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MONTAN WAX FROM CALIFORNIA LIGNITES

A Thesis
Presented to
the Faculty of the Department of Chemistry
College of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Master of Arts

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by
Robert John Kvick
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FOREWORD

Montan wax has been extracted from the lignite deposits of Germany since the early part of the twentieth century. The wax was named by von Boyen (1901). The word Montan is derived from the Latin term montanus meaning "of a mountain." The wax has found extensive uses in polishes, insulating materials, candles, explosives, and special applications in the rubber industry.

The increased demand for waxes for industrial uses and the limited supply of domestic origin has made the study of the sources and characteristics of domestic waxes desirable.

California lignite has been shown to be a valuable source of Montan wax.

The object of this research is to improve upon the physical and chemical properties of the extracted wax.

WAXES

The English term, "wax", is derived from the Anglo-Saxon weax. This was the name used for the material obtained from the honeycomb of the bee. Materials of similar chemical and physical properties were also found in plants. These too were known as weax or wachs. These terms have evolved to the present general term wax. Wax now covers a much broader variety of materials, including all waxlike solids and liquids found in nature and all hydrocarbons, acids, alcohols, and esters that occur individually in waxes.

The general sources of waxes are classified as natural and mineral waxes. The natural waxes are divided into insect, animal, and plant waxes. The mineral classification includes the fossil, earth, and lignite waxes.

The insects of principal importance that produce waxy substance are the various species of the bee. As a rule, the honey-producing bees furnish the larger percentage of wax. Other waxes obtained from insects are: cocoon silk wax, Chinese insect wax from the scale-insect, Coccus pela, and shellac wax from the Lac insect, Carteria lacca.

Waxes are obtainable from both land and marine animals. Wool wax or lanolin from sheep is the most important wax from the land animal sources and spermacetic wax from the sperm whale is the most important marine animal wax.

Wax production in a plant occurs in small quantities in the seeds, the pollen, and in the tissues. It is found as a result of excretion upon their leaves, stems, or fruit. This is especially pronounced in the case of desert and semi-arid plants which secrete a waxy coating upon their leaves to retard evaporation of what little moisture they have. Some of these plants, such as the carnauba palm, from the dry regions of northeastern Brazil; the candelille plant, from the deserts of Mexico; and the bayberry shrubs along the Atlantic Coast secrete enough wax to be of economic and commercial importance.

Constituents of plant and animal waxes are, for the most part, made up of non-glyceryl esters formed in nature through the esterification of the longer carbon chain fatty acids and the higher alcohols. Along with these, there also occur free monohydric alcohols and sterols, free fat and waxy acids, hydrocarbons, and lactones or similar condensation products.

Extraction of ligneous coals yields a mineral wax containing wax esters, free wax acids, ketones, and alcohols. Algae wax, a fossil wax produced by Algae; ozocerite, an earth wax; and montan, a lignite wax, are all types of mineral waxes which are obtained by mining operations and refining processes.

WAX CONSTITUENTS

The constituents of waxes are chiefly acids, alcohols, and esters resulting from the union of the acids and alcohols present. Saturated and unsaturated compounds along with isomers are also found in variations with the above components. Cyclic alcohols or sterols are predominant in fats and oils, but occur in waxes to a small extent, only.

The number of carbon atoms that make up a wax may vary between 14 and 44 (Warth, 1947).

Saturated paraffins, both straight and branched chains are the sole constituents in petroleum waxes and appear to an important degree in other waxes.

The important alcohols in waxes are the aliphatic monohydric alcohols in contrast to the diols and triols which are found in animal and vegetable oils. The acids are separated by saponification with an inorganic base, usually with sodium hydroxide, followed by treatment with an excess of water to remove the resulting salts from the unsaponifiable material. This unsaponifiable material consists of alcohols and other aliphatic substances. Separation of these alcohols and aliphatic substances can be accomplished in most cases by use of a selective solvent, or by fractional crystallization. Little is known of the structure of several of the alcohols encountered in waxes. They are simply referred to as isomers. Carnaubyl alcohol, the alcohol of wool grease, was one of the first isomers to be identified. It is n-lignoceryl alcohol. An isoceryl alcohol also exists. The mixed dimers are responsible for three or more ceryl alcohols, referred to as neoceryl, ceryl and carboceryl ($C_{25}H_{52}O$, $C_{26}H_{54}O$, and $C_{27}H_{56}O$).

