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Review:

Natural montan wax and its raffinates

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Natural montan wax and its raffinates*

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Natural waxes have been used by mankind since prehistoric times. Many uses of wax are based on the imitation of its natural functions. Waxes in nature primarily serve to provide protective barriers on the surfaces of living organisms. Their functions are also determined by wax characteristics such as adhesion and cohesion, as well as slip and deformation effects. In ancient times, for example, wax seals were used to help preserve food and beverages. Beeswax has remained an important material for manufacturing candles up to the present day. Recent vegetable waxes have been used in industry since the mid-nineteenth century, for example in care products. Refined and chemically processed montan-based waxes are quite similar to naturally occurring vegetable ester waxes in their structure and application characteristics. They are similar in their environmental characteristics and are also nontoxic. Crude montan wax itself belongs to the naturally occurring waxes of vegetable origin such as candelilla wax and carnauba wax.

Keywords: Montan wax, carnauba wax, application, analysis, refining.

1 Introduction

Waxes are usually relatively stable nontoxic substances, which mankind has used for a variety of purposes since prehistoric times. The English term wax is derived from the Anglo-Saxon *weax*, which was the name applied to the natural material gleaned from the honeycomb of the bee. When a similar substance was found in plants it also became known as *weax* or *wachs*, and later *wax*. In modern times the term has taken on a broader significance and is generally applied to all wax-like solids and liquids found in nature, and to those that occur individually in waxes, such as the hydrocarbons, acids, alcohols and esters, irrespective of their source or method of preparation, provided such constituents are wax-like in their properties. Certain synthetic compounds which are not waxes from the standpoint of chemical composition, but do have waxy physical characteristics, are included because of their value in technical use as wax substitutes.

The Egyptians in 4200 B.C. found numerous and distinct uses for beeswax. For example they used it to preserve mummies and they are also known to have made square wax writing tablets that could be rubbed down and reused [1]. Wax seals were also used to help preserve food and beverages. Since ancient times beeswax has remained an important material for manufacturing candles up to the present day [2]. The use of waxes for skin care, e. g., is known from the ancient Egyptians and Romans. Waxes generally have a protective function against environmen-

tal influences. Many plants, especially those in tropical or subtropical climates and those subject to long dry spells, form thick layers of wax to protect against excessive water loss and UV radiation. Waxes are also highly resistant to biodegradation. They are practically indigestible when orally ingested by humans or animals and therefore are not metabolized. Many uses of wax are based on the imitation of its natural functions. Waxes in nature primarily serve to provide protective barriers or promote such effects on the surfaces of living organisms. Their functions are also determined by wax characteristics such as adhesion and cohesion, as well as slip and deformation effects. Even insects have wax on their body surfaces. They use it to protect themselves against desiccation, injury and penetration of microorganisms, but also as a lubricant to facilitate the rapid motions of their limbs.

Recent vegetable waxes have been used in industry since the mid-nineteenth century, for example in care products. Partially synthetic hard waxes based on montan wax are quite similar to naturally occurring vegetable ester waxes in their structure and application characteristics. They are similar in their environmental characteristics and are also nontoxic [3]. Crude montan wax itself also belongs to the naturally occurring waxes of vegetable origin such as carnauba wax and candelilla wax. Montan wax is a fossilized vegetable wax extracted from lignites, principally from the central German brown coal reserves west of the Elbe river. Montan waxes of minor quality and quantity have also been mined in Australia, New Zealand,

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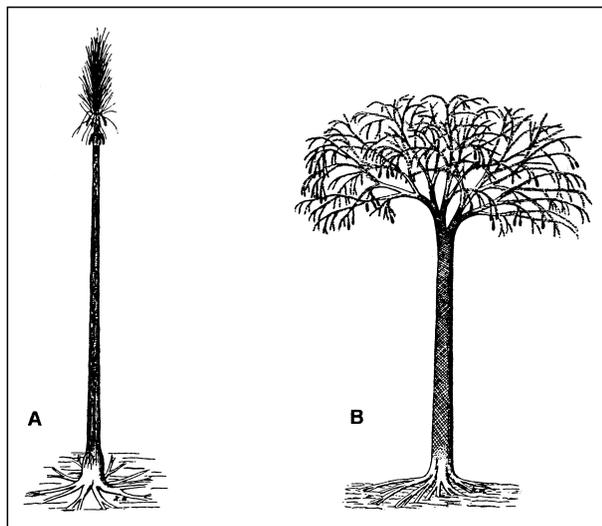


Fig. 1. Coalification of wax coated plant material in pre-historic times created deposits of montan wax. **A** *Sigillaria*, **B** *Lepidodendron*.

Czechoslovakia, Russia, Great Britain, China and the United States. Based on the remains of portions of plants found in the central German seams, researchers have concluded that the typical forests 30 to 40 million years ago included swamp cypresses, *Sigillaria* and *Lepidodendron* trees (Fig. 1), and other conifers. This is thought to be the origin of the wax-containing coal. Prehistoric palm trees as well as laurel, camphor, and cinnamon trees are indicative of subtropical flora [4]. Over the course of the earth's history, specific geological conditions have resulted in the formation of brown coal reserves in which the non-decomposed waxes of the earth's early vegetation have accumulated over millions of years.

However, in contrast to recent natural waxes, montan wax is of fossil origin like petroleum paraffin. Montan wax differs from recent vegetable waxes in that it is polygenetic, which is attributable to the wax-forming flora of a large number of successive vegetation periods. The yield of recent waxes cannot be increased indefinitely, for example because the wax-producing plants are not suitable for cultivation [5]. These waxes are subject to price fluctuations in years with poor harvests.

