water evolved during the condensation suggested that the product must also contain an appreciable quantity of free carboxyl groups. Electrometric titration of one of the polyesters prepared from 9,10-dihydroxystearic acid and maleic anhydride in 80% ethanol showed this to be true. It titrated as a monobasic acid (pK ≅ 7.2, N.E. = 386).

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The Extraction and Constitution of Peat Wax. A Review of Peat Wax Chemistry

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EXTRACTION of peat with organic solvents produces a crude dark-colored wax in about 5 to 15% yield. Interest in such extracted waxes has arisen for two reasons: (1) the fact that peat can be regarded as a precursor of coal suggests that a comparison of extracts obtained from peat with those obtained from coal might yield interesting information on the mode of formation of coal, and (2) the close similarity between peat and lignite suggests that extracts of peat might have properties and industrial uses similar to montan wax and its derivatives. It was particularly with this second aspect in view that a detailed examination of the extraction of peat wax has been carried out in the laboratories of the Department of Industrial and Forensic Science, and coupled with this, an examination of the chemical nature of the wax. This paper presents a review of earlier studies on the extraction and chemistry of peat wax and the related montan wax.

Peat—Its Formation and Occurrence

Peat is a term used to describe the material produced by the incomplete decomposition of vegetable matter either under water, or in the presence of water, under anaerobic conditions. The texture and uniformity of peat depends upon the conditions under which it was formed, and upon the nature of the vegetation which contributed towards its formation. Although the accumulation of living, dead, and partially decomposed vegetable matter usually known as "bog" contains a very large number of species of plants, only a comparatively small proportion of this number has supplied the bulk of the contents of bogs. Prominent among peat-forming plants are: mosses such as *Sphagnum* and *Hypnum*; marsh plants such as *Nymphaea* and *Calla*; heath plants including several species of *Erica* and *Vaccinium*; grasses, rushes, sedges, ferns, algae; marine plants such as *Phragmites, Scirpus,* and *Equisetum;* the leaves of trees and sometimes their trunks and roots.

Peat in its natural state ranges in color from yellowish brown to jet black. A freshly cut surface of raw peat usually tends to darken on exposure to the air. The most characteristic feature of peat in its natural state is its high moisture content which may rise to 97%, a range of 92 to 95% being commonly encountered.

As would be expected from the nature of the processes involved in the formation of peat there is considerable variation in its chemical composition. Some typical figures quoted by Miller (1) for Irish peat are shown in Table I.

TABLE I

Ultimate Analysis of Irish Peat

	Percentage of dry weight
Ash	1.5 – 5.0
Carbon	50.0 – 62.0
Hydrogen	3.0 – 7.0
Sulphur	0.15 – 0.6
Nitrogen	0.5 – 1.7
Oxygen	30.0 – 38.0

The organic constituents of peat are essentially the substances present in the plants forming the peat together with their decomposition products, and the material obtained when peat is extracted with organic solvents has been called variously peat bitumen, peat wax, or crude peat wax.

Crude Peat Wax

Crude peat wax is regarded as consisting of three main components, namely, asphalt, resins, and wax, although there are very many different methods of fractionation into these groups. For example a recent definition of the terms used in this connection is that of Boyd-Barrett and co-workers (2). They regard the resins as highly polar compounds readily absorbed by activated earths because of polar groupings and extractable from the crude wax by virtue of their solubility in cold methyl or ethyl alcohol. The term wax is reserved for the fraction soluble in light petroleum, and miscible in all proportions with paraffin. The asphalt fraction derives its name from its insolubility in light petroleum; the definition of asphalt in the petroleum industry, for example, is any substance present in petroleum, other than inorganic constituents, not soluble in such solvents.

In addition to Boyd-Barrett several workers have published schemes for the separation of the crude wax into resin, wax, and asphalt fractions which have been based on the work of Graefe (3) with montan wax in which asphalt is classified as material insoluble in hot alcohol, wax as that which is soluble in hot but insoluble in cold alcohol, and the resins as that part soluble in cold alcohol.

In the formation of peat wax it is thought that simultaneously with the humification process, the resin and wax parts of the peat-forming plants are accumulated and concentrated in the peat without being decomposed to the same extent as the other plant material. Consequently the more highly humified peats yield more crude wax. Sundgren, Ekman, and Rauhala (4) on the other hand report that they have found samples of peat obtained from two bogs with identical botanical composition and ash content, but with different wax content and wax composition.

