



1957

## The urea adducts of the constituents of California montan wax

Alan Howard Vanderbilt  
*University of the Pacific*

Follow this and additional works at: [https://scholarlycommons.pacific.edu/uop\\_etds](https://scholarlycommons.pacific.edu/uop_etds)

 Part of the [Chemistry Commons](#)

---

### Recommended Citation

Vanderbilt, Alan Howard. (1957). *The urea adducts of the constituents of California montan wax*.  
University of the Pacific, Thesis. [https://scholarlycommons.pacific.edu/uop\\_etds/351](https://scholarlycommons.pacific.edu/uop_etds/351)

This Thesis is brought to you for free and open access by the Graduate School at Scholarly Commons. It has been accepted for inclusion in University of the Pacific Theses and Dissertations by an authorized administrator of Scholarly Commons. For more information, please contact [mgibney@pacific.edu](mailto:mgibney@pacific.edu).

THE UREA ADDUCTS OF <sup>2</sup>  
THE CONSTITUENTS OF CALIFORNIA MONTAN WAX

---

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

---

by  
Alan Howard Vanderbilt  
...  
June 1957

#### ACKNOWLEDGEMENT

The author wishes to express his appreciation for the assistance given him by the faculty of the Department of Chemistry of the College of the Pacific in conducting this research. Appreciation is especially expressed to Dr. Emerson G. Cobb for his helpful criticism and guidance in this work.

## TABLE OF CONTENTS

	PAGE
Introduction . . . . .	1
Wax . . . . .	4
Constituents of Wax . . . . .	4
Occurrence of Waxes . . . . .	7
Montan Wax . . . . .	10
Methods of Extraction . . . . .	10
Purification and Refining . . . . .	13
Constituents . . . . .	14
Urea Adducts . . . . .	18
Methods of Formation . . . . .	18
Structure . . . . .	19
Stability . . . . .	19
Experimental . . . . .	21
Preparation of the Wax . . . . .	21
Determination of Constants . . . . .	22
Preparation of the Urea Adducts . . . . .	28
Decomposition of the Urea Adducts . . . . .	32
Discussion of Results . . . . .	36
Summary . . . . .	40
Literature Cited . . . . .	42

## LIST OF TABLES AND FIGURES

TABLE	PAGE
I. Odd-Carbon Acids Reported Isolated	
From Natural Sources . . . . .	6
II. Uses of Montan Wax . . . . .	11
III. Effects of Pressure on Yield	
Benzene Extraction of Montan Wax . . . .	12
IV. Acids Reported Recovered From Montan	
Wax . . . . .	16
V. Extraction Schedule . . . . .	23
VI. Precipitated Waxes . . . . .	24
VII. Properties of Wax Extracts . . . . .	29
VIII. Properties of Wax Recovered From	
Urea Adducts . . . . .	34
IX. Maximum Average Chain Length of Acid	
Constituents of Montan Wax . . . . .	39
 FIGURE	
1. Acid, Saponification, and Ester Values of	
the Extracts of Montan Wax . . . . .	35
2. Acid, Saponification, and Ester Values of	
Waxes Recovered from the Urea Adducts. .	35

## INTRODUCTION

Interest in the chemical constitution of montan wax began with the work of Von Boyen, who in 1901 showed montanic acid to be a constituent of the wax. In the years that followed the literature has been rich with respect to investigations of montan wax. Most of the literature concerns itself with the technology of the wax, its uses, methods of refining and purification. Much has also been written on its chemical make-up.

The literature is rife with apparent contradictions, principally as regards the number of carbon atoms in the wax constituents. Reports of odd numbers of carbon atoms are repeatedly made, which, if correct, refute the rule that only even-carbon compounds of more than seven carbons occur in natural materials. These findings have not gone unchallenged, however, as many investigators believe that reports of odd-carbon compounds result from incorrect identification of mixtures of even-carbon compounds.

That such confusion exists is not surprising in view of the high molecular weights of the substances occurring in waxy materials. The molecular weight of octacosanoic acid is 480, whereas that of its homolog, nonacosanoic acid, is 494. This difference of only 14 in molecular weights is reflected in very similar properties, hence great difficulty of separation if both occur together.

Another fact giving rise to apparent contradictions as to the chemical nature of montan wax is that the composition of the lignites from which the wax is obtained varies considerably, depending upon the regions from which it is mined. The wax itself is a mixture of natural vegetable waxes occurring in the living plants that contributed to the coal forming deposits. Because the nature of these plants would vary geographically, and because the conditions of carbonification would also vary, it should not be expected that the montan wax recovered from the lignites of Saxo-Thuringen would be identical with that recovered from the lignites of Lone, California.

Past work on the isolation and identification of the constituents of montan wax followed the classical method of analysis of esters and ester constituents. That is, for the acid components, the analysis usually consisted of saponification, separation of saponifiable materials from non-saponifiables, regeneration of free acid from the saponified portion, fractional vacuum distillation, titration of fractions to determine the average equivalent weights, hence the molecular weights, of the acids. For the alcohols it consisted of acetylation of the non-saponifiable portion, fractional crystallization, and determination of the saponification numbers of the acetate fractions. Because of the small differences in molecular weights of homologs of these acid and alcoholic constituents, results obtained by these

means were usually sufficiently inconclusive to be challenged by other workers.

In this laboratory it is felt that by forming urea complexes of these wax constituents the differences in homologous molecular weights will become sufficiently great to enable more conclusive results to be obtained.

It was the purpose of this research to explore the possibility of forming urea adducts of the normal components of montan wax, and to investigate the properties of the adducts and the waxes regenerated from the decomposed adducts.



