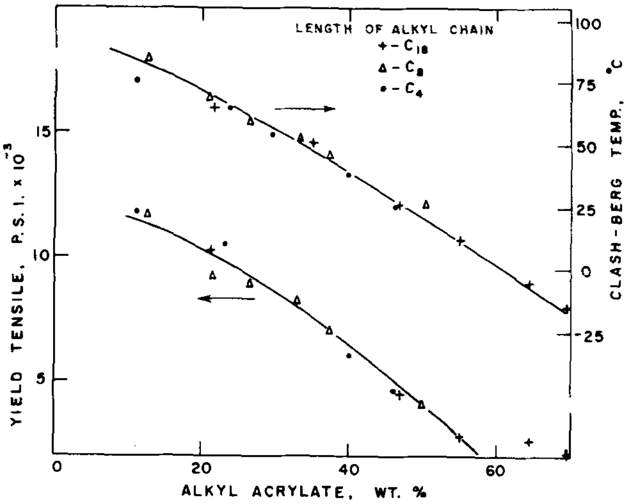

FIG. 1. Variation of yield tensile strength of Clash-Berg temperature of copolymers of acrylonitrile with alkyl acrylate contents.

to 1,000% at the rate of 0.2 in. per minute. The tensile strength was thereby increased approximately three-fold. An x-ray diffraction study of the unstretched and stretched films revealed that orientation of the polymer backbone was only slight. Representative copolymers containing octadecyl acrylate showed scattering maxima at 5.3 and 4.3 Å, which are characteristic of polyacrylonitrile and poly(octadecyl acrylate), respectively. Therefore it is probable that the octadecyl acrylate segments and the acrylonitrile backbone segments crystallized separately. This behavior is similar to the separate crystallization found in copolymers of vinyl alcohol and vinyl stearate (7).

Resistance to Chemical Reagents. Because a possible use for copolymers of acrylonitrile and alkyl acrylates lies in the field of laminations, tests were made to determine their resistance to selected chemical reagents. Samples were immersed at room temperature in soybean oil, 50% alcohol, 1% sodium hydroxide, and 3% and 30% sulfuric acid. The percentage increases in weight were determined after 160 hrs. of immersion. The increase in weight was less than 1% for all samples for all the reagents except 50% alcohol. In the latter the weight percentage increase varied from 1 to 3%, increasing with acrylate content and decreasing with the alkyl chain length of the acrylate. The use of a long-chain acrylate thus imparts slightly greater chemical resistance to the acrylonitrile copolymer.

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On Free Hydroxy Acids of Peat Wax

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Further examination of peat wax has not resulted in the isolation of chemically pure compounds, but data presented below make it seem probable that peat wax contains aliphatic monocarboxylic acids with a molecular size of about C_{19}–C_{22} and aliphatic monohydroxy acids with a molecular size of the order of C_{20}–C_{21}.

WHEN INVESTIGATING the chemical composition of the wax component of peat, the author has found that, in addition to aliphatic monocarboxylic acids, it also contains unknown free hydroxy acids (1). These hydroxy acids are seldom mentioned in the literature (2); nor have they been closely investigated. Certain circumstances indicate that, when extracting peat bitumen with hot solvents, reactions of a polycondensation type take place in the wax fraction and that the hydroxy acids possibly take part in these reactions (3). These reactions cause a decrease of the amount of wax yielded by extraction, and therefore their investigation and control carry theoretical as well as practical importance.

In the present investigation the analysis of the acid part of peat wax has been carried out, and the purpose has been to isolate the free hydroxy acids in as pure a state as possible and thus obtain information about the reactions. The word bitumen is used to designate that part of peat which is obtained by extraction with a hot neutral solvent under normal pressure; crude peat wax refers to that part of the bitumen which is soluble in boiling technical ethanol but is precipitated at a temperature of −7°C. The crude resin then remains in solution.

Materials

Acetic acid, glacial, reagent grade; aluminum oxide, for chromatographic analysis, standardized according to Brockmann; benzene, technical grade, boiling range <0.5°C., total sulfur <0.2%, Br No. <0.4, evaporation residue <5 mg./100 ml.; benzene, thiophene-free, reagent grade; ethanol, technical grade, 94.5% purity; methanol, anhydrous, reagent grade; petroleum ether, boiling range 30–80°C.; pyridine, reagent grade; and $CaCl_2$, HCl (36.4%), H_2SO_4 conc., KOH, reagent grade.

Analytical Methods

In wax investigations chemical characteristics are utilized to depict the composition of complicated mixtures. However, as different methods are used for the determination of each characteristic and because the result depends on the method used, it is necessary, in order to make reproduction possible, clearly to describe the methods used. The characteristics were determined by the following methods: the acid and saponification value by the method by Pschorr, Pfaff, and Berndt, which is suitable for very dark waxes (4); the hydroxyl value by the Freed and Wynne method (5); the carbonyl value by the method of Findley and Brown, using 0.3-N. $NH_2OH \cdot HCl$-solution and potentiometric titration (6); and the iodine value by the method of Hübl (7).

