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PROCESS FOR IMPROVING THE PROPERTIES OF MONTAN WAX

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It is already known that crude Montan wax or such as has been freed from resins or otherwise treated may be bleached by treating it with oxidizing agents, especially chromic acid in acid, for example a mineral acid, solution.

We have now found that particularly valuable products are obtained by treating crude or deresinified Montan wax with only such amounts of chromic acid as are sufficient for bleaching the Montan wax in sulfuric acid solution, if the working conditions, such as concentration and acidity of the oxidizing agent, temperature and duration of treatment be so adjusted in relation to each other that yellow to pure white products are formed with very similar properties to those of carnauba wax but which are considerably easier to saponify and emulsify than the said wax or the crude Montan wax.

In order to obtain this result the working conditions must be so chosen that not only are the coloring constituents eliminated from the Montan wax, but the wax itself is also chemically changed. With this object in view the treatment of the Montan wax is carried on in a sulfuric or phosphoric acid solution of such strength that extensive saponification takes place without the wax being destroyed or carbonized to any considerable degree. Thus for instance sulfuric acid of about 30 to 60 per cent strength or phosphoric acid of a corresponding acidity which is an equivalent of sulfuric acid for the purposes of the present invention may be used. The employment of a sulfuric acid of over 70 per cent strength, however, should be avoided as the wax would be spoiled by the action of an acid of such high strength. The employment of sulfuric acid of the said concentration entails the further advantage that solutions of chromic salts are obtained in the process of a concentration suitable for regeneration by electrolytic methods so that the regenerated solutions of chromic acid can directly be used in the process. In a solution of the said acidity, not only does the chromic acid destroy the coloring matters of the Montan wax, but at a suitable high temperature, i. e., above 100° C., oxidizes to the corresponding fatty acids the alcohols set free by the saponification. By a suitable selection of the temperature and continuing the treatment until the above-mentioned quantities of the oxidizing agent are used up, the fatty acid content of the wax is considerably increased and the proportion of unsaponifiable constituents correspondingly lowered.

The bleaching of crude or deresinified Montan wax in sulfuric acid solution by means of chromic acid is difficult to carry out owing to the formation during the process of pasty masses. Although the formation of these pasty masses can be prevented by the addition of organic solvents or emulsifying agents, such for example as benzene, benzine or carbon tetrachlorid, these additions at the same time render the subsequent recovery of the chromic acid solutions by electrolytic methods difficult.

The said troublesome formation of pasty masses during the bleaching of Montan wax with chromic acid in sulfuric acid solution is prevented, and the spent chromic acid regenerated without difficulty, if the Montan wax be first suspended in a solution of a chromic salt, and then treated with chromic acid in the presence of sulfuric acid. This process may be carried out for example, by stirring up the Montan wax to be bleached, in the warm, in a solution of a chromic salt, for which purpose a solution of chromic sulfate may be employed which has already been used for bleaching and has thereby undergone reduction. The requisite amount of chromic acid solution to effect the bleaching is then run into the fine, stable emulsion obtained in the said manner and heat is applied.

The preferred range of temperature used is between 105° and 120° C. At lower tem-

peratures not only the saponifying action of the mineral acids is inferior, but also the chromic acid is not used up. When working, however, at temperatures above 125° C., the Montan wax darkens more or less extensively. The bleaching process is preferably conducted while continuously evaporating water for the purpose of gradually raising the temperature.

It is advantageous to add the chromic acid solution very slowly at the beginning of the reaction for obtaining a bleached product of a high acid value and using up the chromic acid almost completely. By this manner of working the concentration of the chromic acid in the bleaching liquor is never too high and nevertheless the bleaching process proceeds simultaneously with the oxidation of the free alcohols obtained by the saponifying action of the acid liquor. Moreover, an unduly high concentration of chromic acid in the bleaching liquor would cause a violent reaction which leads to the formation of undesired products. When using, however, a solution of chromic acid of not too high a concentration, such as is obtained by the electrolytic regeneration of a spent bleaching liquor containing chromic salts, and when adding same to the suspension of the wax in sulfuric acid, the action of the chromic acid is fairly rapid initially, but gradually diminishes when adding further amounts of the said chromic acid solution as the bleaching liquor becomes more and more dilute so that owing to the large volume of the liquid, the complete utilization of the chromic acid takes a comparatively long time. Moreover, working with such dilute solutions is a far more troublesome matter, and requires very much larger apparatus.

The beforementioned drawbacks may be overcome by dividing the chromic acid needed for the bleaching into portions and by more or less completely withdrawing the more or less spent portion of solution before adding a fresh portion of chromic acid solution after separation of the reaction mixture into layers by leaving it to stand for awhile.

