4. Phenolphthalein indicator. Dissolve 1 g. of phenolphthalein in 100 ml. of alcohol.

C. Procedure

1. Dissolve the appropriate amount of KOH (35 g. for 0.5 N; 14 g. for 0.2 N) in 20 ml. of distilled water and dilute to a liter with alcohol in an alkali resistant bottle. Mix well and allow to stand overnight. Decant the clear supernatant solution into a brown glass bottle with a rubber stopper without exposure to carbon dioxide.
2. Weigh accurately sufficient dried $KHC_8H_4O_4$ to require about 40 ml. of the potassium hydroxide solution to be standardized and transfer it to a 300-ml. flask that has been swept free of CO_2. Add 50 ml. of cool CO_2-free water. Stopper the flask and swirl gently until the $KHC_8H_4O_4$ is dissolved.
3. When the sample is in solution, add 3 drops of phenolphthalein indicator and titrate to the first persistent faint pink color with the solution to be standardized, taking precautions to exclude CO_2.
4. Determine the quantity of the potassium hydroxide solution required to produce the same pink phenolphthalein end point in another flask containing the indicator and the same volume of CO_2-free water. Subtract the amount from that used in the first titration.
5. Calculate the normality of the standard solution by the following equation:

$$\text{Normality} = \frac{\text{Grams of } KHC_8H_4O_4}{\text{Ml. of KOH} \times 0.20422}$$

Recommendations

THE reports of the subcommittees and the specifications for the preparation of the most used standard solutions have been reviewed by the Seed and Meal Analysis Committee. Its recommendations are:

1. That the recommendations of the Subcommittee on the Analysis of Tung Fruit and Meal be adopted. They are
   - a) That method Ad 1-48 for sampling tung fruit be revised to include sampling of hulled tung fruit and be continued tentative.
   - b) That method Ad 2-48 for the determination of moisture in tung fruit be revised to include the determination of moisture in hulled tung fruit, made official, and designated as Ad 2-52.
   - c) That method Ad 3-48 for the determination of oil in whole tung fruit be made official and designated as Ad 3-52.
   - d) That method Ad 4-48 for the physical analysis of tung fruit be made official and designated as Ad 4-52.
   - e) That method Ad 5-48 for the determination of oil in tung kernels be made official and designated as Ad 5-52.
   - f) That the proposed method for the determination of oil in hulled tung fruit be adopted as tentative and designated as Ad 6-52.
2. That the recommendations of the Subcommittee for the Analysis of Castor Beans and Pomace for the adoption of methods for the analysis of castor beans and pomace as tentative be accepted. The methods involved are
   - a) Determination of moisture and volatile matter in castor beans.
   - b) Determination of oil in castor beans.
   - c) Determination of free fatty acids in castor beans.
   - d) Determination of moisture and volatile matter in castor pomace.
   - e) Determination of oil in castor pomace.
3. That the proposed specifications for the preparation of standard solutions for volumetric analysis be adopted. They are those for the standardization of
   - a) Sodium hydroxide solution,
   - b) Sulfuric acid solution,
   - c) Hydrochloric acid solution, and
   - d) Alcoholic potassium hydroxide.

These recommendations have received the unanimous approval of the committee with the exception that two members voted against the specifications for the standardization of the acid solutions by use of acid potassium phthalate. They have a strong preference for the use of sodium borate.

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Effects of Heat on Crude Peat Wax

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IT has been observed that the yield of bitumen extracted from peat depends on the temperature at which the peat has been dried, and Sundgrén (6) has reported that drying at a temperature of only 100-105° reduces the yield. In this paper bitumen refers to the material extracted from peat with a hot neutral solvent under ordinary pressure, which contains mainly waxes and resins. Crude wax is the part of bitumen left when the crude resins are separated from it.