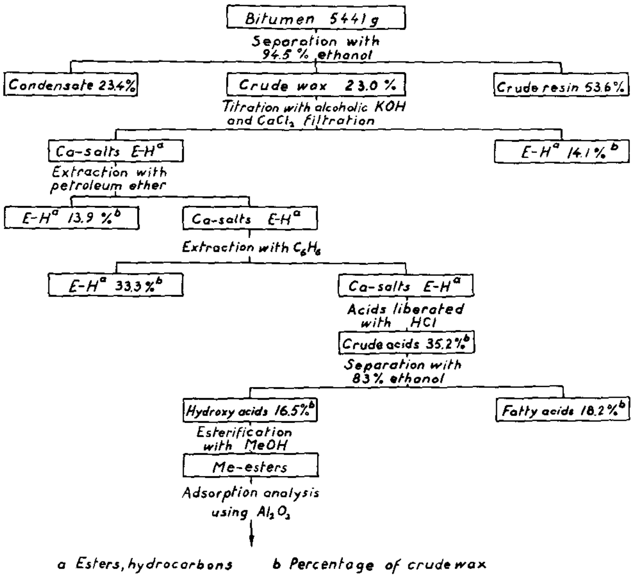

FIG. 1. Analysis of crude peat wax.

The Wizöff method (8) previously used by the author (1,3), which was developed for fats but also recommended for waxes, has proved unreliable in very dark solutions. The detection of a very small part of the wax sample which may not dissolve in the solvent is almost impossible, especially if it is present in the form of a gel.

Experimental

The bitumen used in this investigation was obtained, by extraction with ethanol-benzene (1:9) on a pilot-plant scale, from hydro peat originating from the Kivisuo bog owned by the Leivonsuo Company. The average yield was 10%, based on the dry weight of the peat. The bitumen, amounting to 5,441 g. was analyzed as shown in Figure 1. Using technical ethanol as the solvent (bitumen:solvent = 1:20), the bitumen was divided into the following fractions: a) insoluble in boiling ethanol, polycondensation products, 23.4%; b) soluble in boiling alcohol, crystallizes at −7°C., mainly wax, 23.0%; c) remaining in solution at −7°C., mainly resin, 53.6%.

The wax fraction was purified by recrystallizing twice at −7°C. from technical ethanol (wax:solvent = 1:10). The characteristics of the wax fraction were as follows: melting point, 79–82°C.; acid value, 51.3; saponification value, 126.9; ester value, 75.6; hydroxyl value, 90.3; and iodine value, 33.6.

The free acids of the wax thus obtained were separated as potassium salts, which were then converted into calcium salts. The salts were purified by extracting first with petroleum ether, then with benzene.

The acids were liberated with hydrochloric acid and washed with water. The sum of the fractions were 96.5% of the raw wax; the analytical loss at this stage was 3.5%. The acids still contained some components of the ester type, as shown by the following characteristics: melting point, 77–80°C.; acid value, 91.6; saponification value, 159.4; ester value, 67.2; hydroxyl value, 111.2; carbonyl value, 3.0; and iodine value, 32.2.

In order to increase the hydroxy acids in the soluble fraction, the crude acids, amounting to 415.5 g., were divided into two parts by dissolving in boiling 83% ethanol. The free hydroxy acids thus obtained were esterified by absolute methanol and sulfuric acid. Chromatographic analysis of the methyl esters, amounting to 38.72 g., was carried out in a tapering column, 2.16 m. long (9), using Al_2O_3 as the adsorption medium. The esters were dissolved in benzene and eluted in two stages, first with benzene-methanol (CH_3OH, 20% by volume), then with pyridine-acetic acid (CH_3COOH, 10% by volume).

The progress of the separation was followed by both refractive index and ultraviolet light. No clear fractionation could be noticed on the basis of refractive index, therefore a rough division was made by the sections visible in daylight and in ultraviolet light. The results of this adsorption analysis are given in Figure 2, which symbolizes the analysis. Results have been divided into sections proportional to the masses of the fractions themselves. The analytical results and characteristics of the fractions are shown in Table I.

TABLE I

Characteristics of the Methyl Ester Fractions

Fraction	Molecular weight, Rast	Melting point, °C.	C%	H%	OH-value	Iodine value
I	254.3	55–59.5	77.48	12.66	6.6	43.6
II	307.3	62–63	76.74	12.61	28.3	147.6
III	303.7	65–66	77.63	12.88	39.8	123.3
IV	333.3	71–76.5	73.78	11.48	122.5	210.9

It may be mentioned that none of the methyl ester fractions gave a positive reaction with Noller's triterpene reagent (10) and, on heating, they gave a very unpleasant ("rotten") odor.