The existance of the monomeric alcohols with odd numbers of carbon atoms is unusual. However, montanyl alcohol, in its natural state in montan wax, or in cotton, appears to be a 29-carbon alcohol; and melissyl alcohol of the waxes of arid plants, appears to be a normal alcohol of 31 carbon atoms. Synthetically prepared alcohols having 29 and 31 carbon atoms have the same physical and chemical properties as the corresponding natural alcohols.

Sterols, polycyclic alcohols of the cyclopentanophenanthrene structure, occur, to a certain extent in waxes of both plant and animal origin. They are water insoluble and appear in the unsaponifiable residues of the waxes in significant quantities. Cholesterol, a sterol, is an important constituent of lanolin, a natural material found in the extraction of oils from wool. Associated with cholesterol in wool is 7-8 dihydrocholesterol, which when subjected to ultraviolet light can be activated to a form of vitamin D.

Cholesterol forms esters with lauric acid, myristic acid, palmitic acid and stearic acid that are of a waxy nature and are used extensively in the manufacture of cosmetics.

Ketonic alcohols and lactones are encountered rarely as components of waxes.

Some of the alcohols, their natural occurrence and melting points are given in Table I. (Warth, 1947, pp. 9-14)

	Alcohol	Number of Carbons	M.P.	Source
1.	Cetyl	16	49-50	spermacetic
2.	Stearyl	18	58.5	Montan wax
3.	Ceryl	26	19.5-80	Chinese Insect Wax
4.	Montanyl	29	84.5	montan wax
5.	Myricyl	30	86.5	Japan Wax Carnauba beeswax
6.	Melissyl	31	87	beeswax
7.	Lacceryl	32	89	carnauba stick-lac

The fatty acids in waxes appear both free and combined. The unsaturated acids are valuable in the formation of emulsions and in liquid waxes. Fatty acids of plant origin are generally found to contain an even number of carbon atoms and only a small percentage of waxes contain acids with odd numbers of carbon atoms.

Warth, in his book, "The Chemistry and Technology of Waxes," (1947) has set up a group of acids showing their association with well known fats and waxes. From butter, butyric acid can be obtained; cocoanut oil gives capric acid; human fat gives caprylic acid; cocoanut fat gives capric acid; palm kernel and sperm head oil gives lauric acid; cocoanut oil, spermaceti, and wool waxes yield myristic acid; carnauba wax yields myristic acid; beeswax gives cerotic, montanic and melissic acids. The wax acids have eight or more carbon atoms. Acids of less than eight carbon atoms have not been detected, even in the liquid waxes.

Dibasic acids, hydroxy acids, polyhydroxy acids, unsaturated acids and lactones are encountered in rare instances. They are more closely associated with sugars and starches, and when found with waxes, are considered as impurities. Shelloic acid and certain similar acids found in beeswax are examples.

Alkyl esters resulting from the union of acids with higher aliphatic alcohols, and less often with cyclic alcohols, such as the sterols, are the principal components of the natural waxes. The esters encountered in nature appear to have an even number of carbon atoms, with the possible exception of the esters of an extremely high molecular weight. There is apparently a tendency for an acid of an odd number of carbon atoms to combine with an alcohol with an odd number of carbon atoms to form an ester of an even number of carbon atoms, e. g.,

$C_{28}H_{57}COOH$	$HOC_{29}H_{59}$	$C_{28}H_{57}COOC_{29}H_{59}$	H_2O
Montanic acid	Montanyl alcohol	Montanyl montanate	water

The naturally occurring esters of high molecular weight are extremely difficult to synthesize in the laboratory. Acids isolated from waxes are readily converted to ethyl or other low alkyl esters for purposes of identification. The esters of low alkyl alcohols are separated by distillation or recrystallization. The boiling points of the ester derivatives are commonly used as a means of identification for the acids.