E. Riebeck [6] in 1880 was the first to extract pyropissite, a brown coal with a very high bitumen content, with solvents and to isolate a dark, hard, wax-like substance. Since the industry of the time was dependant on imported wax for such products as cleansers, attempts were soon made to substitute the imports with inexpensive domestic products. The initial result of these efforts was a fundamental patent, granted in 1897 [7]. The first montan wax factory began production in Völpke, Germany, as early as 1900.

2 Composition

Montan wax is a mixture of chemical compounds that can be divided into three substance groups: waxes, resins and asphaltic substances.

Like existing vegetable hard waxes such as carnauba wax, the pure wax substance in montan wax mainly consists of esters of long-chain acids with long-chain alcohols and free long-chain acids. Other components such as free wax alcohols or ketones, paraffins or terpenes are usually present only in small quantities (Tab. 1). There are usually an even number of carbon atoms in the long-chain wax acids and alcohols, although the respective chain lengths between them can contain uneven numbers of carbon atoms.

Tab. 1. Example of typical composition of crude montan wax [4].

Component	Approx. [%]	Component	Approx. [%]
Wax esters	50–60	Resin acids	10–15
Wax acids	20–25	Resin alcohols	1.5
Wax alcohols	1–1.5	Polyterpenes	3.5
Wax ketones	1–1.5	Volatile terpenes	0.1
Hydroxy wax acids	1.0	Ash	0.5
Paraffins	1.0		
Short-chain fatty acids	0.1		

3 Analysis

3.1 Standard procedures for specifying montan waxes

Tab. 2 summarizes the familiar standard procedures for classifying montan waxes. It gives a brief overview of the composition of these waxes, as for instance the contents of wax acids and esters as well as the physical behavior (for example dropping point, hardness, viscosity). Of prime importance in determining the quality of crude montan wax are the parameters acetone soluble amounts ("resin content") and isopropanol insolubles ("asphalt content"). The isopropanol insolubles indicate the amount of difficultly refinable parts of the wax. Samples with a content of over 8% are very difficult to refine or the resulting products are unusable. However, modern instrumental analyses are becoming increasingly important in quality control of waxes. Gas chromatographic (GC) analyses, infrared spectrometry and element screening tests are particularly important for sensitive applications such as food-contact products [8].

Tab. 2. Standard procedures for specifying montan waxes.

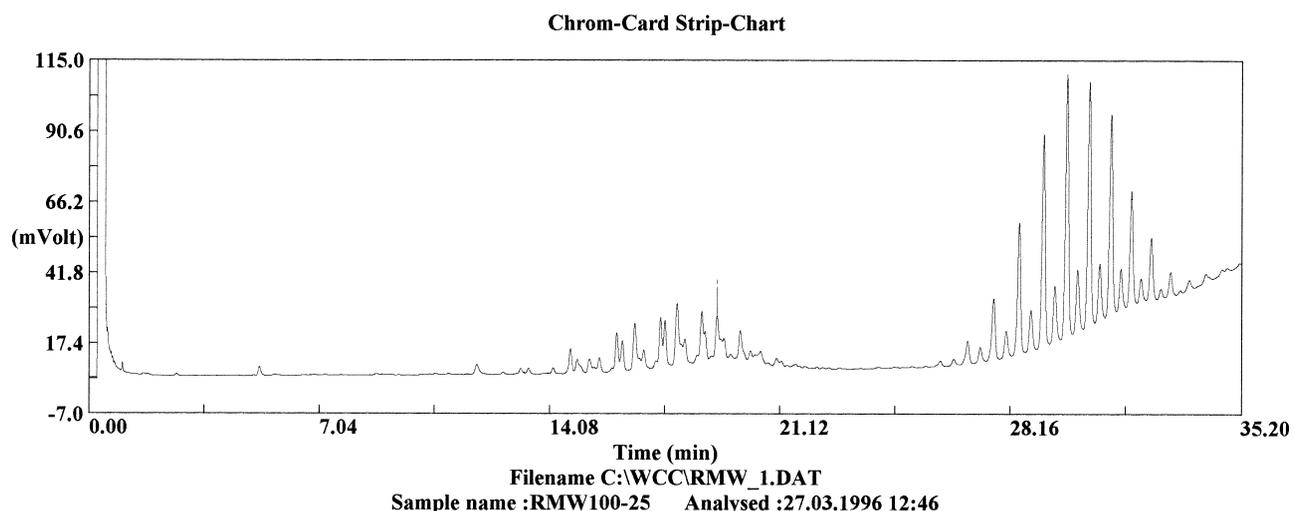
Analysis	Unit	Methods		
		DGF	DIN	ASTM
Acetone soluble amounts	[%]	M-VI 1	–	–
2-Propanol insoluble amounts	[%]	AA-QS-W-01.02 (VMW method)	–	–
Acid number	[mg KOH/g]	M-IV 2	53402	D-1386
Saponification number	[mg KOH/g]	M-IV 2	53401	D-1387
Dropping point (Ubbelohde)	[°C]	M-III 3	51801	D-3954-80 (<i>Mettler</i>)
Congealing point (rotating thermometer)	[°C]	M-III 4a	ISO 2207	D-938
Melt viscosity at 120 °C	[mPa s; mm ² /s]	M-III 8	51562	D-2126
Penetrometer value at 23 °C	[dmm]	M-III 9b	51579	D-1321
Höppler hardness at 23 °C	[bar]	M-III 9a	–	–
Density at 23 °C	[g/cm]	M-III 2a/b	53479	D-792

3.2 Gas Chromatography

Testing to verify the identity and purity of montan wax and its derivatives is of great interest. Therefore, GC studies of waxes have repeatedly been published during the last few years. As a result, the fingerprints with the individual peaks of the most important commercially available waxes are now familiar [9]. Modern temperature-resistant capillary columns for high-temperature analysis now permit much better resolution (Figs. 2–4) [10]. The fingerprints obtained by this method (Tab. 3) permit better identification of montan wax samples of varying quality or origin. The second group of GC signals representing substances of longer retention on the GC column like long-chain esters or diester is specially suited for comparison. Moreover it is possible to distinguish carnauba wax or even mixtures by comparison of GC patterns and/or co-chromatograms.

