Montan wax: The state-of-the-art review

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ABSTRACT

Montan wax origins from ancient plant which leads a long and slow way towards becoming lignite thousands of years ago, their composition is very complex. Crude montan wax is obtained after organic solvent extraction from lignite, then deresined wax is acquired by cooling the extracted solvent toluene, last refined wax called S wax could be made after a series oxidation process, which can be used as basic raw materials for production of more valuable synthetic wax. Montan wax have a wide range of applications in industry, in agriculture, and in forestry. But there are still some problems, for instance, crude montan wax has dark colour, which restricted its application; plenty of by-product resin increase the production cost. Given the montan wax’s wide range application value and the crucial role in the national economy, we should strengthen the study of montan wax and find the way to comprehensive utilization. The author has systematically summarized the research progress of the montan wax and analyzed the deficiencies and problems in china, in order to speed up the montan wax research process.

Key words: montan wax; fundamental research; production; application progress.

INTRODUCTION

Montan wax is natural wax obtained from lignites, which contains pure wax (50-80%), resin (20-40%) and bitumen (10-20%). Due to its good physical and chemical properties, montan wax is often an ideal substitute for the expensive Carnauba Wax. It is widely used in daily chemical industry, wax polish industry, carbon paper industry, electrical industry, machinery industry and many other industries using wax. Germans were the first to extract montan wax from lignite in 1897. The United States, Ukraine, the Czech Republic have had established montan wax industry successively in 1905[1]. Wolfmeier et al.[2] have reported that the annual market demand for montan wax has reached 25,000 tons in 2005. But, montan wax industry starts relatively late and is characterized by weak foundation and backward research in china. The domestic heyday of the research on montan wax was during 1980s~1990s. Since the 20th century, very few people were involved in the research about montan wax and only a few reports were made about it.

Fundamental research of montan wax

Montan wax is brown-black solid, non-toxic, tasteless, high melting point. It has good gloss and chemical stability, can be dissolved in many kinds of organic solvent, and be easily saponification and emulsified. The main index to evaluate the quality of montan wax are melting point, acid value, easter value, saponification value.
Montan wax consist of three separated parts: long chain wax alcohols, long chain wax acids and wax esters formed by them, the carbon number of which is in the range of C_{26}-C_{30}. Baocai Li et al. used an anion exchange chromatogram column and a silica gel column to divide the de-resination montan wax and its oxidized wax into four parts: the free acid, ester acids, alcohols, hydrocarbons, and proved that the method had ideal performance of the separation by the infrared spectrum. Baocai Li et al. continued to use methods such as GC-MS to analyze the structure of montan wax produced in Xundian and Shulan, the results showed that the literature of the past which regarded montan wax made from n-alkanes, normal alkane alcohols, was not accurate. In fact, Montan waxes extracted from different lignite differ greatly in their constituents and content. For example, free acid contained in waxes produced in Xundian and Shulan, the results showed that the literature of the past which regarded montan wax contains a lot of substances not the normal monobasic alkane acid, while free acid contained in waxes produced in Xundian contains a lot of substances not the normal monobasic alkane acid, but some others. The alkane component is the minimum part in the montan wax, and the content of other three parts varies widely depending on different sources.

Some researchers were found that the aliphatic constituents of wax are C_{14}-C_{42} n-alkanes with high coefficients of oddness, C_{14}-C_{30} saturated alcohols, C_{14}-C_{50} higher fatty acids and ester. The contribution of unsaturated compounds was found. The structure and formation conditions of coal are considered. In 2008, L.P. Noskova analyzed the alkaline hydrolysis products of montan wax with chromatograph, IR and NMR, the study showed that the de-resination wax could be divided into four parts: hydrocarbons, alcohols, acids and unsaponifiable esters, which was in accord with Baocai Li trial papers in the 1990s.

