 BDH Analytical Reagent "Analar."

[b] From Hydro-Peat of Kivisuo.

[c] Calculated using the equation, $\sigma = \pm \sqrt{\frac{\Sigma (m - x)^2}{n - 1}}$

The Pschorr, Pfaff, and Berndt Method (3) was modified slightly by employing *0.5 N* solutions instead of *0.1 N* solutions. This is suitable for the analysis of dark products.

In the Potentiometric Method, preparation of the sample was the same as in the "Ordinary Method." After the saponification was completed, the excess potassium hydroxide was acidified with alcoholic sulfuric acid (1 part concentrated sulfuric acid in 5–10 parts ethanol) to pH 3.

Using the titrimeter, the sample was then titrated with 0.5 N alcoholic potassium hydroxide; the amount consumed was indicated by two inflection points, the first being the end-point of the strong acid (H_2SO_4), and the second, the end-point of the liberated, high-molecular organic acids. The saponification value is calculated from the amount of hydroxide used between the two points described. The results are given in Table II.

Hydroxyl Value. The method of Freed and Wynne (4), an outgrowth of procedures by Verley and Bölsing (5) and others, was found to be suitable, with slight modification, for the determination of the hydroxyl value in peat wax.

A 100 ± 2-mg. sample was weighed into a 25-ml. Pyrex test tube, and exactly 2 ml. of pyridine-acetic anhydride reagent (12 wt. % pure anhydride in dry redistilled pyridine) were added. The mixture was heated until the solution boiled, and for one minute

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[1] Edited and revised by W. E. Parker, Eastern Regional Research Laboratory, Philadelphia, Pa.

[2] Described in A.S.T.M. D 399-52.

TABLE II

Saponification Value

Material analyzed	Method	Number of determinations	Mean value	Range	Standard deviation
Ethyl Benzoate[a]	Ordinary	14	378.9	349.2–396.0	16.2
	Pschorr *et al.* (3)	7	357.8	320.2–382.5	23.6
	Potentiometric	11	374.5	370.0–379.0	3.0
Crude Wax[b]	Pschorr *et al.*	10	136.0	127.1–144.9	4.8
	Potentiometric	11	144.9	139.6–148.3	2.4

[a] Theoretical saponification value for Ethyl Benzoate, 373.6, BDH Laboratory Reagent.

[b] From Hydro-Peat of Kivisuo.

longer. (This step should be accurately timed.) After the solution was cooled to room temperature, it was diluted with 5 ml. of carbon dioxide-free water and transferred to a 250-ml. Erlenmeyer flask. The test tube was washed with 10 ml. of water and twice with 10 ml. of ethanol; the washings were added to the solution. After 50 ml. of ethanol were added to the flask, the sample was titrated with 0.1 N aqueous potassium hydroxide, using phenolphthalein as an indicator. Blanks were run simultaneously. If the material contains acids, the acid value of the sample should be determined and the hydroxyl value corrected. The results are given in Table III.

TABLE III

Hydroxyl Value—Method of Freed and Wynne

Sample	Number of determinations	Mean value	Range	Standard deviation
Salicylic acid, BDH analytical reagent "Analar," theor. (OH value = 406.3)............	10	406.6	370.9–448.2	27.4
Crude wax from hydro-peat of Kivisuo (Acid value = 56.5)...	7	121.5	112.3–130.6	7.1

Carbonyl Value. The most common procedure for the determination of the carbonyl group is the reaction of the ketone or aldehyde with hydroxylamine hydrochloride to form the oxime and hydrochloric acid. The acid is then titrated with a standard base. A somewhat modified method of Findley and Brown (6) has been followed.

The reagent, 0.3 N hydroxylamine hydrochloride in absolute ethanol, was freshly prepared, and just before analysis it was titrated with 0.1 N alcoholic potassium hydroxide to pH 3, using the titrimeter. A 200 ± 10-mg. sample was weighed into a 100-ml. beaker and dissolved in 20 ml. of warm toluene; 20 ml. of hydroxylamine hydrochloride were pipetted into the solution, and then the solution was boiled on a steam bath for 7 min. After the solution had cooled to 65°C., it was titrated potentiometrically to pH 3 with 0.1 N alcoholic potassium hydroxide. The solution was boiled again for 7 min. and titrated to pH 3.[3] Blanks were run simultaneously. Results are given in Table IV.