Tab. 3. GC conditions.

Unit:	<i>Fisons Instruments</i> GC 8160	
Column:	<i>Chrompack</i> WCOT ULTI-METAL 10 M x 0.53 mm Coating HT SIMDIST CB DF = 0.17 µm	
Detector:	FID 440 °C	
Injector:	Cool on column	
Carrier:	Nitrogen (10 kPa or 1.45 psi)	
Solvent:	Toluene	
Concentration:	(0.3 g/100 ml)	
Injected quantity:	1 µl	
Temperature program:	Isotemp #1	90 °C
	Isotime #1	2 min
	Rate	10 °C/min
	Isotemp. #2	440 °C
	Isotime #2	60 min

**Fig. 2.** High-temperature GC of crude montan wax.

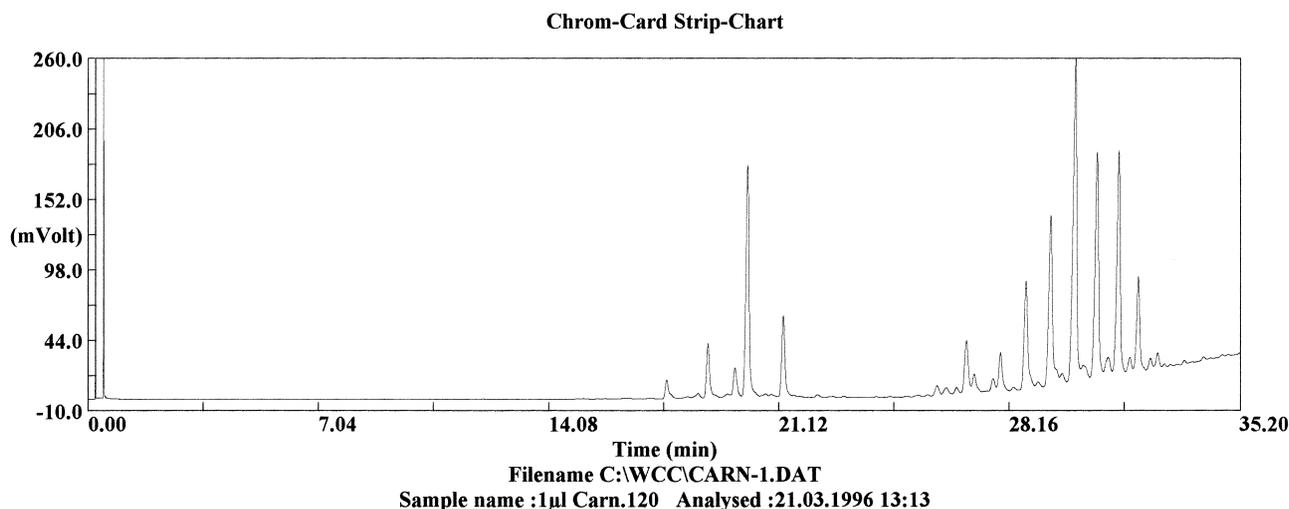


Fig. 3. High-temperature GC of carnauba wax.

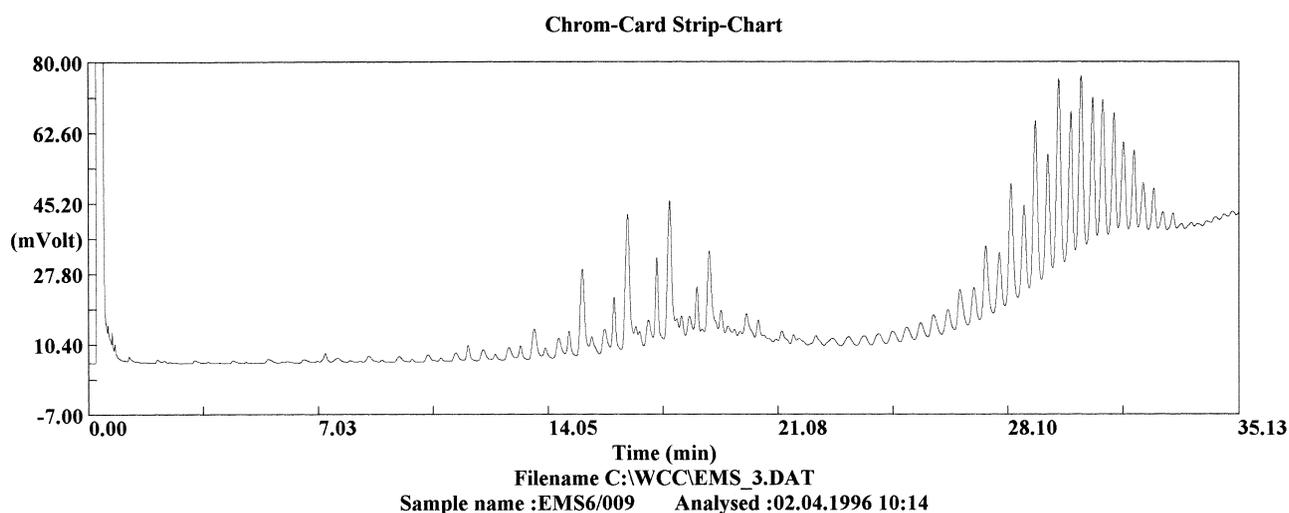


Fig. 4. High-temperature GC of refined and modified montan wax (type EMS).