### Table 1 Quality index table of the main domestic montan wax origin

<table>
<thead>
<tr>
<th>Origin</th>
<th>Sample</th>
<th>Melting point (°C)</th>
<th>Acid value (mg KOH/g)</th>
<th>Easter value (mg KOH/g)</th>
<th>Saponification value (mg KOH/g)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yunnan</td>
<td>Crude wax</td>
<td>83.2</td>
<td>48</td>
<td>32</td>
<td>80</td>
<td>Dark brown</td>
</tr>
<tr>
<td></td>
<td>Refined wax</td>
<td>85.1</td>
<td>49</td>
<td>49</td>
<td>98</td>
<td>Light brown</td>
</tr>
<tr>
<td>Yunnan Xundian</td>
<td>Deresined wax</td>
<td>83.4</td>
<td>47</td>
<td>49</td>
<td>96</td>
<td>Light brown</td>
</tr>
<tr>
<td></td>
<td>Refined wax</td>
<td>84.6</td>
<td>106</td>
<td>52</td>
<td>158</td>
<td>Light yellow</td>
</tr>
<tr>
<td>Yunnan Zhaotong</td>
<td>Deresined wax</td>
<td>84.2</td>
<td>43</td>
<td>52</td>
<td>95</td>
<td>Light brown</td>
</tr>
<tr>
<td></td>
<td>Refined wax</td>
<td>84.1</td>
<td>125</td>
<td>15</td>
<td>140</td>
<td>Creamy white</td>
</tr>
<tr>
<td>Heilong-jiang</td>
<td>Crude wax</td>
<td>80.5</td>
<td>31</td>
<td>35</td>
<td>65</td>
<td>Dark brown</td>
</tr>
<tr>
<td></td>
<td>Refined wax</td>
<td>81.5</td>
<td>31</td>
<td>37</td>
<td>68</td>
<td>Light brown</td>
</tr>
<tr>
<td>Shaangyashan</td>
<td>Crude wax</td>
<td>83.4</td>
<td>59</td>
<td>105</td>
<td>164</td>
<td>Creamy white</td>
</tr>
</tbody>
</table>

Pre-treatment of raw materials

China has the lignite of relatively high moisture content with an average of about 30%. It’s not conducive for transportation, causes extra cost and influences its economic efficiency. In the view of the characteristics of domestic high moisture lignite, drying before utilization seems particularly important. Domestic literatures showed that lignites before being dried was studied as a type of energy fuel used in combustion, pyrolysis and gasification. However, as a type of physical resource for montan wax extraction, there are scarcely any studies about its treatment.

Researchers at abroad show that, compared with other factors, the water content has the greatest impact on the amount and rate of extraction in lignite. Even if the lignite is dried to a constant weight, when it is rewetted to contain 20% moisture content, we can still obtain the extraction content, which is the same with that of 20% moisture content lignites. When the moisture is in the range of 10% -20%, it reaches the maximum extraction rate, then it tends to be stable. If drying almost completely, about 1% moisture content, the extraction efficiency of lignites is the minimum. This phenomenon might be explained by two reasons: first, the lignite contains so many hydroxyl, carbonyl, carboxyl and carbon-hydrogen bonds on its surface which causes lignite to form hydrogen bonds and Van Der Waal’s Force (VDW) with the residual water on its surface. Second, the lignite will shrink distinctly when the water content is excessively low, which results in inadequate pore diameter and low rate of diffusion. When the montan wax’s extraction time is about 180 minutes, it gets the maximum amount of extraction.

The drying temperature of lignite has almost no impact on the extraction of montan wax. Therefore, the drying temperature can be increased to reduce the drying time. However, the temperature can not exceed 135 °C, which will cause lignite to spontaneously combust. The data shows under the presence of oxygen, the linolenate oxidation occurs at 105 °C and above, considering the drying process may cause the wax’s oxidation, the drying temperature is better to be controlled at below 105 °C.
Crushed lignite particle size has little impact on the montan wax extraction process. Its size is generally required at between 0.1 and 3.5mm\[14\]. Larger particle size will reduce the extraction efficiency of montan wax. Particles of smaller size has a larger contact area with solvent, the montan wax extraction efficiency can be improved. But when the size is excessively small, make solid-liquid separation more difficult, and the output of montan wax contains solids residue, and subsequently affect the quality of lignite (higher ash content, exceeded benzene insolubles). Therefore, the excessively small sizes of grains will be screened and dumped. Particle size below 500μm will be re-pelletized\[15\]. Extracting the montan wax under the vacuum conditions has minor advantages, and its value on industrial application is insignificant.

The above research results provide extremely high application value on improving China’s utilization efficiencies of lignite resources and theoretical basis for montan wax extraction. Zhang Huifen\[16\] has studied the optimal technological conditions for extracting montan wax using orthogonal design, extraction temperature: 90℃, extraction duration: 1.5h, solid to liquid ration: 1.5(g/mL), water content: 14.64% and particle size: 0.5-1.0mm, which coincide with that achieved by the foreign researchers.

