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OXIDIZED WAX AND PROCESS FOR PRODUCING SAME

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The present invention relates to the art of separating wax from wax-bearing oil, and more particularly the invention pertains to a method in which certain materials are added to the wax-bearing oil to condition the latter so that the wax may be more readily separated from the oil. The invention also relates to a process for the production of materials which when added to a wax bearing oil, condition the latter so that the wax may be more readily removed therefrom. The invention is also applicable for the separation of oil from wax such as slack wax, wax cakes, etc. This application is a continuation in part of our copending application Serial No. 37,940 filed August 26th, 1935.

Many oils contain relatively large quantities of wax which impart a high pour point to the oil and thereby render these oils unsuitable for use as they are solid and will not flow at ordinary temperatures. In order to render these oils fluid at ordinary temperatures, it is necessary to remove the wax present. This is usually accomplished by adding a suitable diluent to the wax-bearing oil, chilling the diluted oil to a temperature sufficiently low to precipitate or solidify the wax and then separating the precipitated wax from the diluted oil by settling, filtering or centrifuging.

We have discovered that wax present in oils may be more readily separated by mixing the wax-bearing oil with certain materials which render the wax more readily separable from the oil. Hereinafter, the materials which we employ to condition the wax present in wax-bearing oils in order that the wax may be more readily separated from the oil will be referred to as "wax modifiers" or "wax separation aids".

In general, the wax separation aids which we employ to condition the wax-bearing oil to render the wax more readily separable, comprise oxidized paraffinic substances. Such oxidized paraffinic substances include oxidized waxes, such as scale wax, slack wax, chemically refined water white high or low melting point waxes, oxidized petrolatum, oxidized ceresin, oxidized oils containtaining large or small quantities of wax and/or petrolatum, oxidized raffinates produced by solvent extraction of oils and which may be substantially free from wax or may contain large or small quantities of wax, oxidized petroleum distillates either substantially free from wax or containing large or small quantities of wax and oxidized petroleum residues either substantially free from wax or containing large or small quantities of wax. We have discovered that the foregoing oxidized wax separation aids are quite active in conditioning the oil to be dewaxed so that the wax may be more readily separated from the oil. The reason for this phenomenon is not definitely known but we do know that when small amounts of the oxidized material are added to the oil to be dewaxed, an improvement is obtained with respect to the yield of dewaxed oil, filter rate or rate of wax separation and melting point of the separated wax. When the same amount of the materials prior to their oxidation are added to wax-containing oils, the improvement obtained is not sufficiently increased with respect to yield, filter rate and quality of the wax separated over the unaided dewaxing process as to warrant their use in commercial dewaxing processes.

In general, the oxidized wax separation aids may be produced by subjecting the unoxidized waxes or oils to the action of an oxygen-containing gas such as air, oxygen or ozone, preferably at an elevated temperature. Certain types of materials among those mentioned above require no treatment, chemical or otherwise, previous to oxidation to produce the active wax separation aid. However, it is beneficial in the case of certain stocks, such as crude slack waxes, to prepare them for more effective oxidation by a preliminary removal of undesirable impurities, such as resins, reactive oil fractions, etc.

Preferably, when producing the wax separation aid from slack waxes or waxes containing considerable quantities of oil, the crude wax is first deoiled to a low oil content. This may be accomplished by dissolving the wax in a suitable solvent, then chilling the solution to reprecipitate the wax and filtering the mixture. As deoiling solvents, we may employ any of the solvents mentioned hereinafter for diluting the wax bearing oil in the dewaxing thereof. We prefer, however, to employ the liquefied normally gaseous hydrocarbons such as ethane, ethylene, propane, propylene, butane, butylene or mixtures thereof. Of these, we prefer to use propane or butane. It is preferable to effect the deoiling of the wax at a higher temperature than the temperature at which the slack wax was separated from the oil which in propane dewaxing is approximately —40° F. Thus, we may dissolve the slack wax separated from lubricating oil at a temperature of about —40° F. in propane or butane at a temperature sufficient to dissolve the wax, for example 110° F. to 150° F., chill the solution to about 25° F. and separate the liquid constituents from the crystallized wax by filtra-