During 1934–1940 an extensive program of work on the analysis and practical applications of peat wax was undertaken by a group of research workers in Ireland under the direction of Reilly at University College, Cork. Following up the earlier work of Ryan and Dillon (5), Reilly and Kelly (6) investigated the possibility of extracting wax from Irish peat and the subsequent refining of the crude material. In England during 1940–1945 extensive researches were carried out at the Fuel Research Station of the Department of Scientific and Industrial Research by Cawley and King (7) in an attempt to find indigenous substitutes for montan wax. In Finland workers in the State Fuel and Oil Research Station under the direction of Sundgren (8) have carried out many investigations on peat wax. Other workers who have been prominent in this field in recent years are Risi *et al.* (9) in Canada, Macpherson (10) in New Zealand, Kwiatkowski (11) in Poland, and a number of Russian workers, particularly Rakowski and Edelstein (12). Only two earlier reviews are available, those of Reilly and Kelly (6) and of Kiebler (13).

Extraction Yields. The solvent influences both the yield and the type of extract. The yields and properties of waxes obtained from Irish peat were determined by Ryan and Dillon (5) and by Reilly and Kelly (6). They studied single solvents, azeotropic mixtures, and two- and three-phase systems, and in general found that higher yields were obtained with solvent mixtures than with single solvents.

Although extraction with alcohols or mixtures of alcohols with benzene produces the highest yields, recent work by Ackroyd (14) suggests that the constituents of peat may react with alcohol during the extraction. Alcohol extracts contain large amounts of oxygen and may not be suitable for commercial purposes without extensive processing. Although petroleum ether and various petroleum fractions give lower yields of crude wax, these extracts contain a greater proportion of wax and smaller amounts of resins and asphalts.

Both Ackroyd (14) and Boyd-Barrett and his coworkers (2) therefore favor the use of petroleum solvents as yielding a product with high wax content and a high degree of miscibility with paraffin, an important characteristic when the wax is intended for the manufacture of polishes. Typical results obtained by Howard and Hamer (15) with peat from a bog situated in Co. Londonderry, Northern Ireland, are shown in Table II.

TABLE II

Yield of Crude Wax from Peat

Solvent	Yield (% dry peat)
Benzene	10.6
Ethyl alcohol	10.4
Dichloroethane	11.0
Esso solvent 20	7.0
Esso solvent 50	7.8
Hexane	6.7
Methyl ethyl ketone	12.2
Benzene/ethyl alcohol (9:1)	14.1
Benzene/ethyl alcohol (7:3)	14.6

Very high yields can be obtained with high boiling solvents such as cellosolve and pyridine, but the extracts are not waxlike in character and contain much asphaltic material. These high-boiling solvents are extremely difficult to remove from the extract.

Another factor influencing the yield of wax is the pretreatment of the peat before extraction. Schneider and Schellenberg (16), for example, have shown that in the extraction of air-dried peat with benzene more material is dissolved than from peat which has previously been dried at 100°C. Strache and Lant (17) expressed the view that this temperature was too low to favor the formation of insoluble material by a polymerization mechanism, and they suggested that a fusible substance in the peat, insoluble in benzene, might melt and cover the benzene soluble component and thus inhibit its solution in the solvent. This explanation does not appear to be satisfactory, however, as the experimental results of other workers have shown that the solubility of peat wax does in fact decrease when it is heated or stored even at relatively low temperatures. An investigation of this phenomenon has been reported by Sundgren and Rauhala (18) who concluded that heating crude peat wax formed a product which was insoluble in ethanol and certain other solvents, also, that in the crude resin fraction of the extract, products insoluble in alcohol were not formed at temperatures below 80°C. Even at 100°C. the amount was insignificant compared with that formed from the crude wax fraction under the same conditions. This latter finding is in direct contrast to the conclusion of Stadnikow and co-workers (19), who expressed the opinion that the polymerization process was especially noticeable in the resin fraction. Later work by Sundgren and Rauhala (20) has shown that even at 60°C. the wax tends to become less soluble. Additional confirmation that the effect is due to polymerization processes has been obtained by Ackroyd (14), who found a steady increase in the molecular weight of peat wax with time of heating ranging from 860 at the commencement to 1,130 after 72 hours at 100°C.

It may also be noted here that the yield of wax obtained with a given solvent often varies considerably with the source of peat, mountain bogs tending to give higher yields than midland or lowland bogs, but Boyd-Barrett *et al.* (2) showed that there is little difference in the composition of the extracts obtained.

Peat Wax Components

Among the early attempts to determine the constitution of peat wax by solvent fractionation procedures was that of Thiessen and Johnson (21). These workers first separated peat into water soluble, alcohol soluble, alkali soluble, humic acids, lignin, cellulose, insoluble constituents, and mineral matter. A later paper by Johnson and Thiessen (22) dealt with the composition of the alcohol soluble fraction and also of an ether soluble fraction. A wax resembling montan wax was separated from the ether soluble fraction and purified. A green substance which was invariably found in the ether soluble fraction was identified as chlorophyll but the other fractions were not characterized further.