According to this manner of working the operation is conducted throughout with a small volume of liquid, so that a comparatively small apparatus is needed. Moreover, fresh chromic acid in stronger concentration is available for effecting the final bleaching of those constituents of the wax which are most difficult to decolourize, whereas, in the ordinary way, the chromic acid solution used at the end of the process is in a nearly exhausted condition.

Owing to inclusion of compounds of trivalent chromium, the Montan wax bleached with chromic acid has a more or less decided green coloration. The removal of these pigmentary salts presents considerable difficulties, which are met with not only in the case of Montan wax but also, as is known, in other products, such as paraffin wax, beeswax and the like treated with chromic acid. The purification of such products is usually effected by repeated extraction with boiling dilute sulfuric acid, oxalic acid and similar substances.

The elimination of the pigmentary chromium compounds contained in the bleached Montan wax, beeswax, paraffin wax and similar organic compounds which can be melted without undergoing decomposition, can be effected in a simple manner by allowing the mixture of chromic acid and bleached wax, or the bleached wax alone, after drawing off the chromium solution, to settle down for a sufficient length of time, preferably in heated and well insulated settling vessels. In this case molten, but still greenish, wax first collects on the surface of the chromic solution. After a short time, however, a separation of the wax and the chromium compounds finely distributed therein takes place, the latter compounds settling down and leaving a perfectly white, colorless wax behind. The chromic salt solution may also be drawn off after the still colored wax has separated out, the wax being then left to itself in the warm.

In this manner a complete, or almost complete, separation of the wax and the chromium compounds may be obtained. In the latter event, a single short extraction with boiling dilute sulfuric acid is sometimes advisable in order to obtain complete separation.

In comparison with other bleaching processes which also set up a partial chemical alteration of the esters contained in the Montan wax, the method of working above described has the advantages that no loss of valuable constituents is entailed and that no difficult aftertreatment is necessary, but a high-grade yellow to white product is obtained directly, which is quite on a par with carnauba wax with respect to its properties, such as hardness, power of hardening, gloss, feel and the like, but can be saponified far better than the latter, or raw or commercial refined Montan wax, and can be made into stable emulsions even with admixture of substances which emulsify with difficulty or not at all.

In comparison with the carnauba wax residues obtained by saponification with alkali in bleaching carnauba wax, and valued for the ease with which they can be saponified, the product obtained according to the present process has the advantage of a considerably higher melting point (81° centigrade as compared with 63° to 64° centigrade) and the other consequent valuable properties, which otherwise are peculiar to grey carnauba wax alone.

The following examples will further illus-

trate the nature of the said invention which however is not limited thereto.

Example 1

100 kilograms of crude Montan wax are heated to about 100° centigrade while stirring, in association with 500 litres of a sulfuric acid solution of chromium sulfate, containing 400 grams of free sulfuric acid and 300 grams of chromium sulfate together with a little free chromic acid if required per litre. The temperature is then gradually raised to about 108–115° centigrade and 100 kilograms of chromic acid, dissolved in sulfuric acid of 40 per cent strength, are slowly run in. The chromic acid will have become exhausted in a short time, and the bleached Montan wax will float on the solution of sulfuric acid and chromium salts.

Example 2

100 kilograms of crude Montan wax are emulsified, at about 100° centigrade, in 400 litres of spent chromic acid solution containing about 45 per cent of sulfuric acid. The mixture is stirred and heated to about 109° centigrade while 1200 litres of electrolytically regenerated chromic acid solution are run in. This solution contains about 92 grams of free chromic acid, 108 grams of chromium compounds calculated as Cr_2O_3 and 510 grams in total of sulfuric acid, including 410 grams in the free state per litre. The bleaching will be complete by the time the whole of the chromic acid is exhausted.

Example 3

100 kilograms of crude or deresinified Montan wax are suspended in 1600 litres of 42 per cent sulfuric acid, and the mixture is heated to 105° centigrade, whereupon 150 kilograms of chromic acid dissolved in 150 litres of water are slowly added, while stirring. The Montan wax will be bleached in a few hours. It is advisable to raise the temperature to from 115° to 120° centigrade towards the end of the treatment.

Example 4

100 kilograms of Montan wax are emulsified by energetic stirring in 1200 litres of 50 per cent sulfuric acid or 66 per cent phosphoric acid, the temperature being raised to 105° centigrade. A concentrated aqueous solution of chromic acid, containing 160 kilograms of CrO_3, with or without the addition of mineral acid, is then allowed to run in slowly. The temperature is raised, at the same time, to the boiling point of the mixture, and water is then slowly evaporated therefrom so as to cause the temperature to rise still further. In so doing, the supply of heat is regulated in such a way that, at the end of about 5 hours, the temperature of the bleaching liquor will have gradually risen to about 120° centigrade. After stopping the stirring mechanism and the supply of heat, the bleached Montan wax will collect on the surface of the acid chromium solution after standing for a while.

