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OXIDATION OF PETROLEUM CERESIN AND NOVEL PRODUCT OBTAINED THEREBY

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This invention relates to a novel method for the oxidation of petroleum ceresin and to the novel oxidized wax product obtained thereby.

Previous methods of oxidizing petroleum ceresin have been generally unsatisfactory in that they produce oxidized wax compositions which are substantially softer than the original wax. At least in some uses of oxidized microcrystalline waxes, such as oxidized petroleum ceresins, it is desirable that the oxidized wax be hard and in such cases, the tendency of prior art oxidations to result in a softening of the wax is disadvantageous. In the preparation of oxidized microcrystalline wax for use in wax polishes, for example, it is particularly desirable to obtain a hard product. The present invention provides an improved oxidation process wherein an oxidized wax product can be obtained which is nearly as hard as, as hard as, or harder than the original wax previous to oxidation.

The oxidation method of the present invention is further advantageous in that it produces an oxidized wax product having higher viscosity than prior art oxidized waxes produced by previous oxidation methods. Such higher viscosity provides beneficial effects as subsequently more fully described, in the use of oxidized petroleum ceresin in wax polish compositions.

The novel oxidation method of the present invention involves oxidation of a petroleum ceresin to a saponification number above 65 with control of the rate of oxidation in order to obtain a low rate of increase in saponification number. The relatively slow oxidation according to the invention produces the unexpected results of producing a hard oxidized wax with high viscosity, whereas the relatively fast oxidations of the prior art do not provide these beneficial results.

The rate of oxidation according to the present invention is controlled within the range equivalent to 0.05 to 1.25 increase in saponification number per hour. Oxidation rates below the lower limit of the range are generally not economical, and oxidation rates above the upper limit generally result in failure to obtain the advantageous hardness and high viscosity of the oxidized wax product.

The rate of oxidation is also preferably controlled within the range equivalent to 0.01 to 0.30 increase in acid number per hour. Generally, this result is obtained concurrently with the saponification number increase equivalent to 0.05 to 1.25 per hour, since slow oxidation rates as applied to oxidation of petroleum ceresin according to the invention generally result in a high ratio of saponification number to acid number, e. g. 3 to 10, and frequently in the neighborhood of 5.

The oxidation according to the present invention is continued until the saponification number of the oxidized

wax is above 65, since it has been found that the penetration of the oxidized wax generally increases with increasing saponification number in the early stages of the oxidation, and then after passing through a maximum, the penetration ceases to rise substantially and generally decreases with increasing saponification number during the remainder of the oxidation; oxidation to a saponification number of 65–75 generally carries the oxidation beyond the point of maximum penetration, so that the beneficial effect of subsequent reduction in penetration is obtained, or at least so that the penetration levels off and does not substantially increase upon further oxidation. Generally, the most advantageous results according to the invention are obtained by oxidizing to a saponification number not above 150, and preferably not above 100. The oxidation is preferably terminated when the saponification number is within the range 75 to 150, more preferably not above 100. At a typical rate of saponification number increase, 0.35 per hour, the time required to obtain saponification number in the range 75 to 150 is about 210 to 420 hours.

The required oxidation rate according to the invention can be obtained by proper selection of the various conditions which affect the oxidation rate, such as temperatures, catalyst, catalyst concentration, air rate, air-wax contacting conditions, etc. In the light of the present specification, a person skilled in the art can select the conditions which will provide a saponification number increase within the required range of 0.05 to 1.25 per hour. Generally suitable temperatures will be found within the range from the lowest temperature at which the wax is molten, up to about 300° F., and generally suitable air rates within the range of 1000 to 5000 cc./minute/1000 grams of wax. It is to be understood, of course, that other free-oxygen-containing gases can be used instead of air; exceptions, however, are sometimes noted in the case of air containing substantial amounts, e. g. as much as one percent, of ozone. Such ozonized air has been found to be unsuitable for producing the advantageous results of oxidation according to the present invention; and therefore the oxygen containing gases used should be substantially free from ozone, though some small ozone contents may not be detrimental.