SOURCE OF MONTAN WAX

Montan wax is classified as a mineral wax, or more specifically a lignite wax. This classification is not considered mineral or lignite by strict definition but is so specified because of its geological occurrence.

The lignitic coals which yield wax are brown and soft with fragments of the plant structures readily recognizable. Microscopic examination reveals not only abundant cellular tissues but also seed bodies, spores and resinous particles which contain the waxy constituents.

Every coal variety is dependent on many factors. The characteristics of the original vegetation from which the deposit was produced, the degree of decomposition and the following geological history which involves the degree of pressure and heat to the mass of the peat, all influence its properties.

Through a series of transformations, peat deposits have been gradually converted to coal. The classification of a coal is dependent upon the degree of conversion from the initial peat deposit. Lignite represents the lowest degree of conversion whereas anthracite is the result of maximum transformation.

During the degradation of plant ingredients, it is known that protoplasm and oils decay relatively rapidly.

Cellulose and lignin decay more slowly; and the spores, pollens, waxes, and resins remain intact long after other parts of the plant matter have been completely degraded. Because of their high resistance to chemical change, they often remain unchanged during the coalification period.

The conversion of peat into coal is believed to be due largely to the pressures resulting from shifting strata and earth disturbances. Heat generated from these pressures contributes to these changes, and the mineral matter collected in the laying down of vegetation has also influenced the results. The duration and severity of the conditions to which the layer of peat is subjected during this period, as well as the organic deposit, probably determine the kind of coal formed from the original peat deposit.

Lignite is the name applied to the material resulting from the first stages of coal forming. It may or may not be woody and is more compact in structure than peat. It is dark brown to nearly black in color. The lignite taken directly from the mine contains from 20 to 45 percent moisture. It slacks readily and falls to pieces on exposure to weather. The heating value ranges between 5500 and 8300 B.T.U. per lb. of undried lignite, and between 10,000 and 12,000 B.T.U. on the moisture and ash-free basis (Wilson, 1950).

There are tremendous quantities of lignitic coals in the United States which have been exploited commercially only on a very limited scale for fuel purposes because of the available higher-grade coals and the large supplies of petroleum and natural gas.

The lignite deposits in America have a common characteristic with respect to their geological age, in that they are believed to have been developed during the Paleocene and Eocene epochs of the Tertiary period.

The Gulf states, the Northern Great Plains states, and the Pacific Coast states are the three main areas of lignitic coal deposits in the United States (Selvig, 1950).

Alabama, Arkansas, Louisiana, Mississippi, and Texas are included in the "Gulf province" of Campbell's (1929) geographical division of American coal deposits. Campbell grouped these deposits on the basis of geological relationship and geographical distribution. The deposits in North Dakota, Montana and South Dakota, which make up the "Northern Great Plains province", are the most extensive in the United States as far as quantity is concerned. In the "Pacific Coast province", deposits are located in Oregon, Washington and California. Probably the most important lignitic coal deposits of this "province" are located in Amador County, California. The lignite in the neighborhood of Buena Vista and Ione is the best known and was exploited in a small way from about 1871 to 1912.

The fuel values of these coals are very poor but the extractable materials have great potentialities for commercial consumption. Montan wax is considered the most important material taken from lignite. Work is being done on the humic acid or sodium humate extracts from the coal as a vicosity control of mud used in oil well drilling. Aside from the extractable substances, experiments are being conducted on the possible value of the lignite as a fertilizer.

CONSTITUENTS OF MONTAN WAX

The isolation and identification of the various chemical components of montan wax has been the subject of a considerable number of investigations. The constituents contained in montan wax are chiefly esters of monohydric alcohols, and free alcohols and acids of high molecular weight.

Pschorr and Pfaff (1920) isolated various alcohols from ether and acetone extracts of the wax. The ether extract yielded free acids and the alcohol extract yielded tetracosanol, $C_{24}H_{50}O$. Most of the free wax acids and ceryl alcohol, $C_{26}H_{53}OH$, free and esterified were obtained from the acetone soluble material from the residue of the other extraction. Saponification of the final residue, which was rich in esters, yielded tetracosenol, ceryl alcohol, and myricyl alcohol, $C_{30}H_{61}OH$. These findings have been consistent and in accordance with findings of others. There has been no disagreement as to the alcohols isolated but there has been a fair amount of controversy over the chain length of the acid constituents of montan waxes.