TABLE IV

Carbonyl Value—Method of Findley and Brown

Sample	Number of determinations	Mean value	Range	Standard deviation
Acetophenone, Eastman Kodak Co., highest purity, theor. carbonyl value = 466.0............	14	466.4	451.8–476.1	8.2
Crude wax from hydro-peat of Kivisuo....................................	10	20.6	18.8– 22.2	1.3

Discussion

The potentiometric titration in determining acid values is far superior to other methods investigated in this report; and because the maximum rate of change in pH in titrating crude peat wax was difficult to observe, two end-points, pH 9 and pH 10, were arbitrarily selected. The results show that pH 9 is the more logical end-point (Table I).

The potentiometric titration is also better than the color-indicator method in determining saponification values because there is no difficulty in detecting the points of inflection (Table II). The saponification reaction of complicated, high-molecular organic products, such as peat wax, appears to be a balanced reaction; the equilibrium depends on the reaction conditions. This is brought out in Table V, where the saponification time and the size of sample are varied. The results in Table V also reveal that an exact knowledge of these conditions is imperative in order to obtain consistent results.

TABLE V

Saponification Value
Crude Wax from Hydro-Peat of Kivisuo
Potentiometric Method

A. Time (hrs.) Sample of 1.00 ± 0.01 g.	Saponification value	B. Sample wt. (g.) Time 1 hr.	Saponification value
1	141.8	0.5	153.4
2	146.5	1.0	148.5
3	150.8	1.5	136.9
4	153.6	2.0	125.8

The hydroxyl value as determined by the method of Freed and Wynne is in many respects suitable for such high-molecular weight products as crude peat wax although the individual results vary greatly (Table III). However the mean value of 10 analyses appears to be satisfactory. Since the method is rapid and simple, the hydroxyl value may be determined quite successfully. The Witzöff hydroxyl value determination method which the authors used in their previous work (7) is not applicable to crude wax because, depending on the degree of polymerization, a particular part of the wax may be insoluble in the solvent used in this procedure.

A modified Findley and Brown method for determining the carbonyl value (Table IV) is useful for dark products, such as crude peat wax, especially if the color-indicator titration is replaced by the potentiometric titration. It can be said generally that the potentiometric titration clearly shows the end-point and thus prevents human error which may be considerable in color-indicator methods.

Summary

1. The potentiometric titration method is superior to color-indicator methods in the determination of acid and saponification values of earth waxes.
2. The saponification reaction in determining saponification values of earth waxes is a balanced one; therefore the equilibrium depends on conditions under which it is run.
3. Hydroxyl and carbonyl value methods have been modified to make them suitable for earth (mineral) waxes.

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[3] If necessary, this was repeated once again.

4. The values obtained on high-molecular weight peat waxes are not absolute, but rather they serve to characterize and identify these products.

5. The methods explained in this report may perhaps be found suitable for other natural products, such as montan wax.

Acknowledgment

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REFERENCES

1. Koettstorfer, J., Z. anal. Chem., *18*, 199–207 (1879).
2. Fischer, E. J., "Laboratoriumsbuch für die technischer Wachs-, Harz und Ölgemenge," pp. 64–65, Verlag von Wilhelm Knapp, Halle (Saale) (1942).
3. Pschorr, R., Pfaff, J., and Berndt, W., Z. angew. Chem., *34*, 334–336 (1921).
4. Freed, M., and Wynne, A. M., Ind. Eng. Chem., Anal. Ed., *8*, 278–279 (1936).
5. Verley, A., and Bölsing, F., Ber., *34*, 3354–3358 (1901).
6. Findley, T. W., and Brown, J. B., J. Am. Oil Chemists' Soc., *30*, 291–298 (1953).
7. Sundgrén, A., and Rauhala, V. T., J. Am. Oil Chemists' Soc., *29*, 611–613 (1952).