tion or cold settling. This will result in the production of a wax of increased dryness. If desired, the crude wax may be washed with cold propane or other suitable cold solvent to separate the oil from the crude material. Also, if desired, the wax may be sweated to remove the contained oil in accordance with known methods. If desired, the deoiling may be accomplished by extracting the crude wax with a selective solvent such as acetone, mixtures of acetone and benzene or toluene, liquid sulfur dioxide, phenol, chloraniline and the like. We have obtained good results in deoiling slack waxes by the use of a mixture of solvents such as liquefied normally gaseous hydrocarbons, such as propane and an aromatic solvent such as benzene or toluene.

The crude deoiled wax may be subsequently acid treated. This is for the purpose of removing asphalt and other easily oxidized materials which seem to be reactive with oxygen or other oxygen-containing gas in preference to the paraffinic components. In other words, we have found that when wax is contaminated with large quantities of low A. P. I. gravity materials, these latter materials prevent the proper course of oxidation to such an extent that it is not feasible to produce a dewaxing aid from such stocks. The acid treatment also reduces the ratio of oil to wax in the slack wax and leaves only the more stable oils in the slack wax. When the wax has been sufficiently deoiled, the acid treatment may not be necessary providing no considerable proportions of asphalt or resinous materials are present in the wax. If desired, the crude slack wax may be deoiled and deresinated by spraying the wax at a temperature above its melting point into a bath of liquid propane maintained at —40° F. This causes the wax to solidify in discrete particles and sufficient time is allowed for the propane to leach the oil from the solidified particles. The recovered wax may then be heated to above its melting point and allowed to stand. By decanting the wax while fluid, it will be found that the asphalt and resinous materials have settled to the bottom of the vessel.

The acid treatment will, of course, vary with the type of crude wax treated but will usually be at about 10 to 25° F. above the melting point of the wax. The acid treatment should be carried out in stages employing the proper amount of acid, such as 98% sulfuric acid, consistent with good settling of sludge produced by the reaction with the acid. The sludge produced by the first dump of acid may be quite viscous, especially if not withdrawn promptly. Therefore, care should be taken to obtain sufficient agitation and settling without permitting the sludge to have time to thicken excessively. After the last of the sludge is separated from the wax, the latter is heated to a temperature between 140 to 200° F. which is sufficient to reduce the viscosity of the wax for alkali treatment and water washing. The water washing between the acid and alkali treatments may be started immediately after withdrawing the sludge and may be continued as the temperature is raised. The water washing need not be extremely thorough to remove soaps and excess caustic after neutralization. In fact, the presence of a small amount of the sodium compounds have been found to be beneficial in the subsequent oxidation step. As a matter of fact in one run for the production of oxidized wax, none of the sodium hydroxide used for neutralizing the wax was separated and the dehydrated charge, therefore, contained an unusual excess of the caustic which was reflected in a very low acid number (0.1) in the blown product. Nevertheless, this batch of oxidized wax showed a very high filter aid quality.

The wax, either chemically treated and/or deoiled as the case may be, is then subjected to oxidation. The conditions and degree of oxidation will vary with the type and oil content of the wax. In general, the more completely deoiled and refined waxes will tolerate a higher degree of oxidation than waxes which contain substantial quantities of oil. The oxidation consists in heating the wax to a temperature of between 350 and 500° F. and introducing air, oxygen or ozone into the charge until a sufficient oxidation has taken place to render the material active as a wax separation aid and yet retain its compatibility with the oil to be dewaxed. During the oxidation, there is a period of induction during which little or nothing appears to be happening. This may last up to twelve hours or longer, depending upon the degree of contact of the air with the charge and the temperature of oxidation. After this period, the oxidation reactions move fairly rapidly, and it is desirable to stop the oxidation before the charge reaches a stage where it is only sparingly compatible with the waxy oil to be dewaxed.

The degree of oxidation may be determined approximately by measuring the acid and saponification numbers of the oxidized charge. However, these values are not entirely indicative of the wax separation aid effectiveness of the charge since the optimum amount may vary with different types of charging stocks. For example, with an acid treated slack wax, whereas the oxidation should not be carried to an acid number above 5 and a saponification number above 30, in the case of substantially deoiled and refined waxes, the oxidation may be continued until the charge has an acid number between 15 and 100 and a saponification number between 80 and 300. The acid and saponification numbers are determined according to the methods outlined by the American Society of Testing Materials, methods D-188-27T and D-94-28, respectively.