## WAX

The term "wax" is generally applied to any fat-like substance that is not a glyceride, and is derived from the Anglo-Saxon weax which was applied to the solid obtained from the honeycomb of the bee. Today, however, the term "wax" is applied to a great variety of substances of animal and vegetable origin, and even to some synthetics.

The principal constituents of natural waxes---waxes directly obtainable from living organisms---are esters, acids, and alcohols. Mineral waxes---those obtained as a result of mining operations---also contain considerable hydrocarbon material which is believed to have been produced by the pyrolysis of the acids and alcohols.

The alcohols found in waxes are generally monohydric, normal alcohols, varying in chain length from 14 to 44 carbon atoms (Warth, 1947 pp. 9-15). One of the more important low molecular weight alcohols is cetyl alcohol,  $C_{16}H_{34}O$ . The alcohol of highest molecular weight so far isolated from waxes is takakibyl alcohol,  $C_{44}H_{90}O$ , which was isolated from Koryan corn oil, a product of Manchuria.

As was mentioned earlier, all high molecular weight compounds were thought to contain even numbers of carbon atoms. It is, therefore, interesting to note that investigation of waxes has yielded what appear to be odd-carbon alcohols.

The acid constituents of waxes are generally high

molecular weight, monobasic aliphatic acids. Although branch chain acids may exist in waxes, no references to that effect were found. These acids are usually saturated and have chain lengths varying from 14 to 44 carbon atoms. However, those having from 20 to 34 carbon atoms are of principal interest. And it is of interest to note that it is from the investigations of waxes that come the reports of odd carbon acids. Table I summarizes these acids as they are reported by Ralston (1948).

The nomenclature of the acids recovered from waxes is in some instances confusing. This confusion arises from improper identification in the original research, with the result that there are examples of different acids being given the same name, and of different names being applied to the same acid. For example, the following is quoted directly from Warth. "The cerotic acid of scale insect waxes is a C<sub>27</sub> acid, as confirmed by many investigators. The name cerotic was first given to a C<sub>25</sub> acid, which later became known as hyenic acid. Gascard assigned the name neocerotic to the C<sub>25</sub> cerotic acid, and carbocerio to the C<sub>27</sub> cerotic. The name isocerotic infrequently appears in chemical literature for the C<sub>27</sub> acid." The term montanic was first applied by von Boyen to what he believed to be nonacosanoic acid, isolated from montan wax in 1901. Today, however, the name montanic is applied to octacosanoic acid almost exclusively.

TABLE I

## ODD-CARBON ACIDS REPORTED ISOLATED FROM NATURAL SOURCES

ACID	REPORTED SOURCE
Heptanoic (enanthic)	floral waxes (violet leaf oil)
Nonanoic (pelargonic)	oil of rue; Japan wax
Pentadecanoic (hyenic)	yeast fat; bark of <i>Xanthoxylum carolinianum</i> .
Heptadecanoic (margaric)	Gedda wax; lumbang oil
Nonadecanoic	tubercle bacillus wax; leprosy bacillus wax
Heneicosanoic	Japan wax; peanut oil; beef marrow
Tricosanoic (neocerotic)	wax of olive leaves
Pentacosanoic (neocerotic)	beeswax; montan wax
Heptacosanoic (cerotic, isocerotic, carboceric)	beeswax, Chinese wax, montan wax
Nonacosanoic (montanic)	montan wax; bitumen peat wax
Hentriacontanoic	wax esters (not specified)
Tritriacontanoic (psyllic, ceromellisic)	psylla wax; scale insects
Pentatriacontanoic	scale wax; olive wax

Mono and di-hydroxy acids are also found in waxes, and these contribute to the formation of lactones which have also been isolated.

Hydrocarbons of from  $C_{14}$  to  $C_{44}$  are most common in the mineral waxes, but those of higher molecular weight also occur. Chain lengths up to 71 carbon atoms have been reported (Warth, 1947). Hydrocarbons are not found in the natural waxes and are therefore thought to exist in mineral waxes because of the pyrolysis of the other wax constituents.

Other constituents of lesser importance include ketones and sterols. Cholesterol is an important constituent of lanolin, the wax from wool.

Occurrence of Waxes. Wax is produced by a great variety of living organisms. Insects, mammals, birds, plants, and bacteria are some of the life forms from which wax has been obtained. Most of these represent commercial sources of wax, although the wax recovered from bacteria is of scientific interest only. The wax of the tubercle bacillus plays an important role in its resistance to chemotherapy.

There are several insects from which wax is commercially recovered. Beeswax is probably the most common. In Asia a certain scale insect (Coccidae) secretes a protective wax coating, from which is obtained Chinese wax. In Southern Asia the lac insect (*Carteria lacca*) is a source of stick lac.

Certain mammals and birds are commercial sources of wax. The wool "grease" of sheep is very rich in lanolin. The sperm whale (*Physeter macrocephalus*) is the source of

spermaceti. One of the few true liquid waxes is obtained from the "mutton bird", a petrel of the species *Aestrelata lessoni*.

A large variety of waxes is obtained from plants. The outer wall of adult plant leaves are covered by a deposit of cutin, a waxy substance that is highly impermeable to water. This material also covers, but to a lesser extent, the stems and fruit of the plant. Desert plants are highly cutinized, and this plays an important roll in the survival of these plants in regions of low humidity and arid climates. Trees that are highly cutinized are palm trees, olive trees, live oaks, and conifers.

Palm trees are the sources of two important commercial waxes. Carnauba wax is obtained from the carnauba palm Copernica cerifera. The palm Attalea oxcelsa is the source of Ouricuri wax.

Waxes are also obtained from herbs and shrubs in commercial quantities. Candelilla wax is obtained from the weed Pedilanthus pavonis. A wax is also obtained from flax. Japan wax and one of the few naturally liquid waxes, jojoba oil, are plant products. Wax has been recovered from a large number of plants other than those listed here, but relatively few have any commercial importance.