As early as 1852, an acid which melted at 82° was isolated from a brown coal. It was called "geocerinic acid" and the analysis of its lead salt indicated the formula to be $C_{28}H_{56}O_2$. Hell (1900) isolated the free acid by extracting the saponified wax with ligroin and treating the soaps with a mineral acid. The free acids were systematically fractionated by precipitation with magnesium acetate. On analysis, Hell (1900) ventured the formula as $C_{29}H_{58}O_2$. Both of these analyses were on the lead salts and due to the molecular size, the difference between the acids would be close to the experimental error. Other research was done on the difference in molecular weight between the C_{28} and the C_{29} acids which is 14, which is greater than the experimental error. Discrepancies still occurred which were later found to be due to the impurities in the acids. It was believed that the waxy acids were a mixture of acids having an odd number of carbon atoms. Holde, Bleyberg, and Vohrer (1929) reported the separation of a C_{28} acid and an iso-C_{32} acid and suggested that a C_{30} acid was probably an ingredient of montan wax.

A number of acids were prepared synthetically to observe their properties and peculiarities (Francis, Piper, and Malkin, 1930). The melting points of the acids between C_{11} and C_{26} were found to be on two smooth curves, one for the acids having an even number of carbon atoms and the other for the acids having an odd number of carbon atoms. The higher molecular weight acids were found to have melting points which differed slightly from each other depending on the way they were prepared. When the acid was in the form of finely powdered crystals, it had a slightly higher melting point than an acid prepared by using a premelted sample. The melting points were found to be within one degree of each other.

Studies on the large crystal spacing of the pure acids by the same authors and the data obtained from these studies and incorporated with the correct melting point were considered sufficient verification of an acid of high purity.

Samples of acids from montan wax were checked in this manner. It was found that the acids were not pure but were mixtures having either 28 and 30 or of 28, 30, and 32 carbon atoms per molecule. The agreement between the melting points and x-ray spacings of both naturally occuring and synthetic montanic acid, indicate that montanic acid is octacosanoic acid.

The refining of a product is generally a desireable practice. It not only improves the product but opens opportunities for different types and grades of materials to meet specific requirements of the consumer. The purpose of this research is to study the properties of montan wax with respect to refining, bleaching, and blending; and to determine the acid, saponification, ester and Iodine values.

EXTRACTION OF LIGNITE

The extraction of montan wax from lignite is dependent on such variables as the percentage of wax and water in the lignite; the type of solvent used; the time and temperature during the extraction; and the separation of the wax solution from the insoluble material.

The yield of extract from lignite with a given organic solvent may vary over a considerable range depending upon the age of the lignite as well as the origin and method of deposition. It has been found that a maximum yield is reached in the extraction of young brown coals by the use of aromatic solvents (Wakesman, 1930).

Considerable work has been done on the pressure extraction and extraction at elevated temperature (Lowry, 1945). These methods have been used generally in coal analysis. The atmospheric-pressure extraction of brown coals with low-boiling solvents such as alcohol, benzene, and toluene yield waxes and resins chiefly along with small amounts of asphaltic constituents. Extraction of various lignites with the above solvents yielded as low as a fraction of a percent of soluble material to as high as 36.6 percent (Selvig, 1950).

Removal of the waxy constituents from the lignite can be done on a wet or dry basis. The majority of the wax plants in Germany use the von Boyen process which was patented in 1901 in which the brown coal is crushed, clarified and dried before extraction. The only plant in Germany which treat the bituminous lignite in its natural damp state is that of Frank and Zuyler (Warth, 1947). This procedure is designated as the wet extraction process. The two plants that are in actual commercial production of montan wax in the United States use the wet extraction process. One uses a modified wet extraction in which the coal is partially dried.