Comparative table of constants

1. Crude Montan wax	2. Montan wax bleached in glacial acetic acid with chromic acid	3. Montan wax bleached according to the present example.
Acid value, 36	51	132
Saponification value, 101	124	165
Ester value, 65	73	33
Iodine value, 15	0.0	0.0
Melting point, 82°–83° C.	84° C.	81° C.

Example 5

100 kilograms of deresinified Montan wax are suspended in 400 litres of a spent chromic acid solution, mainly containing chromic sulfate and free sulfuric acid, at a temperature of 105° C. 1500 litres of an electrolytically regenerated chromic acid solution are introduced, while stirring, so that during the first hour about 300 litres, during the second hour about 600 litres and the remaining 600 litres are run in during the following half hour. The said chromic acid solution contains 86.5 grams of free chromic acid (CrO_3), 135 grams of other chromium compounds (calculated as $K_2Cr_2O_7$) and 520 grams of sulfuric acid per litre. During the introduction of the chromic acid solution the temperature is raised, while evaporating water, to about 112 to 113° centigrade and during the next two hours to about 117–118° C. After that time the chromic acid is used up and the bleached Montan wax, the characteristic values of which are essentially altered, may be worked up in the usual manner.

Example 6

100 kilograms of crude Montan wax are emulsified in 1000 litres of sulfuric acid of 60 per cent strength at a temperature of 105 to 110° centigrade. 500 litres of a solution of chromic acid and sulfuric acid, containing 360 grams of chromic acid (CrO_3) and 420 grams of sulfuric acid per litre are run in during about 3 hours, regulating the introduction as described in the foregoing example so that initially less and finally more of the chromic acid solution is run in.

After boiling for 6 hours under a reflux cooler while stirring the chromic acid is spent.

The bleached wax is worked up as usual.

Example 7

100 kilograms of deresinified Montan wax are emulsified at a temperature of 105° C. in 400 litres of a spent solution of chromic acid and sulfuric acid of the concentration described in Example 1. 500 litres of a regenerated solution of chromic acid the con-

centration of which being that described in Example 2 are slowly run in during one hour, while stirring. After a further hour during which the temperature is raised to 112° C. the chromic acid is used up, the stirrer is stopped; after standing for half an hour the reaction mixture has separated into two layers and the bulk of the spent chromic acid solution is drawn off from beneath the Montan wax. Again 400 litres of a regenerated chromic acid solution of the said concentration are introduced while heating and stirring. After 2½ hours the spent chromic acid solution is withdrawn for the most part and further 300 litres of the said chromic acid solution are run in. The bleaching process is finished by increasing the temperature within the next three hours to 119° C. while stirring.

What we claim is:

1. In the process of improving the properties of Montan wax the step which comprises heating Montan wax in a sulfuric acid solution of 30 to 60 per cent strength with only such amounts of chromic acid as are sufficient for bleaching the Montan wax at temperatures between about 100 and 125° centigrade until the chromic acid is used up.

2. In the process of improving the properties of Montan wax the steps which comprise suspending Montan wax in a solution of a chromic salt and heating it in a sulfuric acid solution of 30 to 60 per cent strength with only such amounts of chromic acid as are sufficient for bleaching the Montan wax at temperatures between about 100 and 125° centigrade until the chromic acid is used up.

3. In the process of improving the properties of Montan wax the steps which comprise suspending Montan wax in a solution of chromium sulfate and sulfuric acid and heating it in a sulfuric acid solution of 30 to 60 per cent strength with only such amounts of a chromic acid solution as are sufficient for bleaching the Montan wax which is gradually introduced into the reaction mixture at temperatures between 100 and 120° C. until the chromic acid is used up.

4. In the process of improving the properties of Montan wax the steps which comprise suspending Montan wax in a solution of chromic sulfate and sulfuric acid obtained in the process and heating it in a sulfuric acid solution of 30 to 60 per cent strength at temperatures between 100 and 120° centigrade with only such amounts of an electrolytically regenerated chromic acid solution as are sufficient for bleaching the Montan wax until all of the chromic acid is used up, the chromic acid solution being introduced in portions and the spent solutions being at least partially removed before adding a further portion of chromic acid solution.

5. The process of improving the properties of Montan wax which comprises heating Montan wax in a sulfuric acid solution of 30 to 60 per cent strength with only such amounts of chromic acid as are sufficient for bleaching the Montan wax at temperatures between about 100 and 125° centigrade until the chromic acid is used up, allowing the reaction mixture to settle and drawing off the solution of chromic salts.

6. As a new article of manufacture pale-colored Montan wax having a melting point of about 80° centigrade and an acid value of about 130.

In testimony whereof we have hereunto set our hands.

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