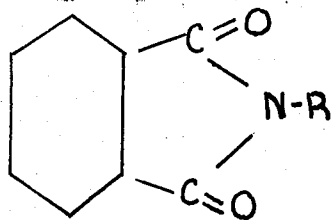
Other waxes, referred to as fossil or mineral waxes, are obtained from the earth as a result of mining opera-

tions. These are waxes that were produced by living organisms sometime in the geological past and have gained their present properties as a result of heat and pressure associated with the formation of the beds in which they are found. Included in this group are the Ozokerites, generally associated with shale; montan wax, present in subbituminous coals, lignite and peat; lignite paraffins; and the paraffin obtained from petroleum.

Today, synthetics are playing a very important role in wax technology, and in many cases are replacing the natural waxes in industrial use. These synthetics are classed as waxes only because of their wax-like properties. Their chemical structures are very different from those of the natural waxes in that they do not contain esters or the high molecular weight acids and alcohols derived from esters.

Polyhalogenated hydrocarbons make up a very important group of synthetic waxes. By varying the degree of halogenation and chain length a wide variety of properties are obtainable.

Another class of synthetic waxes consists of high molecular weight phthalimides of the general formula:



where R is an alkyl radical having six or more carbon atoms (Warth, 1947).

## MONTAN WAX

Montan wax was first extracted from lignite coal by von Boyen, who published his work in 1901. This wax is a hard, very dark wax, melting at about  $86^{\circ}\text{C}$  (by the drop point method). Because of the scarcity and expense of hard, natural waxes, interest developed early in the application of montan wax to commercial uses. Table II indicates some of the uses found for montan wax.

Methods of Extraction. Methods of extraction of montan wax fall into two general categories having many modifications: (1) solvent extraction and (2) distillation. Marcusson and Smelkus (1917) report a 10% to 20% yield when lignite is extracted with benzene at normal pressures. Fischer and Schneider (1917) reported that benzene extraction at increased pressures gave a marked increase in yield, as summarized in Table III.

Schneider and Tropsch (1917) attributed the increase yield observed at  $250^{\circ}\text{C}$  to a cracking process, where a portion of the lignite normally insoluble in benzene is broken down into soluble fragments.

Other solvents have been successfully used in the extraction of montan wax. Acetone is reported by Donath and Brun (1920) to have an advantage over benzene in that moisture does not interfere with the acetone extraction. Meyerheim (1919) found that chlorinated hydrocarbons were effective

TABLE II  
USES OF MONTAN WAX\*

USE	OTHER WAXES IN BLEND
Self-sealing adhesives	Paraffin 133/135
Brewer's Pitch	Natural pitch
Electrical insulation Cable coating wax	Ozokerite
Floor wax	Carnauba, Petroleum ceresin, Paraffin (130°), Beeswax, Japan
Leather dressings	Beeswax, Wool wax, Scale wax
Paper sizing	Paraffin
Carbon paper	Carnauba, Candelilla, Beeswax
Stove polish	Paraffin (40-42)
Buffer wheel polishing compound	Ceresin wax
Shoe polish	I. G. Wax, Carnauba, Candelilla, Paraffin (50-52), Shellac wax, Ozocerite
Phonograph records	

\*This information was summarized from Warth: THE CHEMISTRY AND TECHNOLOGY OF WAXES, Reinhold, 1947.



TABLE III  
EFFECTS OF PRESSURE ON YIELD  
BENZENE EXTRACTION OF MONTAN WAX

SAMPLE	PRESSURE ATMOSPHERES	TEMPERATURE DEG. C	% YIELD
Rhenish lignite	1	80	3-3.5
Rhenish lignite	10	155	4.4
Rhenish lignite	50	250	7
Saxo-Thuringen lignite	1	80	11
Saxo-Thuringen lignite	60	260	25

extracting agents. He used both  $\text{CCl}_4$  and  $\text{CCl}_2\text{CHCl}$  with good results. Davankov and Konovalova (1938) extracted the wax with dichloroethane, and the rapidly expanding Ukrainian montan wax industry is based on this reagent. Fischer (1930) found that certain aliphatic amines such as  $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{NH}_2$  and  $((\text{CH}_3)_2\text{CH})_2\text{NH}$  were excellent solvents for montan wax.

Although most methods of recovery are based on solvent extraction, occasional reference is found whereby distillation is used. Meyerheim reports the successful recovery of the wax with superheated steam.

Purification and Refining of Montan Wax. Crude montan wax contains, in addition to the normal wax constituents, varying amounts of resins and asphaltic materials. Kvick (1952) summarizes the various methods of refining montan wax. These methods include selective extraction with alcohols containing three or more carbon atoms, mixed hexanes (petroleum ether), or aromatic solvents. Extraction with propanol or isopropanol was especially useful as a purification procedure in that the asphaltics are not soluble in the heated reagent, whereas the resins and waxes are. On cooling the solution, the wax crystallizes out and the resins remain dissolved. The wax that is refined in this way is only slightly lighter in color than the crude, however, and this seriously limits the usefulness

of the wax.

Montan wax has also been refined by distillation of the crude. Although distillation at normal pressure produced considerable char, and hence a low yield, distillation at reduced pressure overcame this difficulty. When the steam was superheated to 250° C it was used successfully to separate the useful wax constituents from the other materials present. Extraction of the distillate with benzene, followed by pressing and bleaching, gave in 30% yield a white, crystalline product melting at 70 - 80° C. (Marcusson and Smelkus, 1917).