Discussion

During chromatographic analysis of the methyl esters some fractionation has taken place; the hydroxy acids collected in the latter fractions. As can be seen from Table I, either the hydroxy acids themselves

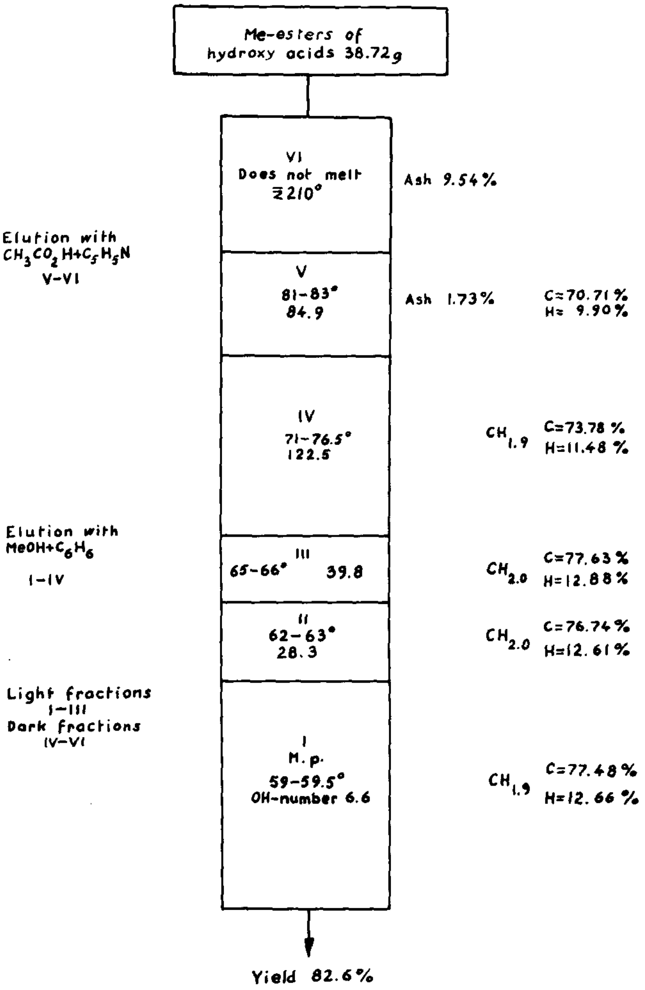

FIG. 2. Adsorption analysis of Me-esters.

are unsaturated, or the fractions in question contain some other unsaturated components.

Data and characteristics concerning Fraction I are inconsistent. It seems that if only the molecular weight and the carbon content are taken into consideration, Fraction II could be the methyl ester of an aliphatic monocarboxylic acid $C_{20}H_{40}O_2$, and Fraction III some methyl ester of the acids $C_{19}H_{38}O_2$–$C_{22}H_{44}O_2$. The hydrogen content however is smaller than in the molecules mentioned above, which can be explained by the unsaturated character of the fractions in question.

If the molecular size of Fraction IV is calculated on the basis of its hydroxyl number, 122.5, and if the presence of an aliphatic monohydroxy acid is assumed, the resultant molecule will be $C_{29}H_{58}O_3$. On the basis of the molecular weight and carbon content our result will be a methyl ester C_{20}–C_{21}, which is also indicated by Beilstein's (11) report about the melting point 70–71°C. of the methyl ester of 20-hydroxy-eicosan-carboxylic acid. Since the hydroxy acid contained in Fraction IV evidently is not pure, the number 122.5 is too small and the molecular weight calculated on the basis of it is too large. Thus the real molecular size would be nearer to the latter alternative, C_{20}–C_{21}. Fractions V and VI have an ash content which obviously is Al_2O_3 carried over from the column.

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Pressure Reaction of Maleic Esters with Vegetable Oils[1]

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The reaction of dimethyl maleate and some related dienophiles with vegetable oils under pressure has been studied successfully. When safflower oil reacts with 100% excess maleate, sulfur dioxide catalyst, and hydroquinone inhibitor at 290° for 1 hr., 80 to 90% yields of adduct fraction, based on linoleate, are obtained. Under the same conditions almost equally good yields result with either linseed or soybean oils. With safflower oil, dimethyl fumarate gave slightly lower yields. Di-*n*-butyl maleate gave even poorer yields, and much residue was formed. Use of anthraquinone as catalyst gave a 53% yield while a nickel conjugation catalyst gave 64%.

If linoleate and linolenate are present, both will react, but the linolenate is more reactive. There is little reaction with oleate, and attempts to force such a reaction lead to decomposition, probably through reversal of the Diels-Alder reaction. The fragments then recombine to form nonvolatile residues.

IN A PREVIOUS PUBLICATION (5) we described the reaction of dimethyl maleate with safflower oil at atmospheric pressure. Using sulfur dioxide catalyst, a maximum yield of 70.3% of adduct fraction, based on linoleate, was obtained.

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