The solvents used in treating the coal commercially are usually of the aromatic type. Several plants in Germany use methanol with benzene generally in the ratio of one to four by volume. The use of methanol is employed in the dry process to prevent a decrease in the yield of extract. Fischer and Scheider (1918) made a study on the yield of wax from dried and wet lignite containing approximately 10 per cent water. They obtained a four per cent greater yield from the wet lignite.

In the wet process, the coal is ground to pass a sixty mesh screen and is then conveyed to an extractor tank where the solvent is added. The time and temperature of actual extraction depends on the nature of the coal. If the temperature is held in the extraction temperature range for too long a period, emulsions which prevent rapid separation of the wax solution from the coal are formed. Some type of a filter cloth which is used in either a vacuum or pressure filter system is the general commercial means of separating the solution from the coal. The solvent is distilled off leaving the crude montan wax.

The crude wax obtained from the extraction of lignite with the lower boiling solvents consists largely of resins, waxes, and asphaltic materials. The percentage of each of these varies with the type of lignite and can be controlled to a certain extent by means of a selective solvent. The segregation of the resins and waxes has received considerable investigation. There are various means of removing the resins from the waxes. A suitable method for commercial extraction would be to dissolve the wax in a hot solvent and then crystallize by cooling. The resins would remain in the solution. Various solvents such as the higher alcohols containing three or more carbons, mixed hexanes or petroleum ether, and the aromatic solvents have been used. The wax crystals produced are not entirely free of resins and a small percentage of wax will remain in the solution, but this amount is very slight as the wax is practically insoluble in cold solvents. The resin content can be separated more completely by fractionation with ether.

In the process used in the German plants, the wax prepared for subsequent processing by oxidation or for selective reactions and for compounding, is extracted to remove the resins. For this procedure the wax is powdered and thoroughly mixed with the solvent mixture, i.e. 20% methyl alcohol and 80% benzene. The wax is removed from the solution containing the resins by filtration. The resins are obtained by distilling off the solvent. Approximately 5% of the total resin remains in the extracted wax (Palmer, 1945).

The amount of the resins varies considerably in different waxes. It was found that montan wax from pyropissite contained as little as 6.64 percent resin; Riebeck montan wax, 16.54; wax from the Heimann firm, 46.6; Bohemian montan, 31.54; and Silesian montan, 65.90 (Lowry, 1947).

Resinous material from the German wax has the following properties: melting point, 65° to 70° C.; acid value, 33; saponification number, 76; and methoxyl number, 3.4.

Investigations have shown the resins to be of a terpene nature. A hydrogenated polyterpene, $C_{20}H_{34}$, has been isolated in small quantities. It was believed to be iosene, a derivative of retene (Soltys, 1929). A petroleum ether extract yielded a saturated tricyclic sesquiterpene with the formula $C_{15}H_{26}$. Along with these polyterpenes, two paraffin hydrocarbons have also been isolated from the petroleum ether fraction. They are triacontane, $C_{30}H_{64}$, melting at 66° C., and dotriacontane, $C_{32}H_{64}$, melting at 70° C. The actual percentages of these hydrocarbons in the resin fraction have not been determined quantitatively, but they apparently dominate because their melting points agree with the melting points of the crude resins. Most of the work on resins has been done on those obtained from German sources.

The crude wax, as extracted, is dark brown to black in color. It has a melting point between 82° C. and 87° C., an acid value of 30-56, a saponification number of 90-110, an iodine number of 17.6, and unsaponifiable material, 36.4 percent (Warth, 1947). The asphaltic, and resinous materials in the waxes alter the wax properties to a considerable degree.

Purification of the crude wax has been investigated. One method used is the treatment of the crude wax concentrated sulfuric acid, its monohydrate, fuming sulfuric, or chlorosulfonic acid, and alkali metal bisulfates. The acid material is added to the molten wax, which is held between 130° C. and 150° C. The mixture is vigorously agitated until the desired purification has been attained. The resulting paste-like material is washed with water and is neutralized with a little alkali metal bicarbonate and then dried. The material may be refined further by extraction with an aromatic solvent (Warth, 1947). This method is inexpensive but the properties of the wax are not improved; in fact there is a tendency to form a char from which low yields of light colored wax are obtained. This wax also has a lower melting point than the crude wax.