None of the purification methods based upon distillation or solvation produced a light wax. In order to obtain a light product bleaching was necessary in each case. All bleaching methods reviewed used the same basic principles - violent oxidation with chromic acid solutions (alkali dichromates dissolved in  $H_2SO_4$ ). This method is very costly because of the amounts of dichromate required. Recent work in the U.S.S.R. has centered around methods of reclaiming spent bleaching solution. These methods have so far met with only partial success.

Constituents of Montan Wax. The composition of montan wax is a subject of much controversy. The first substance reported isolated from montan wax was a fatty acid m.p. 83°C, acid no. 138.3, and was named montanic acid by von Boyen.

The formula of this acid was given as  $C_{29}H_{58}O_2$ . Although other investigators verified this formula for the acid (Hell and Boyan, 1919; Tropsch and Kreutzer, 1922; Stadler, 1933), still others believe it to be in error. This group felt that reports of a  $C_{29}$  acid resulted from improper identification of equimolar mixtures of even carbon acids (Holde, Bleyberg and Vohrer, 1929 and 1931).

The acids reported to be present in montan wax are summarized in Table IV.

Several alcohols have been reported isolated from montan wax. Pschorr and Pfaff (1920), working with montan wax from the lignites of Central Germany, isolated  $C_{24}H_{49}OH$ ,  $C_{26}H_{53}OH$ , and  $C_{30}H_{61}OH$ . Their method involved successive extractions of the crude wax with first ether and then acetone. The two extracts and the residue were then saponified with KOH, and the potassium salts converted to insoluble calcium salts by treatment with  $CaCl_2$ . The mixtures were then extracted with acetone to recover the unsaponifiable material and the regenerated alcohols. These were acetylated with acetic anhydride and recrystallized from alcohol. This procedure was reported as being very effective in the separation of the alcohols from the rest of the wax constituents.

The mixture of acetate esters so obtained was separated further by fractional crystallization, yielding acetates of the three alcohols mentioned above.

TABLE IV

## ACIDS REPORTED RECOVERED FROM MONTAN WAX

## ODD ACIDS

$C_{25}H_{50}O_2$	hyenic acid	Tropsch and Koch	1929
		Tropsch and Kreutzer	1922
$C_{27}H_{54}O_2$	carboceric acid	Tropsch and Kreutzer	1922
		Tropsch and Koch	1929
		Stadler	1933
		Stadler	1934
$C_{29}H_{58}O_2$	montanic acid	von Boyen	1901
		Ryan and Dillon	1909
		Markusson and	
		Smelkus	1917
		Hell and Boyan	1919
		Tropsch and Kreutzer	1922
		Tropsch and Koch	1929
		Stadler	1933
		Stadler	1934
$C_{31}H_{62}O_2$	hentriacontanoic acid	Tropsch and Koch	1929

## EVEN ACIDS

$C_{20}H_{40}O_2$	arachidic acid	Meyerheim	1919
$C_{22}H_{44}O_2$	behenic acid	Meyerheim	1919
		Holde, Bleyberg, and Vohrer	1930
$C_{24}H_{48}O_2$	lignoceric acid	Meyerheim	1919
		Holde, Bleyberg, and Vohrer	1930
$C_{26}H_{52}O_2$	hexacosanoic acid	Holde, et al	1930
$C_{28}H_{56}O_2$	octacosanoic acid (montanic acid)	Holde, et al	1929
$C_{32}H_{64}O_2$ (iso)	dotriacontanoic acid	Holde, et al	1929

Montanyl alcohol,  $C_{29}H_{58}O$ , and stearyl alcohol,  $C_{18}H_{36}O$ , are also reported as being constituents of the wax (Warth, 1947).

The esters of montan wax are mixtures resulting from the various combinations of the acids and alcohols previously mentioned. No references were found to indicate that the structures of these esters were known. This is to be expected, as the methods of analysis all involve saponification.

## UREA ADDUCTS

Methods of Formation. The formation of crystalline complexes of urea with long chain compounds was first reported by Bengen (1940). He found that when an aqueous solution of urea was shaken with a long chain compound a crystalline adduct was readily formed. Such adducts would not form, however, with branched chain compounds.

Interest in urea adducts developed because of the possibilities of using this technique in analytical and technological procedures, with respect to the separation and identification of normal compounds of high molecular weight. Although the urea solvent used by Bengen was water, it was found that methanol was also very effective for this purpose (Zimmerscheid et al, 1949). Other solvents that may be used for this purpose are ethanol, propanol, acetone, methyl ethyl ketone, and the lower boiling amines.

Although the details of forming the complex differ somewhat, the general procedure is usually the same. The compound to be adducted is mixed with a solution of urea in one of the above solvents for from one half hour to twenty four hours, or sometimes even longer, depending upon the stability of the complex and the rate at which equilibrium is achieved. The white, crystalline product is separated by filtration.

Differences of opinion exist as to the feasibility of

washing the crystalline adduct. Many workers report the routine washing of the adduct with pure solvent, but others report that washing the adduct caused decomposition, and that because of this fact impurities could not be removed by this means (Redlich, Gable, Dunlop and Millar, 1950).

Structure. The structure of the urea adducts of normal compounds, specifically hydrocarbons, was determined by the use of X - ray diffraction techniques (Smith, 1952). The unit cell was found to be hexagonal,  $a_0 = 8.230$  and  $c_0 = 11.005$  Å, and to contain six urea molecules. The urea molecules form a hollow channel structure, hexagonal in cross section, in which the hydrocarbon chain is enclosed. The hydrocarbons are in an extended zig-zag configuration with their long axis parallel to the c axis.

The dimensions of the channel are such that it will just accommodate the hydrocarbon molecule when the molecule is unbranched. Therefore only normal hydrocarbons or molecules with terminal functional groups will normally adduct with urea. The channel is constructed of urea molecules arranged in a spiral such that the plane passing through both nitrogen atoms is nearly parallel to the c axis.