Guangzhou Hu\[17\] has conducted a acid and base deashing pretreatment removing part of the ash contained in the lignite, and increased the contact area between the organic material with the solvent to make an influence on the extraction rate and the extraction constituents. Results showed that, acid treatment can improve the extraction rate of montan wax, the stronger polarity of the organic solvent is used, the more obviously the extraction rate increases, and the amount of micromolecules contained in the extractant apparently increases. Results by the alkaline solution treatment showed on the contrary, which caused loss of part of constituents in the extractant. As we all know, The crude montan wax of low quality contains a high content of bitumen, and the ash content is an important part of the bitumen in montan wax, when bitumen content of the montan wax is 14%, the ash content is 3.5% -4.5%\[18\]. Conclusion can be drawn in combination with the above that acid pretreatment can not only improve the productivity, but also reduce the bitumen content to improve montan wax quality.

**The production and deresination of montan wax**

Compared with other coals, lignite has a low degree of coalification with a short coal-forming period, they have rich pores, high oxygen content and low density, it is a low-grade fuel of a high volatile, high moisture, and low calorific value (14MJ / kg). China has abundant lignite resources with an account of about 13% of the national coal resources, which occupies an important position, with a reservation of at least 130.3 billion tons\[10\]. So far, the utilization of lignite is mainly reflected in three directions: solvent extraction of montan wax, oxidative degradation of humic acid, and comprehensive utilization of resin, among which, the montan wax production has the highest industrial value. In 1975-1979, Shulan montan wax factory was established in Jilin province, besides the Northeast montan wax factory, Yunnan Xundian, Yunnan Liaohu, Inner Mongolia Chifeng also began to build montan wax factories. In 2013 the montan wax factory of Yunnan Yuxi launched its production, the annual output was 5,000 tons montan wax. Its montan wax’s quality is currently the most excellent compared with domestic congeneric products. However, the disadvantage of domestic lignite is the montan wax content is generally low and varies between 2% and 9%, which results in high production cost. Normally, the montan wax content is required at 10%(dry basis)\[19-20\] for its production to be cost-efficient. Currently the montan wax factory of Yunnan Yuxi uses residue coals extracted of montan wax to produce humic acid, which greatly increases the economic benefit\[23\].

The montan wax can be extracted through intermittent (pot groups) and continuous approaches. The former requires simple equipment and small investment, but the resources can not be fully utilized. Currently, the latter is more often utilized since its continuous operation is good for achieving mechanization and automation. Continuous extractor includes annular extractor and rotary extractor. Rodeh and Novakovskiy\[22\] once compared these two extractors, but the solvent he used is the benzene which is a strong carcinogen and has now been replaced by toluene. Therefore, it is not very consultative.

Montan wax and its processed products have become indispensably important chemical products in the national economy, especially the refined wax, which is light-colored and purer in wax quality. It accordingly has higher value in use and more expensive in price. Its demand ratio in the market has reached up to 67%\[24\]. The raw material for refined wax production is not the crude montan wax, but the de-resined wax. The crude montan wax contains resin and bitumen, which will consume the amount of the oxidizer in the refining process, cause uncontrollable fierce reaction and subsequently result in dark-colored refined wax. So resin must be removed before producing refined wax so as to achieve good bleaching performance.

Although multiple approaches to remove the resin are available, none of them are mature enough. Vacuum distillation by superheated steam will destroy the structure of wax molecules and the production rate is low. So, it is, from the economic perspective, costly. Freezing distillation is not able to remove the resin effectively and the
de-resinated wax produced can not be further processed. Removing resin with strong oxidizer will destroy pure wax due to oxidization. Besides, the reaction process is difficult to control, the decolorization is incomplete and the production rate is low. Moreover, decomposing resin contained in the montan wax requires a great deal of oxidizer and strong acid, rising production costs and descending utilization. The present relatively effective method is using organic solvent for de-resination under a low temperature condition. In the last century, Beijing Coal Chemistry Research Institute once used cold benzene to remove resin\cite{24} and has significantly improved de-resination wax’s quality. However, many liquid ammonia and cryogenic equipment were used in the production, which would easily cause environmental pollution and equipment jamming, and therefore failed to realize the industrialization. The former Soviet Union has used 24 kinds of organic solvents to study the de-resination\cite{25}, the results showed that the de-resination rate of methylene chloride, carbon tetrachloride, toluene, benzene is high, which were carried out in the laboratory. Looking for extraction agents of high efficiency and low toxicity will be a hot spot of the de-resination technology research in the future.