Another method for the purification of crude waxes consists of separating the acids and alcohols by saponification procedures. The impurities in the alcohol and unsaponifiable portion are removed with a solid adsorbent. The acids are purified by treatment with an oxidizing solution such as dichromate and sulfuric acid or with an alkaline solution of permanganate.

REFINING OF MONTAN WAX

Further removal of the asphalt and resinous material from the crude wax was attempted by the use of methanol, ethanol, propanol, butanol, isopropanol, carbon tetrachloride, and toluene. The crude wax was completely soluble in carbon tetrachloride, toluene, and butanol; and partially soluble in methanol and ethanol. Propanol and isopropanol dissolved the wax and resinous material, leaving the asphaltic material undissolved.

A method of continuous extraction with isopropanol using a modified Soxhlet Extractor was found to separate the asphalt from the other soluble materials in the solution. This refined wax crystallized from the solvent by cooling, and was separated by filtration. The alcohol in the filtrate separated from the resins by distillation.

A sample of crystallized wax was also obtained from a 15 percent solution of crude wax in toluene. The hot solution was cooled and the wax crystals were collected by filtration.

BLEACHING OF MONTAN WAX

The bleaching process was carried out on crude, crystallized, and refined wax. The bleaching solution consisted of a solution of sodium dichromate in sulfuric acid and water. The bleaching combination consisted of 1 part of wax, 1.8 parts of sodium dichromate, 10 parts of water, and 70 parts of 95% sulfuric acid. The mixture was heated to 110° C., at which temperature the reaction became exothermic. However, the reaction was brought to completion toward the end of the oxidation by additional heating.

The residual asphalts and resins are responsible for the color which is removed by their oxidation.

The alkenes were oxidized to glycols and finally to acids. Alcohols present were oxidized to their corresponding acids.

The completion of the bleaching operation was determined by titrating a portion of the bleaching liquor for the chromate ion with standard ferrous ammonium sulfate solution using diphenylamine sulfonic acid as an indicator. The chrome complexes were removed from the wax with dilute sulfuric acid and then treated with water to remove sulfuric acid.

The results obtained were as follows:

Type	Percentage of total chromate used	Color
Crude wax	95	Brown-yellow
Crystallized wax	89	Light tan
Refined wax	75	Pale yellow-white
Asphaltic material	73	No discoloration

ACID VALUE

The acid value is the number of milligrams of KOH needed to neutralize one gram of the wax sample. A general procedure consists of warming 3 to 4 g of the sample with neutralized alcohol in a 250 ml Erlenmeyer flask. Several drops of phenolphthalein solution are added and 0.1 N alcoholic KOH solution is added until the first permanent pink color appears (Crawle, C.M., 1945).

The acid values reported below were obtained by dissolving 0.5 g of the wax in a small amount of warm toluene. When the solution was complete, 200 ml of additional toluene were added. The solution was cooled to room temperature. A few drops of 1 percent solution of phenolphthalein in ethanol were added and titration with alcoholic KOH was carried out as above.

The acid value is the number of ml. of 0.1 N KOH times 5.61 which is the number of milliequivalents of KOH per ml of solution, divided by the weight of the sample.

A comparison of the acid values of the different materials is shown below:

Type	Acid Value
Crude wax	46
Crystallized wax	48
Refined wax	47
Asphaltic material	40.2
Resinous material	60.6
Bleached Crude wax	110
Bleached Crystallized wax	112
Bleached Refined wax	104

SAPONIFICATION AND ESTER VALUE

The saponification value is the number of milligrams of KOH required to hydrolyze 1 gram of wax. The procedure followed was similar to Cawley's (1945). A 0.5 g sample was refluxed in a 250-ml. boiling flask with 20 ml. of 0.5 N alcoholic KOH for 2 hours; 200 ml. of alcohol were added and the solution brought to the boiling point. The hot solution was titrated with 0.5 N hydrochloric acid. A blank determination was made at the same time.

$$\text{Saponification value} = \frac{(\text{Vol. of N HCl in blank--Vol. in analysis}) \times 56.104}{\text{wt. of sample}}$$

The ester values are the differences between the saponification values and the acid values and shows the amount of alkali consumed in the saponification of the esters.