Stability. The stability of the adduct apparently involves hydrogen bonding between adjacent urea molecules, and van der Waals forces between the urea molecules and the hydrocarbon. Each oxygen atom is hydrogen bonded to four nitrogen



atoms, and each nitrogen to two oxygens. In obtaining the bond distances, it was found that there were two lengths of N-H····O bonds in both pure urea and the urea hydrocarbon complex. The longer bond in each was found to be the same length, within the limits of experimental error, but the shorter bond of the complex was 0.05 Å shorter than its counterpart in pure urea. This was more than the probable error in its determination. A shortening of these bonds over those of pure urea apparently contributes to the stability of the adduct.

## EXPERIMENTAL

Preparation of the Wax. The wax used in this experimentation was crude montan wax obtained from lignite coal mined in the region of Ione, California. It was extracted from the coal by solvent extraction, the solvent being a mixture of aliphatic and aromatic hydrocarbons.

The crude wax was in flake form, was hard, brittle, dark brown in color, and had a characteristic waxy feel. When ignited it burned readily, leaving no residue. It had a dropping point of  $86^{\circ}\text{C}$ , acid value 45, saponification value 120, and ester value 75.

The crude wax was subjected to successive exhaustive extractions with methyl alcohol, ethyl alcohol, isopropyl alcohol, and secondary butyl alcohol. The extractions were carried out in a Soxhlet extraction apparatus in the following manner:

10 g of crude wax was extracted with 200 ml of methyl alcohol for 1 hour, at the end of which time the color of the solvent in the extraction chamber was a very pale yellow. The residue in the thimble was then extracted with 200 ml of ethyl alcohol until the color of the solvent in the extraction chamber was a light yellow, slightly darker than that of the methyl alcohol extractate. The residue was then extracted for approximately 1 hour with 200 ml of isopropyl alcohol, and a fourth time using sec.-butyl alcohol. After

each extraction the extractate was slowly cooled to room temperature then cooled to 5° C before filtering. The details of this series of extractions are summarized in Table V.

The precipitated waxes differed from each other both in color and consistency. The waxes extracted with the lower molecular weight alcohols were lighter in color, more gelatinous, and filtered much more slowly than those extracted with alcohols of higher molecular weight. These characteristics of the waxes are summarized with their comparative yields in Table VI.

Determination of Constants. The wax materials were characterized as far as possible by the determination of dropping points, acid values, saponification values and ester values.

Dropping point. Because waxes tend to soften rather than give a sharp melting point, capillary melting points are of little interest. The melting range is too great to be of much significance and the limits of this range are difficult to observe accurately. Therefore in this work the dropping point method was used.

The dropping points were determined as follows: The bulb of a thermometer was dipped into the melted wax and then rotated while the adhering wax solidified in an even layer. The thermometer was then supported in a six inch test tube by means of a cork stopper so that the bottom of

TABLE V  
EXTRACTION SCHEDULE

EXTRACTION	SOLVENT	CHARGE	EXTRACTION TIME	EXTRACTATE COLOR
1st	CH <sub>3</sub> OH	crude wax	1 hour	yellow
2nd	C <sub>2</sub> H <sub>5</sub> OH	residue from 1st extr.	1 hour	dk. yellow
3rd	C <sub>3</sub> H <sub>7</sub> OH (iso)	residue from 2nd extr.	1 hour	brown
4th	C <sub>4</sub> H <sub>9</sub> OH (sec.)	residue from 3rd extr.	1 hour	brown-black

TABLE VI  
PRECIPITATED WAXES

EXTRACTING SOLVENT	NATURE OF PRECIPITATE	COLOR OF DRY FILTER CAKE	COLOR OF RE-MELTED WAX	AVE. % YIELD
CH <sub>3</sub> OH	Very gelati- nous, ex- tremely slow filtering	Light ivory	Light tan	22
C <sub>2</sub> H <sub>5</sub> OH	Gelatinous, slow filter- ing	Dark Ivory	Light brown	10
(iso-) C <sub>3</sub> H <sub>7</sub> OH	Flocculent, fairly rapid filtering	Light tan	Dark brown	19
(sec.) C <sub>4</sub> H <sub>9</sub> OH	Granular, rapid filter- ing	Brown	Brown-black	24
TOTAL AVERAGE AND YIELD . . . . .				75

the bulb was about three quarters of an inch from the bottom of the test tube. The assembly was then immersed in a dibutyl phthalate heating bath equipped with a thermometer and circular stirring rod. The bath was slowly heated with constant stirring such that the bath temperature was maintained about  $10^{\circ}\text{C}$  higher than that inside the test tube. The dropping point was taken as that temperature at which the drop became detached completely from the bulb.

With this type of melting point determination it was observed that, although an excess of wax did not seem to affect the dropping point, care had to be taken that sufficient wax was on the bulb to form a drop. This was insured if a film of wax remained on the bulb after the drop had formed. Carelessness in this respect would lead to abnormally high dropping points.

Acid values. Acid values were determined as follows: Approximately 0.5 g of wax, weighed to the nearest milligram, was dissolved in a small amount of warm benzene. When solution was complete sufficient warm benzene was added to give a total volume of 200 ml, and the mixture was allowed to cool to nearly room temperature. 10 drops of 0.1% phenolphthalein were added and the solution titrated with approximately 0.1 N KOH to the appearance of a pink color that did not fade in 30 seconds. A blank was run concurrently.

The acid value is defined as the number of milligrams

of KOH required to neutralize the free acid present in 1 g of the sample. It was calculated according to the formula:

$$N_A = - \frac{V \times 5.61}{\text{Wt. of sample}}$$

where  $N_A$  = acid value, and V is the volume of base corrected to 0.100 N.