Also, indicative of the degree of oxidation of the charge, are the increases in specific gravity, viscosity and melting point. In general, the oxidation should not be carried to such a point that the viscosity and melting point are excessively high, rendering the subsequent handling of the oxidized material difficult. Also, we have found that too much blowing or oxidation of the wax charge results in the production of a product which causes plugging of the filter cloth in the dewaxing operations.

We have also found that the substances to be oxidized may be efficiently oxidized to produce wax separation aids by the use of hydrogen peroxide. The oxidation with hydrogen peroxide may be carried out advantageously in the presence of a stream of air or oxygen while maintaining the charge at an elevated temperature. The hydrogen peroxide may be added continuously to the charge as a liquid solution while maintaining the charge at an elevated temperature. Preferably, air is simultaneously introduced into the heated charge while adding the hydrogen peroxide. If desired, air may be passed through a separate vessel containing hydrogen peroxide and the activated air or oxygen thence passed into the heated charge. The temperature to which the charge is heated will depend upon the nature

of the particular charge to be oxidized. Paraffins, for example, may be satisfactorily oxidized at a temperature between 350 to 400° F. The use of paraffins oxidized with hydrogen peroxide is advantageous with respect to the color of the oxidized wax obtained. Hydrogen peroxide, in addition to being an effective oxidizing agent exerts a bleaching action on the wax producing a very pale wax which does not impair the color of the dewaxed oil when employed as a wax separation aid.

The oxidation reaction with air, oxygen or ozone or with hydrogen peroxide may be aided when the oxidation reaction is carried out in the presence of catalysts. Catalysts which may be employed for this purpose are metal chlorides, such as the chlorides of iron, zinc, tin, aluminum, metal soaps such as the naphthenates (oleates, stearates, ricinoleates, palmitates) of sodium, copper, magnesium, aluminum cobalt and iron.

In carrying out our invention, a small amount, i. e. 0.3 to 1% by volume of the wax separation aid is mixed or dissolved in the wax-bearing oil after which the mixture is chilled to a sufficiently low temperature to precipitate or solidify the wax in the oil. The solidified wax may then be separated from the chilled mixture by settling, centrifuging or filtering. The added wax separation aid will be precipitated and removed with the wax. If desired, the wax separation aid may be first mixed or dissolved at an elevated temperature such as, for example, about 350° F. in a small quantity of the waxy distillates to be dewaxed. The concentrated solution may then be added to the waxy distillates in such an amount so as to incorporate the desired amount of the wax separation aid.

Better results will be obtained when adding as wax separation aid such oxidized waxes as are produced from the same types of oil as the oil to be dewaxed. Thus, if it is desired to dewax an S. A. E. 20 waxy stock, it is preferable to employ an oxidized wax which was recovered from an S. A. E. 20 waxy stock; if it is desired to dewax an S. A. E. 50 oil, superior results will be obtained by employing an oxidized S. A. E. 50 wax. Likewise, when dewaxing S. A. E. 70 stocks, an oxidized S. A. E. 70 wax should be employed. The reason for this phenomenon is not definitely understood, but we have found that by employing the oxidized wax from the same type oil to be dewaxed, better results will be obtained with respect to the yield of oil, filter rate and quality of the wax.

It is preferable to employ as a wax separation aid, the wax which is removed from the same oil and which is oxidized. This means that the wax removed from the oil will contain a small amount of oxidized wax which was added to the oil to be dewaxed. This mixture is then oxidized and employed for aiding in the wax separation of further quantities of the same oil. By this procedure, better results will be obtained due to the fact that the oxidized wax employed as a wax separation aid in dewaxing oils will produce a wax which will have a lower oil content and thus the separated wax will oxidize into a wax separation aid having superior wax modifying properties than one containing large amounts of oil.