The following data were obtained:

Sample	Saponification Value	Ester Value
Crude wax	104	58
Refined wax	87.9	40.9
Resinous material	91.8	31.6
Asphaltic material	148	108.2
Bleached Crude wax	151.7	41.7
Bleached Crystallized wax	112	87
Bleached Refined wax	155	51

IODINE ABSORPTION VALUE

The iodine number is a measure of the percentage of unsaturated material present in the sample analyzed.

The Hanus method which employs an iodine monobromide solution in acetic acid was used in finding this value.

For the determination of the iodine value, a known weight of the sample, in this case, 0.3 g was dissolved by treating with 20 ml. of carbon tetrachloride. The solution was then cooled to room temperature and a measured volume of iodine monobromide solution was added. The solution was mixed and set aside in a dark room for two hours. A few ml. of 15 percent KI solution were placed in the cup of the ground glass stoppered 250 ml. iodine flasks.

After the waiting period, 10 ml. of KI solution were added and the free iodine was titrated with 0.1N sodium thiosulfate. The results were calculated to give the grams of iodine absorbed by 100 grams of the sample.

Sample	I_2 Value
Crude wax	24
Crystallized wax	18
Refined wax	10
Resinous material	38
Asphaltic material	36
Bleached Crude wax	0
Bleached Crystallized wax	0
Bleached Refined wax	0

MELTING POINT DETERMINATION

The ball and ring method was employed in the determination of the melting point (Selvig, 1950). A melted sample was poured into the ring; on solidification, a steel ball was placed on the sample and both were suspended in a beaker of water. A thermometer was placed along side the sample with the mercury bulb even with the ring. The water was heated at a rate of 1° C. per minute. The melting point was taken as the temperature at which the steel ball dropped through the ring.

The melting points obtained were as follows:

Sample	M.P., ° C.
Crude wax	81.5
Crystallized wax	86.5

Sample	M.P., ° C.
Refined wax	85
Resinous wax	56
Asphaltic wax	92
Bleached Crude wax	84
Bleached Crystallized wax	86
Bleached Refined wax	85

PARAFFIN WAX COMPATIBILITY

Compounding of waxes makes it possible to produce innumerable mixtures or blends of waxes having many commercial uses. A general method of testing a wax is by determining its compatibility with paraffin having a melting point of 56° C.

Tests of the compatibility with paraffin were made with the crude montan wax, crystallized montan wax, refined montan wax, and the asphaltic material. The tests were made by adding 1 gram of the sample to 3 grams of melted paraffin in a small beaker. The waxes were mixed thoroughly while the temperature was held at 100° for a period of approximately two hours.

The crude and crystallized waxes were not completely compatible; the separated asphalt was not compatible and the refined wax showed 100 percent compatibility.

DISCUSSION OF RESULTS

The products obtained from the isopropanol extraction of the crude montan wax were isolated in the following percentages: refined wax- 70.7%, resin- 16.8%, and asphalt 12.5%. This procedure is quite simple. It takes about 30 minutes at a temperature between 75-80° C. for the waxes and resins to completely dissolve, leaving the asphaltic residue.[1] The separation of the wax from the solution is simply a matter of slowly cooling the solution with no agitation so as to obtain large crystals that filter readily. The solvent loss is small because an enclosed system is used. This system of separation was found to be unique in that the asphalt, resin, and refined wax are isolated in the same process.

The bleaching of the different types of materials showed that the asphalt was the main detriment in obtaining a light colored wax. The wax crystallized from toluene was bleached to a color a little lighter than that of the bleached crude wax. This was probably due to the removal of the unsaturated compounds in the resinous material. The removal of the chrome complexes from the bleached crystallized wax proved to be difficult. In the attempted bleach of the asphalt, a dark grey, spongy substance resulted from which it was difficult to remove the chromium complexes. Several acid treatments were necessary to remove the last traces of the chromium complexes. The asphalt as obtained from the crude wax has a dark brown color when air dried. The fused asphalt was a very dark black mass. No color change was noticeable in the oxidized asphalt.