Saponification value. The saponification value is that number of milligrams of KOH required to neutralize the total acid (both as free acid and that acid combined in the wax esters) in one gram of wax. The saponification values were determined according to the following procedure:

Approximately 0.5 g of wax was weighed to the nearest mg into a 250 ml Erlenmeyer flask. To this was added 90 ml of a suitable solvent, and the flask was then heated, by immersing in hot water, until solution of the wax was complete. The material was transferred to a 200 ml round bottom flask, with an additional 10 ml of solvent being used to rinse the Erlenmeyer flask. This rinse solution was also added to the round bottom flask making a total of 100 ml. 10 ml of approximately 0.5N KOH was added, and the mixture refluxed for two hours.

A blank was prepared containing all but the wax sample, and this also was refluxed for two hours.

The saponification values were calculated according to the following formula:

$$V_s = \frac{(V_b - v_w) \times 56.1}{\text{Weight of sample}}$$

where  $V_s$  = saponification value,  $v_b$  = volume of acid required to titrate blank, and  $v_w$  = volume of acid required to titrate wax sample. ( $v_b$  and  $v_w$  corrected to 1.0 N KOH).

The selection of solvent for the determination of saponification values posed a considerable problem, due to the different solubility characteristics of the wax samples. Standard procedures for determining saponification values involve only the use of the alcoholic KOH as the solvent. The samples under investigation here, however; are not soluble in alcohol, except those samples obtained by extraction with methyl and ethyl alcohols.

Although benzene is a good solvent for all the waxes under investigation, attempts to use benzene were not successful because of establishing a two-phase system during the titration. It was found that isopropyl alcohol was a satisfactory solvent for the waxes extracted with methyl and ethyl alcohols. For the wax extracted with isopropyl alcohol, sec-butyl alcohol was used as the solvent during the saponification, and for that extracted with sec-butyl alcohol the solvent was a mixture of 80% sec-butyl alcohol and 20% benzene.

Ester values. Since the acid value is determined as the number of milligrams of free acid per gram of sample, and the saponification value is determined as the number of milligrams of total acid (combined and uncombined) per gram of sample, the difference between these two values would be



the number of milligrams of acid that was combined in the ester linkage, per gram of sample. This difference, therefore, is the ester value of the sample, and may be stated simply as:

$$V_E = V_S - V_A$$

Table VII summarizes the above properties of the different wax samples.

Preparation of the Urea Adducts. Preliminary work indicated certain difficulties that would be encountered in the preparation of the urea adducts of wax constituents---difficulties that would prevent the complexing, or that would lead to a product severely contaminated with the reactants.

As was noted in the works referred to earlier, the urea solvent, or "activator" should be a polar solvent such as methyl alcohol, ethyl alcohol, or water. Any of these are considered excellent. However, since the wax samples have rather limited solubilities in these solvents, it was not possible to form the adducts by addition of the wax to the urea in its solvent for any except the methyl alcohol extract. The waxes extracted with the higher molecular weight solvents would not form adducts in this manner.

The possibility of forming the adducts by shaking saturated solutions of the wax and urea in their respective

TABLE VII  
PROPERTIES OF WAX EXTRACTS

WAX SAMPLE	DROP PT. °C	ACID VALUE	SAP. VALUE	ESTER VALUE
Crude	86	45	120	75
Methyl Alc. Extract	80	81	135	54
Ethyl Alc. Extract	84	67	94	27
Iso-propyl Alc. Extract	88	34	100	66
Sec-butyl Alc. Extract	91	21	105	84

solvents was also investigated. When these solutions were shaken together vigorously, a white, needle-like precipitate formed in large amount. Investigation soon showed, however, that this material was principally urea. Controls were then run in which methanol, saturated with urea, was mixed with two different wax solvents - toluene and 2, 2, 4-trimethylpentane, - solvents in which the wax solubility is good. In each case when the pure solvent was shaken with the urea-methanol solution there was a considerable precipitation of urea observed. It was therefore concluded that attempts to produce the adduct in this manner would not be successful due to the large amount of free urea that would contaminate the product.

Test experiments were then performed, using a wax solvent in which there would be a greater solubility of urea. N-butyl alcohol was selected as the wax solvent, and the following test performed:

0.5 g of methyl alcohol wax extract was dissolved by warming in 100 ml of n-butyl alcohol. When cooled to room temperature no precipitation of wax was observed. 20 ml of methyl alcohol was added, with no precipitation of wax observed.

The urea adduct of the methyl alcohol wax extract was then prepared as follows: 0.504 g of wax was dissolved in 100 ml of n-butyl alcohol, 20 ml of the saturated urea-

methyl alcohol solution was added, and the mixture heated to 40°C. The mixture was then allowed to cool to 30°C, with constant stirring, at which temperature a cloudiness appeared. At this point stirring was discontinued and a copious white precipitate slowly settled out of solution. The mixture was allowed to stand 24 hours before being filtered. The precipitate was crystalline-white in color, consisting of very fine needles.

Attempts to wash the crystalline precipitate with the pure solvents resulted in almost complete decomposition of the adduct. Therefore all melting points reported here are on the crude, unwashed precipitate. The m. p. (capillary method) of the adduct was 139°-141°, indicating a new substance rather than a mixture. Decomposition of the material was observed at the m. p.

The yield of adduct was 1.278 g, which, upon decomposition, yielded 0.296 g of wax, or approximately 59% yield. The wax was a light olive green in color. The recovered wax, in addition to being altered in color, had changed solubility characteristics. The methanol extract was completely soluble in hot isopropyl alcohol, but the wax recovered from the adduct had only limited solubility in this reagent.