The air-wax contacting conditions have a substantial effect on the oxidation rate, and it is possible to obtain the relatively slow oxidation rate according to the invention with contacting conditions which do not provide very intimate contact between oxygen and wax, even though the other oxidation conditions are such that intimate contact between oxygen and wax would result in a higher oxidation rate than that of the present invention under those other oxidation conditions. Factors involved in the air-wax contacting conditions include, in a process where air is bubbled through liquid wax, the number and size of the air bubbles, the degree of mechanical agitation if any, etc.

Oxidation according to the present invention is preferably conducted in the presence of a catalyst, e. g. a catalyst of the "drier" type, as employed in paints and varnishes, etc. Metallic soaps such as manganese, cobalt, lead, or zinc soaps of naphthenic, stearic, oleic, palmitic, or linoleic acids, etc., are suitable catalysts of the drier type. Manganese soaps are particularly preferred. The amount of catalyst employed is preferably such as to provide 0.02 to 2.0 parts by weight of metal, e. g. manganese, per 100 parts of wax.

The petroleum ceresins oxidized according to the invention are high-melting microcrystalline waxes having melting point within the approximate range from 175° F. to 210° F., and most commonly within the approximate range from 180° F. to 195° F.

The process of the present invention produces a novel, oxidized microcrystalline wax product characterized by low penetration, high ratio of saponification number to acid number, and high viscosity. The penetration at 77° F. is not greater than 10, the ratio of saponification number to acid number is at least 3, and the S. U. viscosity at 210° F. is at least 200. The saponification number is above 65 and preferably in the range 75 to 150.

Prior to the present invention, oxidized wax products characterized by low penetration and high ratio of saponification number to acid number have been known, but these prior art products have had lower viscosities than the oxidized wax products of the present invention. The high viscosity of the products according to the present invention is particularly advantageous in use of the products in wax polish compositions, where an unusually high gloss and resistance to scuffing and slipping is provided by virtue of the high viscosity of the products.

The oxidized wax products of the invention may have any penetration at 77° F. not greater than 10, though generally the penetration will be at least 1, and generally in the range 2 to 8. Also, the ratio of saponification number to acid number will generally not be greater than 10. The S. U. viscosity of the oxidized wax according to the invention can vary widely, because of the rapid increase of viscosity with time which is obtained in the novel oxidation according to the method of the invention; thus very high viscosity products, even above 1000 S. U. viscosity at 210° F. can be obtained with long oxidation periods. Highly advantageous oxidized wax products according to the invention are those having S. U. viscosity at 210° F. above 300, more preferably above 500. Generally, the most suitable oxidized waxes will not have S. U. viscosity at 210° F. above 2000 though such oxidized waxes can and have been prepared according to the invention.

The following examples illustrate the invention:

Example 1

In this example, a petroleum ceresin wax oxidized under conditions to provide an average increase in saponification number of about 0.36 per hour and an average increase in acid number of about 0.09 per hour. The total oxidation period was 268 hours, and the saponification number and acid number of the product were 95.3 and 22.6 respectively.

The oxidation charge was a petroleum ceresin prepared by de-waxing a solvent-refined lubricating oil to obtain slack wax, distilling off 70 percent of the slack wax, and de-oiling the residue by dissolving in a solvent comprising methyl ethyl ketone, benzene, and toluene at a temperature above 92° F., cooling to 92° F., and filtering to obtain a filter cake which after removal of solvent and decolorization with clay at 300° F. yielded the present wax, having melting point at 190° F., oil content of 1.1 percent, penetration at 77° F. of 6, and penetration at 130° F. of 16.

The oxidation of the wax was conducted as follows: The wax was heated to 250–270° F. in a vessel, and air, introduced at the bottom of the vessel through two glass spiders, was bubbled upwardly through the molten wax and then withdrawn from the vessel. The air rate for the first 46.75 hours was 3000 cc. per minute per 1000 grams of wax, and for the remainder of the oxidation was 2000 cc. per minute per 1000 grams of wax. The oxidation was conducted in the presence of a manganese naphthenate catalyst in amount equivalent to 0.04 part of manganese per 100 parts of wax. During the oxidation periodic measurements were made of the

properties of the oxidized wax. The following table shows the variation of properties with time:

Time in Hours	Saponification Number	Acid Number	Penetration at 77° F.	Viscosity, S. U. V. at 210° F.
0	0	0	6	85
24	20.7			
46.5	36.3			
116.25	55.2		9	187
140.25	65.4		8	209
164.25			9	246
169.75	67.4		9	
188.25	72		9	
212.25	81.5		8	
239.75	84.0		8	543
260.75			7	
268	95.3	22.6	7	841

The oxidation was terminated at the end of the 268 hour period. The melting point of the product was 175° F. The table shows that the penetration increased during a first portion of the oxidation period and decreased during a last portion of the oxidation period to give an ultimate product having penetration only one point higher than that of the original unoxidized wax. The low penetration of the product is an unobvious and highly advantageous property for oxidized waxes for use in polishes and other applications.