3.3 Infrared spectrometry

In comparison with gas chromatography the information supplied by infrared spectrometry is relatively small. However, the identity of some waxes' type can be made with definite certainty in the so-called "fingerprint" area (ca. 400–1600 cm^{-1}). Substances that show conformity are with high probability, identical. As shown in the spectra (Figs. 5–8), ester waxes give very similar patterns. However it is possible to identify carnauba wax (Fig. 7) *via* the absorbances at 1600 cm^{-1} and 1515 cm^{-1} .

However no information was available to us so far what at least causes these characteristic signals. In all spectra shown in Figs. 5–8 C=O groups of non-esterified acids are represented by absorbances at ca. 1700 cm^{-1} , whereas C=O groups of esters give absorbances at 1740 cm^{-1} .

3.4 Determination of elements by X-ray fluorescence

Energy-dispersive X-ray fluorescence (EDXRF) is a non-destructive analytical technique for the determination of chemical elements in solid, powder and liquid samples. Advantages of EDXRF include simple sample preparation, high reliability and excellent reproducibility of analytical results. The physical basis of the process is the use of X-rays to excite the elements in the sample, causing them to emit characteristic X-ray fluorescence. The energy and intensity of the emitted radiation allow *simultaneous* determination of a wide variety of elements contained in the sample in the ppm range. XRF analysis provides high information content and is therefore a suitable alternative to absorption spectrometry, particularly where nondestructive measuring is required (for example in small samples). Measurements were taken of test samples of crude mon-

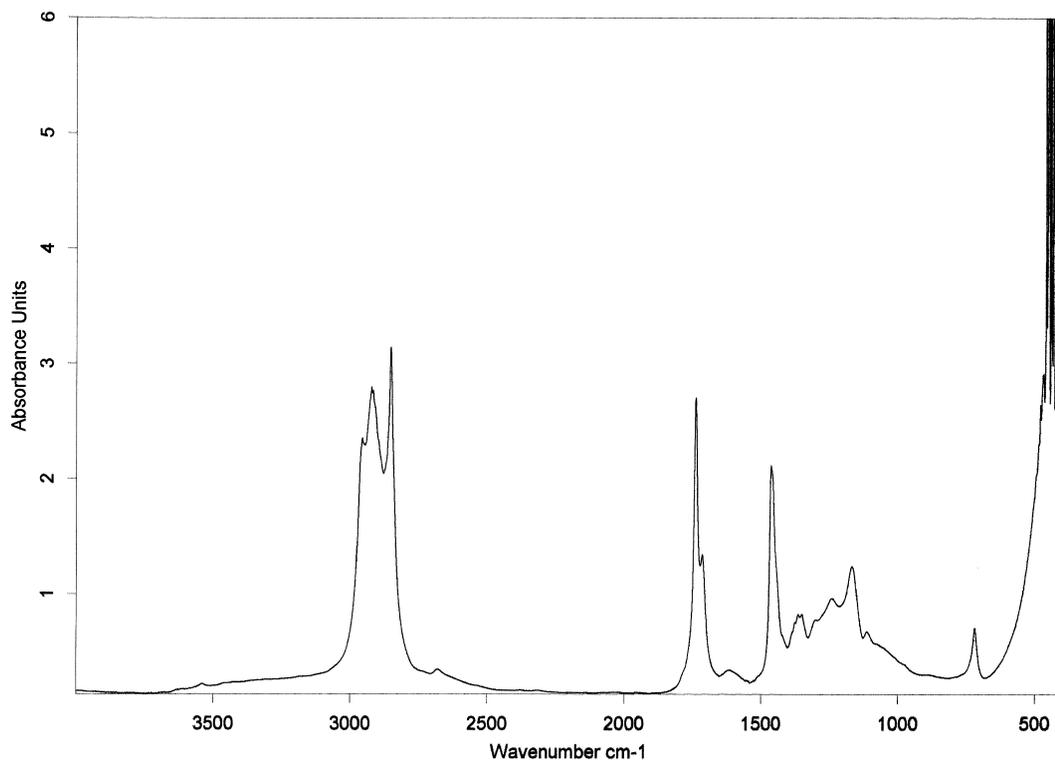


Fig. 5. FT-IR spectrum of crude montan wax .