The adduct of the ethyl alcohol extract was prepared using the same proportions, but starting with 2.000 g of

wax. The yield was 6.106 g of a cream colored precipitate, m. p.  $137^{\circ}$  -  $144^{\circ}\text{C}$ . The weight of the recovered wax was 1.525 g, or 76% of wax adducted.

It was found that the decreased solubility of the iso-propyl alcohol extract prevented the formation of the adduct by the method used for the methyl and ethyl alcohol extracts. When the wax solvent was modified by the addition of 100 ml of benzene, however, the 2 g of wax dissolved completely, and remained in solution when cooled to room temperature.

80 ml of saturated urea-methanol solution was added, and the solution allowed to cool with constant stirring. The stirring was discontinued when the mixture had reached room temperature, and the precipitate allowed to settle out. The precipitate formed two layers, the bottom, more dense precipitate was found to be unreacted wax, while the upper layer, which was silky in appearance, had a melting point of  $138^{\circ}$  -  $141^{\circ}\text{C}$ , indicating it to be the adduct. The weight of wax recovered from the decomposed adduct was 0.249 g, or 12.5% of the original sample.

All attempts to adduct the sec-butyl alcohol extract ended with simple mixtures of urea and wax. If any adduct was produced, it was lost in the large amounts of pure reactants that precipitated out.

Decomposition of the Urea Adducts. The adducts were decomposed by vigorous shaking in 100 ml of cold water.

The urea went into solution, leaving the insoluble wax behind. The wax was separated by gravity filtration, and was air dried.

Where sufficient wax was recovered, dropping points, acid values, saponification values and ester values were determined. These are summarized in Table VIII.

TABLE VIII  
PROPERTIES OF WAX RECOVERED FROM UREA ADDUCTS

ADDUCTED WAX	DROP PT. °C	ACID VALUE	SAP. VALUE	ESTER VALUE
Methyl Alc. Extract	94	83	110	27
Ethyl Alc. Extract	89	57	97	40
*Iso-propyl Alc. Extract	—	29	76	47
*Sec-butyl Alc. Extract	—	—	—	—

\*Not sufficient wax recovered to determine values where blanks occur.

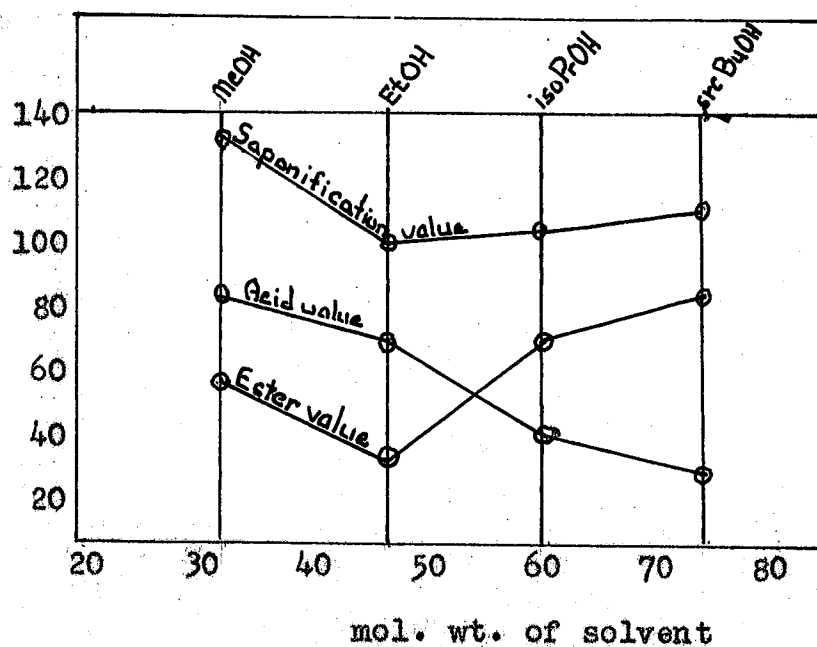


Figure 1. Acid, ester, and saponification values of the extracts of montan wax.

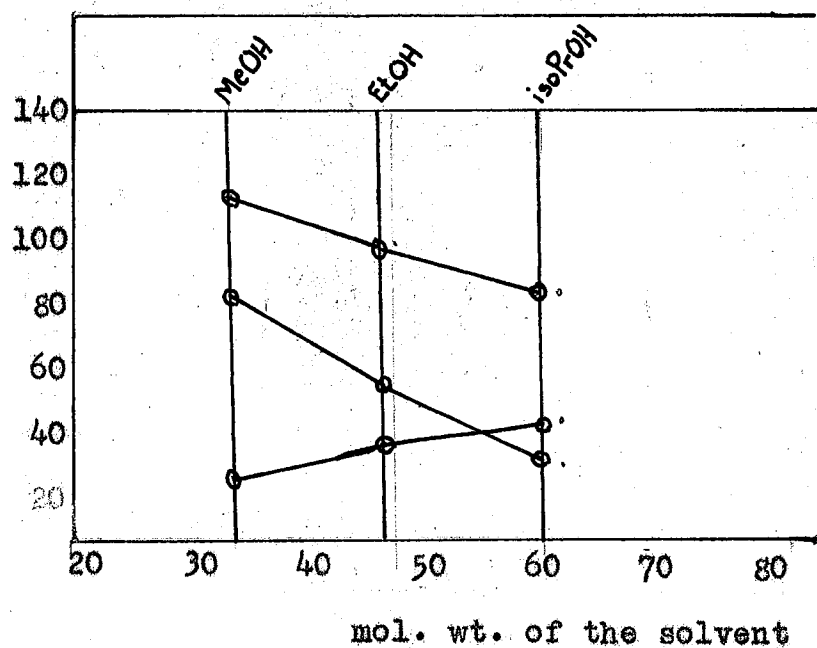


Figure 2. Acid, ester, and saponification values of waxes recovered from the urea adducts.