Currently the industrial de-resination solvent is cold toluene, which can remove 20% of the resin in the montan wax, leaving only 2%-5% of resin residual in the de-resined wax\cite{26}. The principle is that under low temperatures, the resin in the montan wax may be dissolved in an organic solvent, while the wax is insoluble or sparingly soluble so that it can achieve the purpose of the separation of the resin and the wax. However, the resin is not required to be completely removed, the resin content of different requirements depends on the usage, for example, in some cases, the resin is needed to add to the montan wax to achieve a better performance.

The oxidation refining and modification of the montan wax

Crude montan wax and de-resined wax, for their dark color, can only be used in industries which color requests are not high, However, when they are refined through oxidization to produce light-colored wax, their scope of applications will be expanded and the economic value will be improved. There are multiple ways of oxidization available\cite{27} The most commonly used method currently is the chromic acid-sulfuric acid oxidization method, you can get light-colored wax which has white-yellowish appearance, hard and brittle texture with high acid value. However, chromium waste-liquid is difficult to deal with, and can only be used for the tanning industry\cite{28}. This process requires adding glucose to restore the unreacted hexavalent chromium, which subsequently results in high production cost. Therefore, How to effectively solve the chromium-containing waste liquid produced from the production is the key whether it’s the favoring development of montan wax industry. Indirect electrochemical oxidation\cite{29-31} has solved the problem of Chromic-acid oxidization Wastewater in the process of oxidation bleaching of Montan Wax. Currently the oxidation process of montan wax for the industry is: extracting the montan wax with toluene from lignite, continue removing the resin with toluene in the crude montan wax, oxidating with chromic acid and sulfuric acid, pickling, water-washing, and then recycling and circle utilizing\cite{26}. This process can realize pollution-free refining of montan wax.

The light-colored refined wax is then esterified with alcohol (normally ethylene glycol, butylenes glycol or the mixture of the two) under certain conditions to obtain OP-wax, O-wax, E-wax and KP-wax etc. Among those, OP wax, O wax’s oil absorption and lipophilicity are better than the expensive carnaub wax, which are widely used in furniture wax, car wax and polishing wax products etc. E wax is more suitable for undertint wax products which are needed for saponification and emulsification, and it can be used as the lubricant of the plastics industry, to manufacture crayons and colored paper, etc. The other modified waxes also greatly broadens the montan wax of scope of application.

Application progress

Industry

Montan wax and carnauba wax share many similarities in their properties. However, the former’s color is too dark and has limited its applications. When color is not strictly required, the montan wax can serve as a cheap substitute for the carnauba wax. The carnauba wax contained in the shoe polish, floor wax and car wax can be replaced by montan wax.

The montan wax contains much higher aliphatic acid, higher aliphatic ester and alcohol etc. which provide excellent advantages, like oil absorbency and color solubility. When appropriate amount of montan wax is added into the carbon paper recipe, it can absorb excessive oil substances, help to dissolve pigment and provide the carbon paper with smooth, uniform surface and is not sticky. The montan wax is an important raw material in the carbon paper industry.

Since the montan wax is characterized by low electric conductivity and good insulating property, it can be coated on the surface of the electric wires and cables. Moreover, it can also be used on the fixed porcelain insulator and the binding wires as well as the external layer of the mated compensating wires coatings to improve its electric
insulating property, prevent it from being tacky and extend its service life.

Researchers\textsuperscript{32} used TG-FTIR online to analyze the montan wax extracted by six different solvent under nitrogen protection conditions. The results indicate that the temperature limit of montan wax is 260\textdegree C so that it could only be used as polymer precise cast moulding material. when it is served as polished wax, the cover of the automobiles would not endure chemical change under heat, so that it can help to maintain the glossiness. According to the research conducted by Yu Jin\textsuperscript{33}, putting montan wax into the mold material can increase the solubility of EVA and polymerized rosin. Besides, the mold material is smooth, fine and exquisite.

As an excellent road asphalt additive, the polarity and good emulsifying capability of the montan wax enables itself to improve the bonding strength between the asphalt binder and the masonries. The montan wax can also be added into the rubber to serve as dispersant and lubricant.

The approach to add montan wax-bearing mixtures into the concrete and heat the external cured concrete to 90\textdegree C to melt the wax mixture, which will then penetrate into the micro-porous concrete can prevent the water and soluble salt from penetrating and improve the durability of the pavement. The montan wax emulsion is also a type of release agent for concrete members. Spraying it onto the preheated metal formwork can prevent the concrete and the pattern from sticking with each other, make mould release easier and reduce damage to the member surfaces.