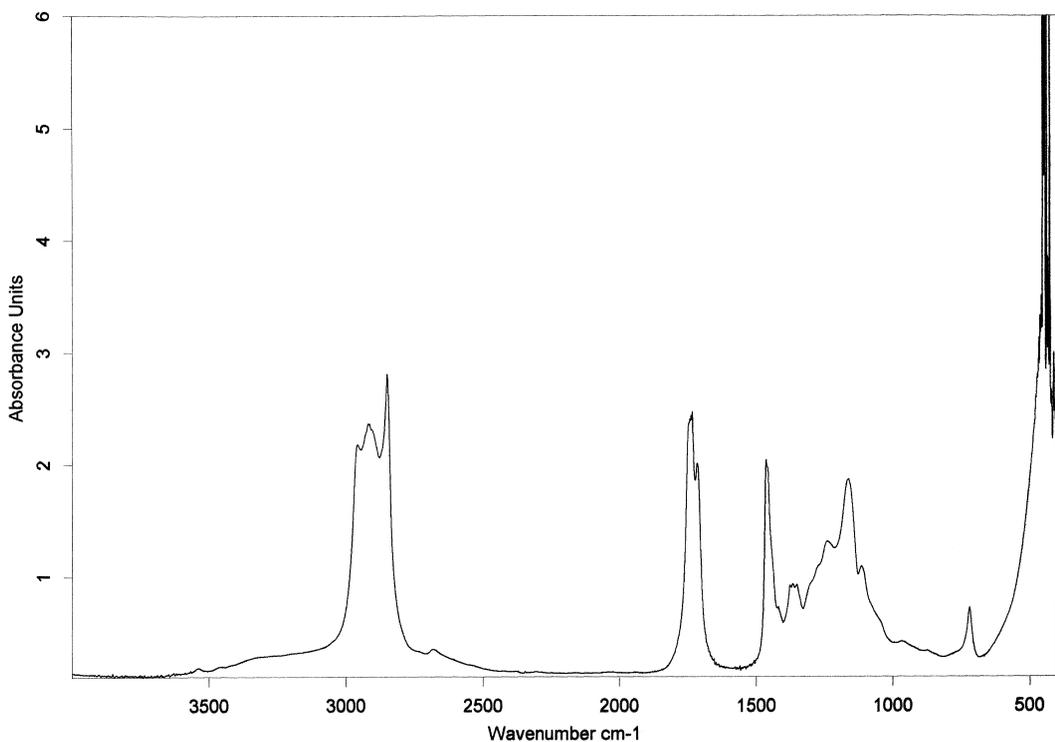


Fig. 6. FT-IR spectrum of refined and modified montan wax (type EMS).

tan wax, S wax, and E wax. The results (Fig. 9) show that refining (type S wax) and, respectively, derivatization and additional cleaning (type E wax) predictably leads to de-

creasing concentrations of almost every element studied, i.e. to increasing purity of the waxes. XRF studies of candelilla wax has been described elsewhere [5].

4 Application

After the resin is extracted, the crude montan wax is refined by saponification and oxidation to yield a light yellow raffinate consisting primarily of long-chain wax acids with chain lengths of 22–34 carbon atoms (Fig. 10). Products such as partially synthetic montan wax derivatives that

are extremely hard with a light color and excellent polishing characteristics are manufactured from this raffinate by esterification.

The range of applications for the various montan wax derivatives is extremely broad: Because they are non-toxic, bleached montan wax derivatives have been

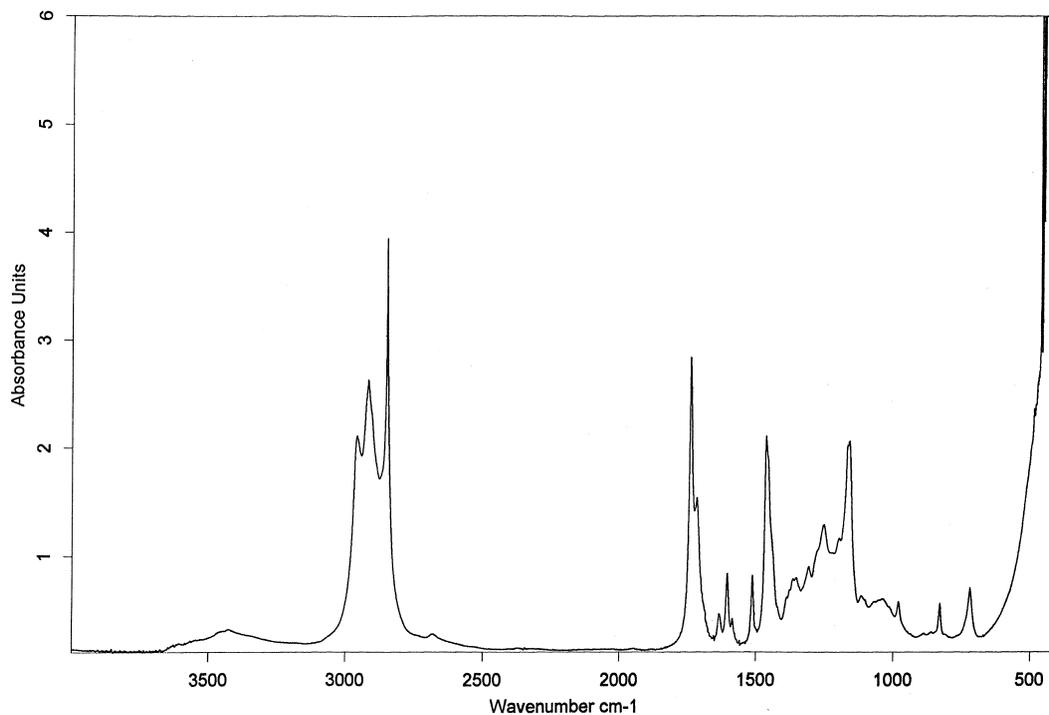


Fig. 7. FT-IR spectrum of carnauba wax.