A paper published by Stadnikow and Titow (23) was one of the first to describe the separation of the crude wax into wax and resin fractions. Successive treatment with petroleum ether and with benzene separated the crude wax into two fractions, about 45% being regarded as wax and the remaining 55% as resin. Sundgren, Ekman, and Rauhala (4) also consider that the crude wax can conveniently be divided into two main fractions which they refer to as crude waxes and crude resins. They state that the former group consists of free higher fatty acids, esters, higher alcohols, partly esterified oxy-acids, and dicarboxylic acids, oxy-acids, estolides, lactones, normal paraffins, isoparaffins, and possibly sterols. The crude resins contained fractions which were termed free resin acids, resin esters, resin alcohols, and resenes.

Some results of Howard and Hamer (15) are summarized in Table III, which shows the percentages of resin, wax, and asphalt in crude waxes extracted with the series of solvents used for the extractions reported in Table II.

TABLE III

Resin, Wax, and Asphalt Content of Crude Peat Wax
(Percentage by weight of crude wax)

Solvent	Resin	Wax	Asphalt
Benzene	21	64	15
Ethyl alcohol	32	56	12
Dichloroethane	20	70	10
Esso solvent 20	10	88	2
Esso solvent 50	12	87	1
Hexane	9	90	1
Methyl ethyl ketone	23	63	14
Benzene/ethyl alcohol (9:1)	39	48	13
Benzene/ethyl alcohol (7:3)	33	49	18

Individual Constituents. Preliminary fractionation with methyl alcohol containing 0.5% acetone enabled Rakowski and Edelstein (12) to separate crude wax, extracted from peat with an alcohol-benzene mixture, into a resin fraction which formed 33% of the crude wax. By extraction with ether and dilute alkali 54% of crude resin acids were separated from the resin fraction. Further treatment of the resin-free crude wax with ethyl alcohol and aromatic free petroleum ether resulted in the separation of a pale waxy material with a melting point of 73 to 77°C. which amounted to 13% of the original crude wax. From this fraction 57% of mixed fatty acids were obtained by saponification and the following acids were separated: $C_{26}H_{52}O_2$, $C_{27}H_{54}O_2$, and $C_{28}H_{56}O_2$. The residual 43% contained hydrocarbons, alcohols, and other unsaponifiable matter.

Shortly after the above report Titow (24) separated the saponifiable fraction into pale yellow wax acids, 37.8% of the original crude wax, and a black carbonaceous mass of resin acids, 15.8% of the crude wax. Further separation of the unsaponifiable fraction yielded the hydrocarbons pentatriacontane and tritriacontane together with what appeared to be an alcohol with the formula $C_{27}H_{56}O$. From the unsaponifiable fraction of the original extract four acids were obtained by fractional distillation of the mixed ethyl esters. These were identified as $C_{12}H_{22}O_2$, $C_{14}H_{26}O_2$, $C_{25}H_{50}O_2$ and $C_{27}H_{54}O_2$. The presence of higher members of the same homologous series of acids was also indicated, but no further members were isolated. In addition evidence was obtained of the presence of an hydroxy acid with the formula $C_{30}H_{60}O_3$. Cyclic acids and esters with cyclic alcohols appeared to be present in the resinous portion of the crude wax.

Using a somewhat similar procedure Zalosiecki and Hausmann (25) were able to isolate acids with the formulae $C_{16}H_{25}O_5$, $C_{21}H_{55}O_7$, and an alcohol $C_{20}H_{40}O_4$. The isolation of an acid $C_{19}H_{34}O_2$ from Finnish peat has been reported by Aschan (26) while the three acids $C_{27}H_{54}O_2$, $C_{28}H_{56}O_2$, and $C_{29}H_{58}O_2$ were reported by Roginskaya (27). Both these workers used techniques somewhat similar to those employed by Titow (24).

The identification of the above acids and other constituents has been based largely on melting point and molecular weight. The results are open to doubt because the experimental error is comparable to the difference between successive members of an homologous series.

Following recovery and analysis of the products of saponification of the resins, wax, and asphalt, Ackroyd (14) concluded that lactones or estolides are a major constituent of the wax fraction since on recovery of the saponification material a substantial ester value is found. A great deal of valuable information is contained in Ackroyd's paper, although he made no attempt to isolate or characterize any constituents.

As in the case of other waxes the saponification products of peat wax have been subjected to fractional distillation, usually in the form of methyl esters. Reilly and Wilson (28) investigated the two fractions of highest boiling point obtained by this method and found them to consist mainly of the acids $C_{26}H_{52}O_2$ and $C_{27}H_{54}O_2$.