Example 2

In the preceding example, the penetration of the oxidized wax at saponification number of 95.3 was only one point higher than that of the original wax. In many instances according to the invention, the penetration of the oxidized wax at saponification number above 65 will be no higher at all than that of the original wax. For example in oxidation of a wax differing from that oxidized in the previous example only in that the present wax had not been decolorized with clay, it was found that after oxidation for 235.25 hours, the saponification number had increased from 0 to 88.2 and the penetration had, after increasing from 5 to 8 in the early stages of the oxidation, decreased again to 5.

Comparison Example 1

In order to compare the oxidation procedure and product with other procedures and products not providing the unusual results obtained according to the present invention, the same wax used in Example 1 was oxidized in the presence of the same catalyst as in Example 1, the air rate being 4500 cc. minute/1000 grams of wax, and the oxidation temperature being 290–300° F. The air was introduced into a lower portion of the body of liquid wax through two fritted glass diffusers, rather than through the two glass spiders employed in Example 1. The effect of the use of such diffusers was to produce a larger number of air bubbles of smaller size, and to provide more agitation of the liquid wax, than in Example 1.

Because of the higher temperature and air rate and the more intimate contact of air with wax, the oxidation rate in the present example was higher than in Example 1. The following table shows the variation of properties with time:

Time In Hours	Saponification Number	Penetration at 77° F.
0	0	6
7	30.5	9
12	46.4	12
14.75	94.3	16
16.75	110.6	17
18.75	126.1	21
20.75	138.9	24

The above table shows that the rapid oxidation of the comparison example results in a steadily increasing penetration which is 24 at a saponification number of 138.9

and apparently still increasing, whereas in Example 1, a slow oxidation according to the invention results in a decrease in penetration as the saponification number rises above 72, the penetration at saponification number of 95.3 being only 7, and a downward trend in penetration being evident. The difference in results is clearly shown in the following table.

	Example 1	Comparison Example
Average Sap. No. Increase/Hr	0.356	6.7
Penetration (77° F.) at 94.3–95.3 Sap. No.	7	16

From the above table, it is seen that oxidation according to the present invention provides a much harder wax from a given charge stock than does a more rapid oxidation of the type employed in the prior art. The oxidation according to the present invention also provides an oxidized wax product having much higher viscosity than that obtained by a more rapid oxidation. This is shown by the following Comparison Example 2.

Comparison Example 2

In this example the same wax employed in the preceding comparison example was oxidized at 240–260° F. in the presence of a manganese-naphthenate-containing catalyst, with 3000 cc./minute/1000 grams of wax being introduced through two fritted glass diffusers. After 32 hours, the saponification number was 113.5, the penetration at 77° F. was 19, and the S. U. viscosity at 210° F. was 156. The difference in results between this example and Example 1 is shown in the following table:

	Example 1	Comparison Example 2
Average Sap. No. Increase/Hr	0.356	3.55
Maximum S. U. V. at 210° F	841	156

The above table shows that oxidation according to the present invention provides a much higher viscosity product than a more rapid oxidation of the type employed in the prior art.

In Examples 1 and 2 and the comparison examples, the difference in oxidation rates was obtained partly by virtue of a different manner of introducing the oxidizing agent into contact with the wax. The decelerating effect of introducing the air in the manner of Examples 1 and 2 is probably due to the smaller amount of surface area of contact between air bubbles and wax, the bubbles being larger and less numerous than in the comparison examples, and to the lesser agitation provided by the air introduction method of Examples 1 and 2. It is to be understood that other methods of providing a relatively slow oxidation can be employed. For example, using the air introduction apparatus of the comparison example, the air could be introduced at a lesser volume rate in order to provide a slower rate of oxidation that would provide the advantageous results obtained in Examples 1 and 2. Other variables, such as oxidation temperature and catalyst, can be regulated in order to provide the proper rate of oxidation. In the light of the present specification, a person skilled in the art can determine the oxidation conditions to provide the proper rate of oxidation.