The removal of the asphalt and resinous material not only eliminated the majority of unsaturated groups, as indicated by the iodine values, but also appeared to remove a majority of the coloring materials. The asphalt was also the cause of paraffin incompatibility. The isopropanol insoluble material proved to be incompatible with paraffin wax.

The refined wax was lighter in color than the crude montan wax. This refined material not only took less of the oxidizing agent but also showed greater change in color. By treatment of the crude wax with isopropanol, the unsaturated compounds in the refined material were reduced to over one-half as those contained in the crude wax.

Comparison of the acid values, saponification values and ester values of the crude, refined, and crystallized waxes with those of their corresponding bleached products show that part of the esters were hydrolyzed and the resulting alcohols were oxidized to acids. There is also an indication that the alkenes were split, forming two carboxylic groups.

The comparison of the melting points of the various separated substances with the melting points of the crude material shows that the presence of resins lower the melting point of waxes.

SUMMARY

An economically feasible procedure for refining crude montan wax has been developed. This procedure consists of the use of isopropanol to dissolve the waxes and resins, leaving the asphaltic material in the residue, and the subsequent crystallization of the wax from the solution, leaving the resins in the filtrate.

The asphaltic constituents were shown to be incompatible with paraffin wax and are not oxidizable by the method used. The refined wax was bleached best and with the least amount of chromic acid. Compatibility of the refined material with paraffin was complete. A large percentage of the coloring material was eliminated by the isopropanol treatment of the crude wax.

No attempt was made to isolate and identify the chemical constituents of the waxy products.

BIBLIOGRAPHY

LITERATURE CITED

A. Periodicals

Cawley, C. M., and J. G. King,
1945--Ester Waxes from British Lignite and Peat: Transcontinental Journal of the Society of Chemical Industry, 237-242.

Fischer, F., and W. Schneider,
1918--Ges. Abhandl. Kenntnes Knoble, 150-63.

Francis, F., S. Piper, and T. Malkin,
1930--Proc. Roy. Soc. (London) A 128, 214-52.

Hell, C. Z.,
1900--Angew. Chem., 13, 556-7.

Holde, D., W. Bleyber, and H. Vohrer,
1929--Brennstoff-Chemie, 10, 101-8, 124-8.

Palmer, G., G. S. Shillitoes, and A. Macmaster,
1945--German Montan Wax Industry, 3-5.

Pschorr, R., and J. K. Pfaff,
1920--Ber, 53 B, 2147-2162.

Selvig, W. A., W. H. Ode, B. C. Park, and H. J. O'Donnell,
1950--American Lignites: Bureau of Mines, Bulletin 482, 31-36.

Soltys, A.,
1929--Monatsh., 53/54, 175-84, 185-6, Monatshefte fur chemie und verwandte teste anderer wissenschaften.

Von Boyen, E.,
1899--Z. Angew. Chem., 12, 64-5, 14, 1110-1.

Wakesman, S. A., and K. Stevens,
1930--Industrial and Engineering Chemistry, Analytical Edition, 2, 167-73.

LITERATURE CITED

B. Books

Campbell, M. R.,
1929--THE COAL FIELDS OF THE UNITED STATES
U.S. Geological Survey Prof. Paper 100, 1-33.

Lowry, H. H.,
1947--CHEMISTRY OF COAL UTILIZATION
John Wiley and Sons, Sec. printing,
New York, 690-697.

Ralston, A. W.,
1948--FATTY ACIDS AND THEIR DERIVATIVES
John Wiley and Sons, Inc., New York, 55-57.

Warth, Albin H.,
1945--THE CHEMISTRY AND TECHNOLOGY OF WAXES
Reinhold Publishing Corporation, New York.

Wilson, P. J. Jr., and J. H. Wells,
1950--COAL, COKE, AND COAL CHEMICALS
McGraw-Hill Book Company, Inc., New York, 63.