Stadnikoff and coworkers (4, 5) reported that the solubility of peat bitumen in certain solvents decreases when the material is heated or stored for some time. They expressed the opinion that this phenomenon is a polymerization process and mentioned especially that the crude resin in peat bitumen is easily polymerized. Zetzsche (8) calls the part of peat bitumen which is difficult to dissolve "Polymer-Bitumen." Cawley and Carlile (1) use the term "asphalt" for the part of peat bitumen insoluble in light petroleum (B. Pt. 80-100°), and the term crude wax for the product extracted directly from peat.

The workers in the present research have reported (7) that the crude fatty acids separated from the crude wax of peat bitumen behave, when heated, in the same way as the bitumen.

As far as is known, none of the investigators mentioned has studied closely the formation of this insoluble or difficultly soluble part. The question is of interest not only as a scientific problem but also as an important factor in the production of these materials from peat on a commercial scale. The Peat

Technical Laboratory therefore has investigated the influence of heat on peat bitumen and especially on its valuable component, crude wax. While studying the conditions under which the insoluble product forms, an attempt has been made to find out the nature of the product. It would then be possible to depart from the hypothetical terms used to describe the insoluble products formed in the bitumen and its crude wax, which give a wrong impression of the process of formation of this product as well as of the composition of the starting material (bitumen or crude wax).

Experimental

The bitumen used in the present investigation was obtained from Aitoneva machine-peat by extraction with a mixed solvent, benzene-ethanol (1:9). The ethanol was of technical grade, 94.5% purity. The bitumen was divided into crude wax and crude resin fractions by dissolving it in boiling hot ethanol and precipitating the crude waxes from the solution at —7°C. while the crude resins remain in the solution. For certain experiments the crude wax was recrystallized from ethanol at +20°C., and the product thus obtained is hereafter called purified wax. These materials were subjected to the following tests:

a) Heat treatment of the bitumen and its components and their storage in air.
b) Heat treatment of the purified wax in solution.
c) Heat treatment of the crude wax in an atmosphere of nitrogen.
d) Heat treatment of the crude wax after bonding of the —OH function.
e) Study of the decomposition products of the heat treatment.

Heat Treatment of Bitumen in the Air. Samples were taken of bitumen and of crude wax as well as of crude resin in ethanol to avoid heat influences by the evaporation of the solvent. The weights of the dry substances of the samples were calculated by means of separate dry-substance estimation. Table I gives the results of the heat treatment and the storage.

Table I and Figure 1 show clearly that the formation of the part insoluble in ethanol begins at about 60°C. in crude wax and at about 80°C. in purified wax. The crude wax is practically insoluble in ethanol when it has been heated for 24 hours at a temperature of 180 ± 3°C. *In the tests it was observed that* the same result is obtained with crude waxes as with bitumen as well as with crude resins if they are heated at a temperature of 260 ± 3°C., for 2 hours. If the crude wax of peat is thus heated either at a temperature of 180 ± 3°C., for 24 hours or at a temperature of 260 ± 3°C., for 2 hours, the product is insoluble not only in ethanol but also in methyl alcohol, ether, acetone, petrol-ether, and benzene (B. Pt. 80-100°C.,) and dissolves only slightly in chloroform, benzene, and toluene.

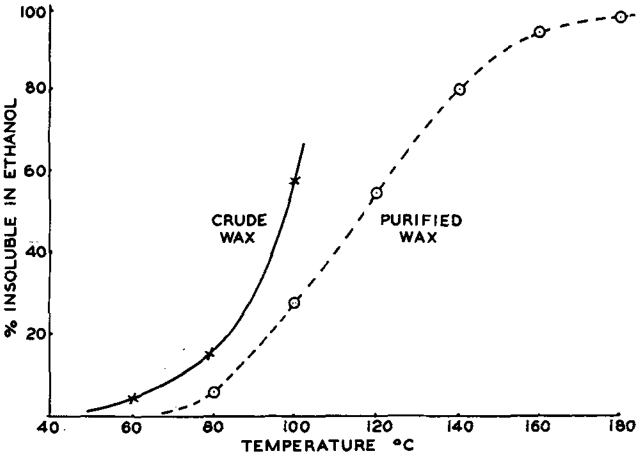

FIG. 1. Relations between temperature of heating and percentage of insoluble in ethanol of crude wax and of purified wax.