Oxidized waxes obtained according to the present invention have novel and advantageous combinations of properties in that they have high ratios of saponification to acid number, low penetrations, and high viscosities. Prior art oxidized waxes do not have this advantageous combination of properties. This is demonstrated in the following table which presents a comparison of properties between several prior art oxidized waxes and two oxidized waxes according to the present invention, oxidized wax 1 being the product obtained in Example 1, and oxidized wax 2 being another product obtained by the process of the present invention:

	Saponification Number	Acid Number	Penetration at 77° F.	Viscosity at 210° F.
Prior Art Waxes:				
A	78	28	9	162
B	76	28	9	123
C	53	24	7	114
Waxes According to the Invention:				
1	95.3	22.6	7	841
2	84.2	19.8	7	890

As seen from this table, the oxidized waxes according to the present invention have much higher viscosities than those of prior art oxidized waxes.

In the preceding description of examples, the oxidized wax product referred to is the total liquid oxidation product, with no separation of the liquid oxidation product into various types of components such as oxidized material and unoxidized material, etc. It is to be understood that such separations can be effected after an oxidation according to the present invention but such oxidation has particular advantage in the preparation of oxidized wax products where the total oxidation product is employed, e. g. in a wax polish composition.

Penetrations given herein were determined by A. S. T. M. standard method of test D5–25 under the standard conditions of 100 grams, 5 seconds, 77° F. Acid numbers were determined by A. S. T. M. standard method of test D974–51T. Saponification numbers were determined by the procedure of A. S. T. M. standard method of test D94–48T except that toluene was used as solvent in place of methyl ethyl ketone.

This application is a continuation-in-part of copending application Serial No. 311,144 of Seymour W. Ferris and Herbert L. Johnson, filed September 23, 1952, and now abandoned.

The invention claimed is:

1. Method for obtaining oxidized petroleum ceresin having low penetration and high viscosity which comprises: oxidizing a petroleum ceresin having melting point within the approximate range from 175° F. to 210° F. at an average rate equivalent to 0.05 to 1.25 increase in saponification number per hour for the period required to reach a saponification number of 65; and terminating the oxidation when the saponification number of the total oxidation product is above 65 and the penetration of the oxidized wax at 77° F. is less than it was at an earlier stage of the oxidation.

2. Method according to claim 1 wherein the average rate of acid number increase per hour is 0.1 to 0.30.

3. Method according to claim 1 wherein the total oxidation time is within the range 210 to 420 hours.

4. Method according to claim 1 wherein the oxidation is conducted in the presence of a "drier" catalyst.

5. Method according to claim 4 wherein said catalyst is manganese naphthenate in amount equivalent to 0.02 to 2.0 parts by weight of manganese per 100 parts of wax.

6. Method according to claim 1 wherein said oxidation is conducted with the wax in molten state at a temperature not substantially above 300° F.

7. Method according to claim 1 wherein said wax is oxidized by contact with air at a rate of 1000 to 5000 cc. of air per minute per 1000 grams of wax.

8. Method according to claim 7 wherein said contact is obtained by passing large bubbles of air through a body of said wax in molten state.

9. An oxidized ceresin composition having saponification number of above 65, ratio of saponification number to acid number of at least 3, penetration at 77° F. not greater than 10, and S. U. viscosity at 210° F. of at least 200.

10. Composition according to claim 9 wherein said viscosity at 210° F. is at least 500.

11. Method for obtaining oxidized petroleum ceresin having low penetration and high viscosity which comprises: oxidizing a petroleum ceresin having melting point within the approximate range from 175° F. to 210° F. to a saponification number of at least 65 mg. of KOH per gram at a rate such that the saponification number reaches 65 within about 140 to 1300 hours; and terminating the oxidation when the penetration of the oxidized wax at 77° F. is less than it was at an earlier stage of the oxidation.

12. Method according to claim 1 wherein the oxidation

is terminated when the saponification number of the total oxidation product is above 75 mg. of KOH per gram.

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