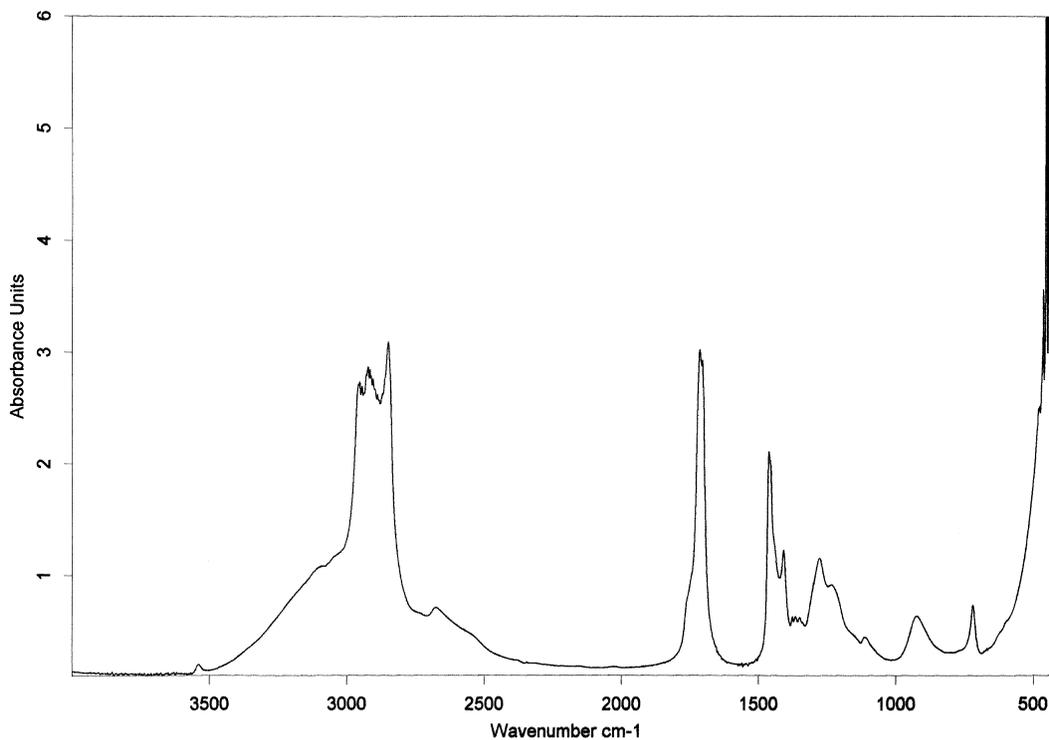


Fig. 8. FT-IR spectrum of refined montan wax (type S).

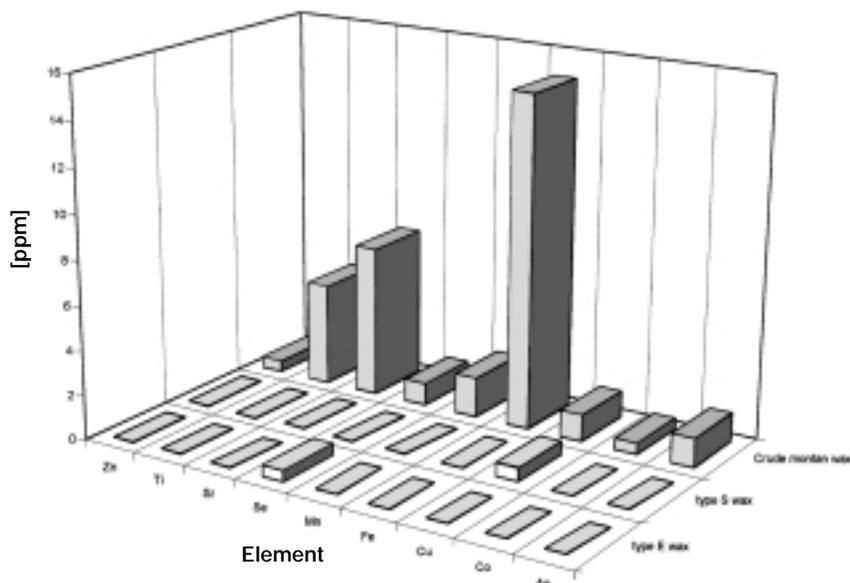


Fig. 9. XRF analyses of crude montan wax, raffinates (type S wax), and derivatives (type E wax).

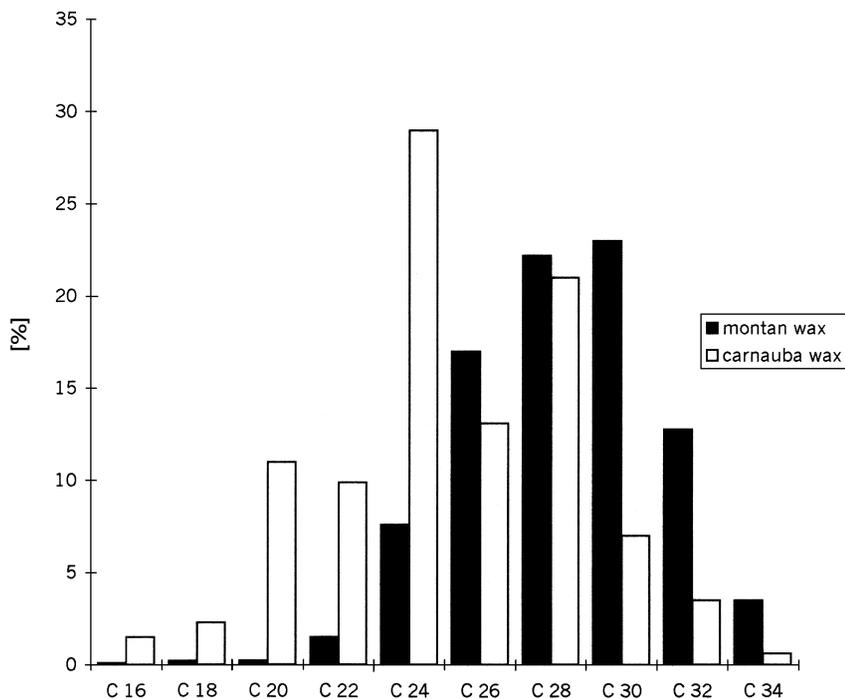


Fig. 10. Typical composition of fatty acids in montan wax and carnauba wax.

approved by the German *Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin* (BgVV), the United States Food and Drug Administration (FDA) and the health authorities of the major European industrial countries for almost all technical applications. Specially cleaned ester waxes (*cera montanglycoli*) meet the specifications of the *Deutsche Arzneibuch* (DAB) and are used in the pharmaceutical industries as coating agents.