## DISCUSSION OF RESULTS

Attempts to form the adducts directly from the crude wax were unsuccessful due to the insoluble components present. Any adduct that was formed was hopelessly lost in this material.

This difficulty was overcome by the method of successive selective extraction reported here. With this preliminary treatment the wax constituents were divided into groups with similar solubility characteristics. It was, therefore, possible to treat each extract according to its own, fairly uniform, solubility characteristics, with no interference from those substances which had been removed through this treatment.

Through this approach it was possible to adduct the constituents and then recover from the adduct the wax in 23.3% yield. (Based on weight of crude wax required.)

A comparison of the properties of the wax extracts with the wax recovered from the corresponding adducts is shown in Figures 1 and 2. It is seen by comparing these figures that a selection possibly occurred when the extracts formed the adducts.

The amount of free acid present in the extracts decreased with each successive extraction, as indicated by the change of acid value from a high of 81 for the methyl alcohol extract to a low of 21 with the sec-butyl alcohol

extract. No such regularity is seen in the data for either saponification values or ester values of the wax extracts.

Figure 2, however, shows a linear decrease in both acid values and saponification values, and a linear increase in ester values.

The maximum chain lengths for the recovered acids consistent with the observed properties may be calculated. This calculation, which will be developed below, is based upon the assumption that the only substances separated by the methods described in this work are esters and monobasic acids. This assumption ignores, of course, the rather obvious fact that free alcohols are quite probably also present. These results are, therefore, not meant to be exact values.

The following calculation is for the methanol extract. The results of similar calculations based upon the other waxes studied here are summarized in Table IX.

Calculations for Methanol Extract:

$$V_A = 81$$

Assuming the acids to be monobasic, the number of equivalents of KOH equals the number of moles of acid.

$$n_A = \frac{V_A \times 10^{-3}}{\text{Eq. wt. of KOH}}, \text{ where } n \text{ equals the number of moles of acid per gram.}$$

$$n_A = \frac{1081}{56.1} = 1.44 \times 10^{-3} \text{ moles of acid/gram of wax.}$$

$$V_E = 54$$

$$n_E = \frac{.054}{56.1} = .96 \times 10^{-3} \text{ moles of ester/gram of wax.}$$

Assuming the chain lengths of the acid and alcohol portions of the ester to be equal and the same as for the free acid,

if  $x$  = mol. wt. of the acid,

then  $2x - 32$  = mol. wt. of the ester.

$$(1.44 \times 10^{-3})x + (.96 \times 10^{-3})(2x - 32) = 1.00 \text{ g.}$$

solving the above, we find:

$$x = 305 = \text{mol. wt. of the acid.}$$

if  $n$  = no. of C atoms in the acid, then:

$$12(n) + 1(2n) + 32 = 305$$

$$\text{or } n = 20 = \text{length of chain in the acid.}$$

TABLE IX  
MAXIMUM AVERAGE CHAIN LENGTH OF ACID CONSTITUENTS  
OF MONTAN WAX

EXTRACTING SOLVENT	ACIDS FROM EXTRACTS	ACIDS FROM RECOVERED WAXES
Methanol	20	27
Ethanol	30	27
Iso-propanol	22	31
Sec-butanol	17	—

The value obtained for the ethanol extract appears out of line. The general increase obtained for the recovered adducts indicates the possibility of some low molecular weight branched chain acids being present in the extract. These would not adduct; therefore the average chain length of the recovered acids would show an increase.

## SUMMARY

A successful method for preparing the adducts of some of the constituents of montan wax has been developed. This method utilized successive extractions of the crude wax with the following solvents: methanol, ethanol, isopropanol, and sec.-butanol. Adducts were obtained from each of the extracts except that of the sec.-butanol. The yield of wax recovered from the decomposed adducts was 23%, based upon the weight of the crude wax required.

The dropping points, acid values, saponification values, and ester values of the waxes were obtained. From this information the maximum average chain length of the acid constituents was calculated. No attempt was made to identify any of the constituents.

**LITERATURE CITED**

## LITERATURE CITED

- Davankov, A., and O. A. Konovalova, Organic Chemical Industry (U.S.S.R.), 4: 276-9, 1937
- Donath, Ed., and Brun, Brennstoff Chemie, I: 86-7, 1920
- Fischer, F., and W. Schneider, Gesellschaft Abhandlungen zur Kenntnis der Kohle, I: 204-10, 1917
- Hell, C. Z., and Boyen, Zeitschrift Angewandte Chemie, 13: I, 556, 1919
- Kvick, Robert J., "Montan Wax From California Lignites", Unpublished Thesis, College of the Pacific, 1952
- Marcusson, J., and H. Smelkus, Journal of the Society of the Chemical Industry, 36: 540, 1917
- Meyerheim, G., Seifenfabr, 39: 365-7, 394-6
- Ralston, A. W., Fatty Acids and Their Derivatives, John Wiley and Sons, Incorporated, New York, 1948
- Redlich, O., C. M. Gable, A. K. Dunlop, and R. W. Millar, Journal of the American Chemical Society, 72: 4153, 1950
- Ryan, Hugh, and Dilton, Thomas, Proceedings Dublin Society, 12: 202-9, 1909
- Schneider, W., and H. Tropsch, Gesellschaft Abhandlungen zur Kenntnis der Kohle, II, 57-64, 1917
- von Boyen, E., Zeitschrift Angewandte Chemie, 14, 1110-1, 1901
- Warth, Albin H., The Chemistry and Technology of Waxes, Reinhold Publishing Corporation, New York, 1947