It will be observed that when referring to an S. A. E. 20, 50, 70, etc. waxy stock, we mean that the waxy distillate will yield upon complete refining, such as after separating the wax and low grade lubricating oil fraction such as those which are soluble in selective solvents such as liquid sulfur dioxide and the like, an oil corresponding to the range of viscosities covered in the S. A. E. designation is employed. By an S. A. E. 20, 50, 70, etc. wax, we mean a wax which is separated from the waxy distillate having the particular S. A. E. designation after dewaxing and selective solvent extraction.

In many cases, it is desirable to dilute the mixture of wax-bearing oil and wax separation aid with a suitable diluent prior to the chilling step in order to render the oil fluent at the dewaxing temperature. As diluents for the wax-bearing oil, we may employ liquefied normally gaseous hydrocarbons such as ethane, ethylene, propane, propylene, butane, butylene or mixtures thereof, light hydrocarbons such as pentane, hexane, heptane octane, nonane, or hydrocarbon fractions such as naphtha, gasoline, kerosene or gas oil. We may also employ such diluents as acetone, mixtures of acetone and benzol, ethyl alcohol, propyl alcohol, butyl alcohol, methyl ethyl ketone, diethyl ketone, methylpropyl ketone, ethylpropyl ketone, cyclohexanone, normally gaseous and normally liquid ethers, methyl chloride, dichlorethylene or trichlorethylene or mixtures of these materials with the aforementioned hydrocarbons.

The use of a liquefied normally gaseous diluent such as liquid propane is preferred since in addition to having the property of retaining less wax in solution at low temperatures, it may be employed to produce the necessary degree of refrigeration to precipitate the wax from the solution by vaporizing a portion of the liquefied normally gaseous material from the diluent oil under reduced pressure.

While the foregoing is specifically directed to the addition of extraneous wax separation aids to oils to be dewaxed, we have also discovered that the dewaxing characteristics of oils may be improved by oxidizing the stock prior to chilling and dewaxing. Thus, by subjecting the oil to be dewaxed to the action of air, oxygen or ozone or even hydrogen peroxide, the wax separation aids may be produced in situ. While this procedure is not to be preferred over the previous method of adding a small amount of the oxidized wax separation aid, since it involves the necessity of oxidizing the entire charge of oil to be dewaxed, it is nevertheless within the scope of our invention.

It is thus an object of our invention to improve dewaxing characteristics of wax-containing oils by adding a small quantity of an oxidized wax to the oil to be dewaxed.

A further object of our invention resides in the use of oxidized petroleum fractions which were either substantially free from wax or contain large or small quantities of wax prior to their oxidation, such materials being added in sufficient quantities of wax-containing oils to improve their dewaxing characteristics.

Another object of our invention resides in a process for separating wax from oils by first oxidizing the wax-containing oil and then separating the wax from the oxidized oil.

It is an important object of our invention to produce an oxidized wax from crude waxes by first subjecting the wax to precipitation and then oxidizing the purified wax with air or other oxidizing gas.

It is a further object of our invention to accomplish oxidation by subjecting the material to be employed as a wax separation aid for the oil to be dewaxed to the action of an oxygen-containing

gas such as air, oxygen or ozone at an elevated temperature. It is also an object of our invention to effect the oxidation by means of such liquids as hydrogen peroxide, preferably by agitating the material to be oxidized with air. It is a further object of our invention to effect the oxidation in the presence of catalysts. It is a further object of our invention to separate as much of the oil contained in slack waxes as is possible prior to oxidation to produce the wax separation aid.

A further object of our invention resides in dissolving the wax-bearing oil to be dewaxed and oxidized wax separation aid or the oxidized oil to be dewaxed in a suitable diluent, chilling the mixture and separating the precipitated wax from the diluted oil. The use of a liquefied normally gaseous hydrocarbon such as propane is preferred because the necessary degree of refrigeration may be accomplished by vaporizing a portion of the diluent under reduced pressure.

It is a further object of our invention to employ as a wax separation aid, an oxidized wax produced from oils of the same character as the oil to be dewaxed.

Many specific objects, features and advantages of our invention will become apparent to those skilled in the art as the description of our invention proceeds in connection with specific examples given below which are not considered as limiting our invention but merely illustrative of methods of carrying it out.