TABLE I

Relations of Time and Temperature of Treatment to the Ethanol Insoluble Fractions of Bitumen, Crude and Purified Waxes, and Crude Resin

Treatment		Percentage of Insoluble in Boiling Ethanol			
Time	Temperature	Bitumen	Wax		Crude Resin
			Crude	Purified	
24 hrs.	40±3°C.	0	0	....	0
24 hrs.	60±3°C.	0	2.8	....	0
24 hrs.	80±3°C.	6.4	12.8[b]	3.1	0
24 hrs.	100±3°C.	30.0[a]	58.9[a, b]	27.1	0.9[a]
24 hrs.	120±3°C.	....	....	52.1	....
24 hrs.	140±3°C.	....	....	81.8	....
24 hrs.	160±3°C.	....	....	94.4	....
24 hrs.	180±3°C.	....	....	97.5	....
1 week	20±2°C.	0	0.3	....	0
2 weeks	20±2°C.	0.8	1.4	....	0
3 weeks	20±2°C.	2.8	1.2	....	0

[a] When ethanol alone, rather than the benzene-ethanol mixture, is used as the extracting solvent, the percentages for bitumen, crude wax, and crude resin, after heating at 100°C., are: 5.1, 21.6, and 0, respectively.

[b] When crude wax is heated at these temperatures in an atmosphere of nitrogen rather than in air, the percentages insoluble in boiling ethanol at 80° and 100°C. are only 3.1 and 26.2, respectively.

Table I draws attention to the fact that for the same increase of temperature, the formation of a product insoluble in alcohol is greater in crude wax than in bitumen. The crude resins, in which the insoluble product formed is small, evidently reduce the percentage of an insoluble component in bitumen.

As shown in footnote a, Table I, there is less tendency for an insoluble fraction to form when ethanol is used as the extracting solvent, rather than the benzene-ethanol mixture.

Heat Treatment of Purified Wax in Solution. Heating purified wax in air increased the percentage which is insoluble in boiling ethanol much more than heating in an ethanol solution at the same temperature. After 24 hours at 78 (+2,—1)°C. the insoluble fractions amounted to 3.1% and 2.9%, but after 168 hours they were 58.0% and 8.9%, respectively.

Heat Treatment in a Nitrogen Atmosphere. The influence of the oxygen in the air on reducing the solubility of crude wax in ethanol is shown by data given in footnote b, Table I. The increase of the part of crude wax which is insoluble in ethanol was less on heating in an atmosphere of nitrogen than in air. However the formation of this insoluble product does not depend on the presence of oxygen even though its presence does promote the formation of that product. Since an insoluble product forms in an atmosphere of nitrogen, an attempt was made to follow the process in crude wax by means of the characteristic values.

It will be observed from Table II that the saponification value increases very little when the crude wax is heated in an atmosphere of nitrogen while the change of the iodine value remains within the limits of errors of the method. On the other hand, the acid and especially the hydroxyl values are reduced considerably by the heating. Thus, naturally, the ester value increases.

TABLE II

Effect of Heating Crude Wax[a] in a Nitrogen Atmosphere on Its Characteristics

Characteristics	Before heating	After heating, 24 hrs. at 80±3°C.
Acid value[b]	66.0	60.7
Saponification value[b]	132.9	136.0
Ester value	66.9	75.3
Hydroxyl value (Witzöff)	50.2	18.3
Iodine value (Hübl)	39.4	40.0

[a] The crude wax used was prepared by evaporating the solvent at a temperature below 30°C.

[b] Method for dark solutions, Holde, D., and Bleyberg, W., "Kohlenstofföle und Fette," 7th edition, p. 972, Hirschwaldsche Buchhandlung, Berlin, 1933.

The changes of the characteristic values caused by the heating in a nitrogen atmosphere indicate the reaction of —COOH and —OH functions. To test this explanation the —OH function was inactivated by acetylation prior to the heat treatment.