There are very few references in the literature to the use of chromatographic techniques for the separation of the constituents of peat wax and these all indicate that other methods such as saponification have been used to reduce the complexity of wax before attempting chromatography. For example in work described by Nillsson, Hansson, and Erdheim (29), crude wax was first saponified and the acids separated, giving 47% of acids and 53% of unsaponifiables. The unsaponifiables were further separated and found to contain 79% of alcohols and 21% hydrocarbons, ketones, etc. Chromatography of both acids and unsaponifiables was carried out on columns of alumina developed with benzene-ethyl alcohol, benzene-acetic acid, or benzene-pyridine. In the case of the unsaponifiables a characteristic yellow band was observed which was considered to be a single substance. Aluminum oxide was found to be too active an absorbent for the mixed acids even when treated with water to reduce activity, and recoveries from this fraction were poor. The method was however reported as promising and capable of further development. Sundgren *et al.* (4) separated the methyl esters of hydroxy acids of peat wax chromatographically but the isolation of definite substances was not reported.

The most extensive investigation of this type so far reported is that of Boyd-Barrett (30). In this series of experiments the crude peat wax was extracted from peat either with benzene/alcohol (9:1 by volume) or petroleum ether. The behavior of the unsaponifiable components of this crude wax on alumina columns was studied. When eluted with benzene, bright yellow bands were observed and these were collected. About

12% of the unsaponifiable matter was thus isolated as a yellow waxy solid. This fraction, when recrystallized from petroleum ether, yielded a small amount of pale yellow crystals melting at 251°C. and having a blue fluorescence in ultraviolet light. Analysis gave C, 91.94%, H, 7.95% corresponding to an empirical formula $C_{23}H_{24}$. Further elution of the column with solvents in order of increasing polarity, toluene, petroleum ether, and absolute alcohol yielded small amounts of material. Only alcohol eluted enough material for further purification and an apparently pure compound, melting point 95 to 96°C., was separated (C, 75.88%, H, 12.92%, and O, 11.20%). Other adsorbents used were silica gel and active carbon but in no case were promising results obtained. The crude waxes were also percolated without prior treatment, but apart from the isolation of a very small amount of the hydrocarbon mentioned above little progress was made. This was attributed to the low solubility of the crude waxes in cold solvents.

A study of steroids and triperpenoids isolated from a sample of peat has recently been reported by McLean, Rettie, and Spring (31). These workers extracted peat with light petroleum and saponified the extracted material. The resultant mixture was separated by chromatography on alumina. The early fractions were hydrocarbons. Crystallization of intermediate fractions gave an alcohol $C_{30}H_{52}O$ identified as friedelan-3β-ol (epifriedelanol). Crystallization of later fractions gave an undisclosed number of triterpenoids and final elution of the column with ether containing a small amount of methanol gave a sterol mixture with constants in close agreement with those reported by Ives and O'Neill (32) for the β-sitostanol which they isolated from peat moss.

Montan Wax

Montan wax is the natural wax most closely related to peat wax and therefore a substance which might provide a working guide to the analysis and possible composition of peat wax. A very great deal of published work is available due to the industrial importance of this wax but mention will be made of only a few important relevant studies.

The similarity between the physical properties of peat wax and montan wax is shown in Table IV.

TABLE IV

Comparison of Properties of Crude Peat Wax and Crude Montan Wax

	Peat wax	Montan wax
Melting point °C.	75	78
Acid value	56	29
Saponification value	116	92
Ester value	60	63

As with peat wax three main component fractions are readily distinguished by solvent fractionation, asphalt, resins, and wax, although the classification here is usually based on solubility characteristics in alcohol. Other methods include the use of acetone at −20° to extract the resin followed by extraction of wax with boiling isopropanol (33); liquid sulphur dioxide (34) and acetone-sulphur dioxide 1:1 (35).

The main components of the resins are dark "resin acids" and "hydroxy resin acids" and probably include estolides, lactones, etc., derived from hydroxy acids, also terpenes and sterols. Little is known about the structure of the asphalt fraction but it includes sulphur-containing hydroxy and resin acids.

After removal of resin and asphalt from crude montan wax the refined wax is pale brown in color (peat wax is very dark brown). Many components have been identified including lactones and estolides, polyterpenes, triacontane and dotriacontane, and higher fatty acids, principally montanic acid. Montanic acid has been the subject of several detailed investigations, including chromatographic analysis and its structure now seems established as n-octacosanoic acid (36).

The presence of triterpenes in benzene extracts of montan wax has been demonstrated by Jarolim *et al.* (37), who used chromatography on neutral alumina followed by fractional crystallization to separate fifteen individual crystalline compounds including hydrocarbons, alcohols, ketones, and lactones.

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