Examples of use of oxidized scale wax

A 6 gallon charge of crude scale wax having a melting point of 123° F. was heated in a still to a temperature of 450° F. after which air was introduced into the charge, first at a rate of 0.27 cu. ft. per minute for approximately 72 hours and then at a rate of 0.40 cu. ft. per minute. The oxidized wax upon completion of the oxidation for 94 hours had an acid number of 7, a saponification number of 65, a melting point of over 300° F. and a specific gravity at 60° F. of 0.865.

The oxidized crude scale wax was mixed in a closed vessel with an S. A. E. 20 waxy lubricating oil distillate obtained by the vacuum distillation of a Santa Fe Springs crude oil. The oxidized crude scale wax was mixed with the waxy distillate at a temperature of about 300° F. and in an amount as to incorporate approximately 0.3% by volume into the waxy distillate. The resulting mixture was then mixed with approximately 4.5 volumes of liquid propane under superatmospheric pressure. The temperature of the resulting mixture was about 130° F. and the pressure was about 250 lbs. per sq. in. The mixture of waxy lubricating oil, propane and wax modifier was then chilled externally at a rate of approximately 3° F. per minute to aproximately —40° F., the refrigeration being accomplished by vaporizing under gradually reduced pressure, a portion of propane in a jacket surrounding the chilling vessel. The chilled slurry of propane, lubricating oil, solidified wax and wax modifier was filtered under a pressure of about 25 lbs. per sq. in. to effect the separation of the precipitated wax and wax modifier from the propane solution of the lubricating oil. The filter rate was 4.9 gallons per square foot of filter surface per hour based on the propane free oil. It will be observed that all determinations of filter rates discussed herein are based on the dewaxed oil after separating the propane therefrom. The filtrate was then distilled to remove the propane. Approximately 81.7% by volume of dewaxed oil was recovered having a pour point of —5° F. The separated wax had a melting point of 130° F. as determined by the Galician method.

In another run employing 1% of the above type wax modifier oxidized 72 hours at 450° F. on another portion of the same oil which was dewaxed under the same conditions as above, except that a propane to oil ratio of 2 to 1 was employed, a filter rate of approximately 3.0 gal./sq. ft./hr. was obtained. Approximately, 80.8% by volume of oil was recovered having a pour point of —10° F. The separated wax had a melting point of 128° F.

The results obtained in the foregoing examples indicated that this type of wax modifier is quite active in dewaxing oils when compared with a blank run wherein no wax modifier is employed. The blank run on the same oil and using same amount of propane and carried out under the same dewaxing conditions as above, showed that only 65.7% by volume of oil was obtained having a pour point of —5° F. The wax separated from the oil had a melting point of only 115° F.

A refined scale wax having a melting point of 123° F., that is, a crude scale wax which was recovered from an S. A. E. 10 waxy distillate and which was deoiled and treated with sulfuric acid, neutralized with alkali and clay treated, was oxidized with pure oxygen at a temperature of 450° F. for approximately 22 hours. The oxidized wax had an acid number of 10.4, and a saponification number of 106.3.

Propane dewaxing runs on an S. A. E. 20 waxy vacuum distillate according to the procedure described in the first example, employing 0.20, 0.50 and 1.00% by weight of the oxidized wax modifier showed filter rates of 8.3, 8.0 and 7.5 gal./sq. ft./hour, respectively, based on the viscous oil, yields of dewaxed oil of 81.9, 85.0 and 85.9% by volume, respectively, each having a pour point of —5° F. and separated waxes of 128, 131 and 131° F. melting point, respectively.

In another run, 1% by weight of the above oxidized refined scale wax was employed as a wax separation aid for dewaxing an S. A. E. 50 waxy distillate according to the propane dewaxing method described in the first example, employing, however, two volumes of propane to one of the oil. A yield of 80.5% by volume of dewaxed oil was obtained having a pour point of —5° F. at a filter rate of 31.1 gal./sq. ft./hr. The melting point of the wax separated was 140° F. according of the Ubbelohde method.