Heat Treatment After Bonding of the —OH Function. Solvent-free crude wax was acetylated according to Witzöff's method (2). A part of the product thus obtained was heated in air at a temperature of 100 ± 3°C., for 22 hours. The acid values before and after heating were 50.5 and 49.5. Since these are within the limits of error of the method, it is possible to conclude that the free carboxyl groups did not react during the heating.

As it now seemed that when the —COOH and —OH functions were free they reacted to some extent between themselves during the heat treatment, a test was carried out to identify products formed.

The Decomposition Products Formed During the Heat Treatment. During the heating of bitumen and crude wax it was observed that gaseous substances were evolved and a loss in weight occurred. To obtain quantitative data a sample of solvent-free crude wax was heated in a current of nitrogen for 48 hours, first at 100 ± 2°C. for 24 hours and then at 150 ± 2°C. for 24 hours. The sample, original weight 0.9392 g., lost 7.8 mg., and 37.0 mg., during the successive periods of heating. The gaseous decomposition products were conducted through absorption tubes filled with ascarite and magnesium perchlorate, both reagents of a quality used in microanalysis. For the two periods of heating the weights of water amounted to 5.8 mg. and 27.0 mg., and of carbon dioxide to 0.4 mg. and 10.0 mg., respectively. The water was identified by means of anhydrous copper sulfate.

The results show that at a temperature of 100°C. splitting of carbon dioxide from crude wax takes place only in a minimal degree; on the other hand, at the same temperature water is generated and escapes in a clearly perceptible amount.

Discussion

Those carrying out the present investigation (7) have proved the presence of hydroxy acids in the crude wax of peat and have indicated the possibilities of the formation of polyesters or estolids:

$$x\cdot \mathrm{HO{-}R{-}COOH} \longrightarrow \mathrm{HO{-}(R{-}COO)_{x\text{-}1}{-}R{-}COOH} + (x\text{-}1)\mathrm{H_2O}$$

The last mentioned circumstance is partly supported by the preliminary results obtained in this research. The decrease of the acid and hydroxyl values caused by the heat treatment and the increase of ester value indicate this (Table II). In addition, the slight increase of the saponification value could be explained by this type of reaction (3). The result obtained by the examination of acetylated crude wax obviously indicates the same conclusion. According to this, the free —COOH and —OH functions react at least to some extent between themselves.

However in the esterification reaction the acid as well as the hydroxyl values should decrease in the same degree. Consequently the formation of polyesters cannot be the only satisfactory explanation in this case, and it is therefore probable that the heat treatment causes other simultaneous reactions in the crude wax of peat. For example, the formation of anhydrides simultaneously with polyesterification would explain that the hydroxyl value decreases more than the acid value.

Considering the low solubility in organic solvents of the product formed by the heat treatment, the simple esters produced from monocarboxylic acids and monohydric alcohols are not a sufficient explanation of the solubility behavior. It is probable that the product in question consists of compounds of larger molecular size.

The above-mentioned facts, and the fact that heat treatment of crude wax at a temperature below 100° C. produces mainly water and liberates only an insignificant quantity of carbon dioxide, indicate that one or several of the reactions taking place are of a condensation-polymerization type. At higher temperatures (beginning from + 150°C.) the formation of carbon dioxide and other gases is accelerated, owing to the increase in the rate of decomposition typical of these temperatures.

Summary

1. On heating, there is formed in crude peat wax a product insoluble in ethanol and several other organic solvents.

2. In the crude resins of peat bitumen a product insoluble in alcohol is not formed at a temperature below 80°C. while at a temperature of 100°C. the quantity formed is insignificant compared with that of the crude wax.

3. When ethanol is used to extract bitumen, less insoluble material forms on heating than when the benzene-ethanol mixture is employed as the solvent.

4. The amount of the insoluble part formed by heating purified wax in an ethanol solution is less than by heating it in air at the same temperature.

5. The formation of an insoluble part in crude wax occurs in the absence of oxygen, but its presence accelerates the rate of formation.

6. In the range, room temperature up to 100°C., one or more condensation-polymerization type of reactions take place in crude wax.

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