Agriculture
At abroad\textsuperscript{34} someone used the emulsion of the refined montan wax as a dispersant in mixture with many other types of pesticides to spray crops to produce a type of rainwater-resistant pesticide. Adding the montan wax emulsion into the herbicide can improve the efficiency of the herbicide. A two-year field experiment showed that the montan wax emulsion did no harm to the crops.

Forestry
In the protection of timber, people put more and more emphasis on environmental protection, along with some of environmentally harmful bio-pesticides and other wood preservatives being banned or restricted, boron-based wood preservatives become the prevailing environmental-friendly preservative in the market, whose major disadvantage is it can easily run off in a humid environment, which limits the application of boron-based wood preservatives areas outdoors. Overseas research indicates that the synergistic effect by using the montan wax emulsion and boron compounds together will not only improve the stabilization of boron constituents, but also strength its resistance against wood-decaying fungi\textsuperscript{35}. Montan wax emulsion prevents the boron compounds from running off not only by the hydrophobic effect of wax surface. Microscopic observation\textsuperscript{36} indicates that lignite emulsion can form thin film inside the cell walls, and this film can not only delay the diffusion of water and enzyme, but also reduce the run off of boron substance. Boron substance and montan wax emulsion’s synergistic effect has enough resistance against at least two kinds of wood decay fungi, and montan wax emulsion’s adding can decrease the minimum fungi concentration of the boron substances. The waterproof agent used for wood protection is normally paraffin\textsuperscript{37}. This is the most important application besides used as candles\textsuperscript{38}. Montan wax having one of the most important advantages over paraffin is that it can form a thin layer of waterproof film\textsuperscript{39}, which can both prevent water from penetrating into the wood and improve the wood anti-corrosive capabilities\textsuperscript{35,36,40}. Researches showed that montan wax is more superior to paraffin in terms of wood protection.

Existing Problems and Deficiencies
Still a lot of people lack adequate awareness about lignites and burn it as an ordinary fuel, which can otherwise be used for montan wax production. Its combustion value is low and will create pollution. The lignite resources are unduly destroyed. The montan wax has extremely high value in use and is the resource that both in domestic and international market are in scarcity and in shortage of. Its current price is rising and will maintain this strong momentum. China needs to strengthen researches on its basic applications and bring closer cooperation between academies and enterprises.

There is no patent aiming solely at de-resination technologies. Some foreign reports once mentioned the de-resination methods and its patented technology, which involved methods like vacuum distillation by superheated steam, freezing distillation, and oxidation by strong oxidizers (eg. H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{3} + K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, KMnO\textsubscript{4}), but none of them were feasible in terms of the economic cost or industrialization. German owns the industrialized de-resination technology, but it is difficult to obtain due to technical security and monopoly. In China, there are no proprietary intellectual property rights available in relation to the de-resination wax technology, nor are there any industrialized production lines or equipment. Somebody once attempted to remove resin using refrigerated centrifugation technology, but finally failed. In his trial production, the product could not flow to the following refining process and therefore failed to realize industrialization. How to produce de-resinated waxes which are suitable for producing
refined waxes in an industrialized scale, and control the production cost within an acceptable range remain difficult for de-resinatation technology.

In China, the production of montan wax mainly focused on crude wax, and exquisite product categorized based on its specific applications in the next step is necessary. In German, it is categorized into several types according to its applications, like ROMONTA665, which is suitable for using as raw material for producing solvent-bearing ornaments and polishes; ROMONTA6715, which contains low resin content and relatively higher asphalt, is a special wax for producing disposable carbon paper. In addition to this, there are still ROMONTA Y type waxes dedicated for use in investment castings in German.

In Japan, the montan wax has been registered as a food additive applied in fruit handling, because it can reduce the rate of water loss in fruits. Besides, it also has applications in cosmetics, because it is a natural product and deemed nontoxic. That is why no research about the minimum dosage that can create side effect is available at present, and this is not good for the development of its applications in food and drug. More and further research about its pharmacological action is urgently expected.

There are no evaluations in terms of resin application value in medical field. As the by-product during production of de-resinated waxes from the crude waxes, the montan wax resin was not rationally made use of, and was the last present, and this is not good for the development of its applications in food and drug. More and further research about its specific applications in the next step is necessary. In German, it is categorized into several types according to its application value is urgently expected.

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