Montan wax emulsions (type LG wax) are also used in temporary anti graffiti coatings (Tab.4) [11]. Annually,

Graffiti is a damage factor which costs multimillions domestically [12].

Among the various preventive methods is an application of coating products on the exposed surfaces. For example, these can be protected against the penetration of color sprays by being initially treated by wax emulsions (*L. Matthies, Untersuchungen zur Wasserfestigkeit von Wachsemulsionen für temporäre Anti-Graffiti-Beschichtungen, unpublished*)

The removal of said wax coatings is done very simply with steam under high pressure. Simple cleaning machines

Tab. 4. Anti-Graffiti Emulsion (type AG160699-8). Manufacture: Melt waxes and emulsifier at max. 110 °C. While stirring add hot water and bring to a short boil; then add cold water and cool rapidly to 40 °C. The solid material content can be varied; the consistency can also be adjusted with thickening agents [11, modified].

Component	Supplier	Amount [g]
LG-wax	Voelpker Montanwachs GmbH, Voelpke	4.2
Paraffine 52/54	TotalFinaElf	2.7
Emulan OC (APEO free)	BASFAG, Ludwigshafen	1.2
Water, hot		15.0
Water, cold		76.9

can be used. The fundamental requirements for a most effective and at the same gentle pretreatment of surfaces of buildings in order to protect them against colored spraying are compiled in the WTA-Recommendation "Protective Systems with respect to Graffiti Soiling". This document is meant to be used by architects, planning engineers and craftsmen. In relation with the most frequently used building materials the different possibilities of protection of buildings and their handling are outlined. Permanent, semipermanent and temporary protective systems are to be distinguished. Mechanisms of different protective systems are explained. Test methods are suggested in order to assess the functioning, the resistance against weathering and the influence of a protective treatment on the physical building behavior of materials [13].

A number of ester waxes are used as lubricants in the plastics industry [14, 15, 16]. Ester wax in powder form is excellent for processing rigid and plasticized PVC mixtures in calendar, extruder and injection molding machines. Even addition of slight quantities improves both the internal and external lubrication effect. OP-wax is also a PVC lubricant with internal and external properties, although the external lubrication effect predominates. It is

excellent for processing rigid PVC in calendaring, extrusion, injection-molding and blow-molding processes.

OP-wax is extremely hard, imparts an excellent gloss and binds well with solvents such as white spirit, turpentine oil and according to new findings [17] also orange terpenes (d-limonene). The wax still forms perfectly bound pastes when mixed with these solvents at a weight ratio of one part wax to twenty parts solvent. For this reason it is a popular ingredient in classic solvent pastes (Tab. 5) such as floor wax, shoe polishes, furniture care products, etc.

Tab. 5. Solvent paste with OP Montan Wax (Lab scale). Manufacture: The individual components are melted together in the order shown at 110 °C. Then 46 ml of white spirit or orange terpene are carefully stirred into the mixture, which is then allowed to cool to approximately 60 °C. Then the mixture is poured into cans at approximately 48 °C and allowed to harden.

Component	Supplier	Amount [g]
OP-wax	Voelpker Montanwachs GmbH	3.0
Ozokerite	Th.C. Tromm GmbH, Cologne	1.0
Paraffine 52/54	TotalFinaElf	9.0

Montan wax esters are typically easy to emulsify. The self-polishing films adhere very well to floors or other surfaces. They resist soil and are particularly resistant to mechanical loads. Traffic marks are easily removed by polishing. These waxes are compatible with other waxes such as microcrystalline waxes, paraffins or emulsifiable polyethylene waxes. Various ester waxes were specially developed for manufacturing dry-bright floor polishes and wax cleaners for both household and industrial use.

Emulsifiers developed especially for waxes and wax compounds are best for nonionic, self-polishing emulsions. These include such products as Emulan OC (BASF); Mulsifan (Zschimmer & Schwarz); wax emulsifier 4106 (Clariant). It is advisable to experiment to find out which emulsifier is best suited for each application in order to

Tab. 6. General recipe for cold-process car polish with ELE Montan Wax (Lab scale). Manufacture: Add water to container. Mix Carbopol thoroughly with diatomaceous earth and stir into water. When this mixture is homogenous, slowly add the silicon components and then the wax emulsion. The acrylate polymerizes and thickens only when the basic amino siloxane is added. The wax emulsion is produced beforehand by emulsifying solid flakes.

Component	Supplier	Amount [g]
Water		45.4
Thickener (acrylate polymer)	BF Goodrich, Brussels	0.2
Diatomaceous earth	Lehmann & Voss, Hamburg	5.0
40% Amino siloxane emulsion	Th. Goldschmidt AG, Essen	7.6
35% Silicon oil emulsion	Th. Goldschmidt, Essen	8.6
ELE wax emulsion (12%, APEO-free)	Voelpker Montanwachs GmbH, Voelpke	33.2

obtain optimum emulsion characteristics such as dry-bright finish, wetting, hardness and water resistance of the dry film, etc.