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Epoxidized Esters of Fatty Acids as Internal and External Plasticizers for Polyvinyl Acetate[1]

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A GROWING MARKET has been developing for polyvinyl acetate emulsions as a component of water-base paints. The wide use of these emulsions is attributed to the availability of their components, low cost, ease of formulation, ease of application in painting, and the resistance of the film to degradation by sunlight. However fusion of the drying latex[4] to form a uniform film at the usual ambient temperatures encountered in outdoor painting fails to occur unless the polyvinyl acetate has been modified. In one method of modification, external plasticizers (liquids compatible with polyvinyl acetate and having high boiling points) are added to the latex. These liquids function by lowering the fusion temperature of the film. The most widely used external plasticizers belong to the general class of esters, of which the esters of dibasic acids and of phosphoric acid are the most important commercially. Simple glycerides and other monobasic fatty acid esters are unfortunately incompatible with polyvinyl acetate, thereby limiting their use as polymer modifiers (5).

In an alternate modification technique (internal plasticization), copolymers of vinyl acetate having lower fusion temperatures than polyvinyl acetate are used in its place. As co-monomers for internal plasticization, alkyl acrylates (8), chloroprene (8), and vinyl esters of long-chain fatty acids (6) have been reported.

As part of a general program of this laboratory for discovering new uses and applications for fats, an investigation was undertaken on the modification of fatty acid esters to produce plasticizers for polyvinyl acetate. This paper describes the use of esters of epoxy, hydroxy-acetoxy, and polyacetoxystearic acids as external plasticizers for polyvinyl acetate latex and the preparation of emulsions of copolymers of vinyl acetate and vinyl epoxystearate. The role of the epoxy group as an acetic acid scavenger (2, 4) under emulsion conditions was also investigated. Such scavenging action is desirable to prevent container corrosion and to promote emulsion stability.

Experimental and Results

Materials. Vinyl acetate obtained from a commercial source was fractionally distilled before use. The fraction boiling at 72°C. was used in this investigation. Vinyl epoxystearate was prepared by the method of Silbert *et al.* (7). The esters studied were epoxidized soybean oil (ADMEX 710,[5] oxirane oxygen, 5.87%) from Archer-Daniels-Midland Company; butyl epoxystearate (Estynox 403, oxirane oxygen 4.02%), butyl hydroxy-acetoxystearate (Estynox 203), and butyl polyacetoxystearate (Estynox 206) from the Baker Castor Oil Company. Acetostearin (acetyl stearyl glycerides) and aceto-olein (acetyl oleyl glycerides), prepared from soybean oil, were obtained from the Southern Regional Research Laboratory. These oils were used without further purification.

A mixture of acetyl epoxystearyl glycerides (oxirane oxygen 4.50%) was prepared by direct epoxidation of aceto-olein by the method of Findley *et al.* (2). 2-Methoxyethyl 9,10-epoxystearate was prepared by the epoxidation of 2-methoxyethyl oleate, an ester obtained by the acid-catalyzed esterification of oleic acid with methyl cellosolve.

Sulfonated red oil, Pluronic F68,[6] and Triton W-31,[7] are commercial emulsifiers and were used without further purification. Reagent grade potassium persulfate was the polymerization initiator used.

Screening Tests. Proposed plasticizers were first screened for compatibility by preparing solutions of each ester with polyvinyl acetate in toluene and coating films from these solutions onto glass plates. The solutions, consisting of 90 g. toluene, 10 g. polyvinyl acetate, and 2.2 to 5.4 g. plasticizer, gave concentrations of plasticizer ranging from 18 to 35% in the plasticized polyvinyl acetate films after complete evaporation of the toluene solvent. After complete drying at room temperature, the films were examined for evidence of separation of the plasticizers. A plasticizer was considered to be compatible if the resulting film was clear and flexible and showed no separation of oil. The results of these tests are listed in Table I.

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[1] Presented at the Fall Meeting, American Oil Chemists' Society, Philadelphia, Pa., October 11, 1955.

[2] Fellow of the National Renderers' Association.

[3] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

[4] A latex is defined as an aqueous dispersion of colloidal polymer particles which has been stabilized by an emulsifier.

[5] Reference to commercial products in this publication is not intended to be a recommendation of these products by the U. S. Department of Agriculture over others not mentioned.

[6] A condensate of ethylene oxide with a hydrophobic base formed by condensing propylene oxide with propylene glycol.

[7] Sodium salt of an alkylaryl polyether sulfate.