According to *Stache* [18], alkylphenoethoxylates (APEOs) have for some time been considered undesirable as emulsifiers. Investigations in Switzerland have shown that, upon biological breakdown, short-lived products are formed that are even more poisonous to fish than APEOs itself. Not all experts are convinced as to the validity of these tests. However, in Germany several producer groups have decided not to use emulsifiers containing APEOs. Emulsifiers in use now are mostly mixtures of fatty alcohol ethoxylates. An interesting new ecological concept for the future seems to be the use of alkylpolyglycosides (APG) [17].

The emulsions are manufactured by melting wax and emulsifier together and adding boiling water while continuously stirring the mixture. The mixture is brought to a boil and then quickly cooled to 40 °C.

Emulsification of solid flakes is the most widely used emulsifying process. The wax flakes are slowly strewn into the boiling water (Tab. 6). The temperature should not drop below 92 °C while the flakes are added. Rapid stirring is not necessary; slowly stirring the developing emulsion with an agitator blade or similar tool will be sufficient. The emulsion is brought to a boil for one to two minutes and then quickly cooled to room temperature. It is not advisable to disperse the wax flakes into cold water and then heat it to a boil. Emulsification of solid flakes is not a suitable process if the emulsion is to include other waxes such as microcrystalline waxes or paraffins. In such cases, all the waxes should first be melted together. The two processes described below may be used in that case.

In the water-in-wax process, the molten wax is heated to 100–110 °C while the emulsion is stirred continuously. The boiling water is added slowly at first, then more quickly. The mixture is then brought to a boil for one to two minutes. Prolonged boiling should be avoided as this can reduce the gloss of the dry film. Then the emulsion is rapidly cooled to room temperature. It should be slowly stirred while cooling.

In the wax-in-water process, the molten wax is heated 100–110 °C and added to the boiling water while the emulsion is stirred moderately quickly. The emulsion is briefly brought to a boil and then quickly cooled to room temperature.

Nonionic emulsions of montan wax esters can usually be produced with water of up to medium hardness as the nonionic emulsifiers are largely unaffected by hardening elements in the water. Tap water with a hardness of ap-

proximately 3.6 mmol/l of calcium ions (corresponding to 25 ° Clark) may be used. Extremely hard water should be softened prior to use.

Generally the final concentration of the wax emulsions will be between 10% and 15% of the total content of solid components. For subsequent mixing with other substances or to conserve storage space, concentrations with a wax content of up to 30% can be produced by rapidly bringing the emulsion to a boil and quickly adding cold tap water to achieve the desired final concentration (dilute emulsion). The higher the wax content, the more solid the consistency of the emulsion will be; any consistency from a liquid to a solid paste may be achieved.

Anionic emulsions can be created when wax acids and, in applicable cases, additional fatty acids (such as oleic acid) react with alkalis (such as amines or potash) to form the respective soaps. Particularly suitable amines include diethylethanolamine, 3-methoxypropylamine, amino-methylpropanol, and triethanolamine. However, finished or semifinished soaps (such as sodium stearate) may also be used. The soaps and saponification components such as amine or potash (K_2CO_3) are dissolved by warming them to approximately 75 °C in a portion of the water. This solution is then slowly poured into the molten wax (approximately 90–100 °C) and, in applicable cases, fatty acids while slowly stirring. While the mixture is stirred constantly, slowly at first and then progressively faster, boiling distilled water or softened water is then added (water-to-wax process). A wax-to-water process may also be used. Here, the major portion of the molten wax with added amines or alkali is slowly added to the boiling water while it is constantly stirred. A small portion of the amines or alkali is also added to the boiling water beforehand. In both cases, an oil-in-water emulsion is obtained. However, the water-to-wax process initially yields a water-in-oil emulsion which is only converted to the other type of emulsion by adding more water past what is known as the inversion point. Anionic self-polishing emulsions can be visually distinguished from nonionic emulsions by their greater transparency. They appear slightly brownish because the smaller particle size (<100 nm) results in greater light dispersion than reflection.

The hardening elements in the water combine with the fatty acids to form insoluble precipitates and in doing so can prevent the formation of amine soaps. Therefore, soft water should be used when manufacturing self-polishing emulsions, at least during the emulsifying process itself. An alternative is to use tap water that has been softened beforehand [19].

Additional applications include leather and car care products and applications in the plastics and paper industries, for example:

- Auxiliaries used in preparing leather to improve its grip, flexibility and gloss.
- Finishes for the shoe industry.
- Anti-blocking agents for PVDC and other polymer coatings (aroma-tight food packaging).
- Mold release agents for resin coatings (laminated boards for furniture).
- Slip agents for injection molding and for manufacturing foamed plastics such as polyurethane hot foam.
- Slip agents for hot-stamped foils.
- Corrosion protection.

The manufacturers' wax tables may also be consulted for the full range of applications [20].

The adhesiveness and ability of aqueous montan wax dispersions to form films are exploited in processes for temporarily binding dust on dumping grounds or when planting poor quality land subject to erosion. After the wax dispersion is applied to such surfaces, the water gradually evaporates. The montan wax then binds the thin uppermost layer of soil into a stable layer that protects against water and soil erosion and prevents the soil from drying out too quickly. The hydrophobic effect of montan wax dispersions is also exploited in a newly developed low-cost technique for drying out damp basements. To moisture-proof the basement, a spear-like rod is driven into the soil as deep as the bottom level of the foundation. A montan wax dispersion is forced through two lateral openings at up to 40 MPa. The high pressure causes it to slice through the soil along the walls and finally form a waterproof envelope approximately 10 cm (4 inches) thick. Similar processes are used to seal the sides and floors of sanitary landfills.

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