Example of use of oxidized S. A. E. 50 wax

A slack wax obtained by dewaxing an S. A. E. 50 waxy distillate which was produced by the vacuum distillation of a Santa Fe Springs crude oil was first deoiled by dissolving it in propane and chilling the solution to reprecipitate the wax and recovering the precipitated wax by filtration. The deoiled wax was subsequently given a heavy acid treatment and then wet neutralized preparatory to oxidation with pure oxygen. The acid treatment was carried out with 20 lbs. per barrel of 103% sulfuric acid at a temperature of 210° F. It was neutralized with 35% of 5% caustic soda solution at 210° F. and water washed with three dumps of 100 volume percent each of water. The treated wax had a melting point (Galician) of 150° F. This material was then oxidized at a temperature of 450° F. with pure oxygen for approximately 10 hours. The finished product had an acid number of 16.0 and a saponification number of 82.2.

When an S. A. E. 20 vacuum distillate was dewaxed in the presence of 1% of this material according to the propane dewaxing method outlined in the first example, a yield of 83.0% by volume of —10° F. pour point oil was obtained and a wax was recovered having a melting point (Galician) of 130° F. The filter rate was approximately 6.6 gal./sq. ft./hr.

It is significant to note that when the unoxidized wax was employed as a dewaxing aid in dewaxing of the same character oil, according to the same procedure, the yield of oil obtained was only 69.2% by volume. This does not represent sufficient improvement over the blank run described in the first example to indicate appreciable modifier action on the part of the unoxidized S. A. E. 50 wax.

In another run, crude slack wax was obtained from a Santa Fe Springs S. A. E. 50 waxy distillate having a melting point of 131° F. as determined by the Ubbelohde method and an oil content of 50.3% as determined by the acetone-benzene method. The latter method consists in extracting the oily wax with a mixture of 65% by volume acetone and 35% benzene in an amount of 50 ml. of solvent to 1 gram of wax and separating the wax at —10° F. by filtration. The amount of oil dissolved by the acetone-benzene mixture represents the amount of oil originally present in the wax. The aforementioned slack wax was acid treated first with 30 lbs. and then with 45 lbs. of 98% sulfuric acid per barrel of wax at a temperature of 145 to 165° F. The acid treated wax was then washed at 175 to 200° F. with 20% of 2.5° Baumé caustic soda, followed by water washing and then blowing bright with air at 240° F. A neutral wax was recovered having an oil content of 35.7% and a melting point (Ubbelohde) of 138° F. This material was then oxidized by blowing it with air at a temperature of 450° to 500° F. for about 26 hours, samples being taken at the end of 16, 24 and 26 hours of blowing with air.

Test runs in dewaxing an S. A. E. 20 vacuum distillate obtained from Santa Fe Springs crude oil were made employing 1% of each of the oxidized samples. Dewaxing was carried out in accordance with the procedure outlined in the first example. Yields of dewaxed oil of 81.2, 81.9 and 83.0% by volume having pour points of —5° F., —5° F. and —10° F., respectively, were obtained when employing the 16, 24 and 26 hour air blown samples, respectively. The melting points (Ubbelohde) of the separated waxes were 125, 127 and 125, respectively, and the filter rates were 8.1, 10.6 and 11.1 gal./sq. ft./hr., respectively.

Another portion of the above oxidized acid treated S. A. E. 50 wax was added to an S. A. E. 50 waxy distillate in amount as to incorporate 0.5% by weight of the oxidized wax. The oil was dewaxed according to the propane dewaxing method described above employing, however, a volumetric ratio of two volumes of propane to one of the oil. A yield of dewaxed oil of 84.0% by volume was obtained having a pour point of —15° F. The melting point (Ubbelohde) of the wax separated was 145° F. The filter rate was 5.8 gal./sq. ft./hr.

From the foregoing example compared with the example of dewaxing the S. A. E. 50 stock employing the S. A. E. 10 oxidized wax as a wax separation aid, it will be observed that better yields and filter rates were obtained by using the oxidized S. A. E. 50 wax on the S. A. E. 50 waxy distillate. However, the S. A. E. 10 oxidized wax was more effective as a wax separation aid in dewaxing the S. A. E. 20 waxy distillate. This indicates that the nearer the oxidized wax resembles the type of wax in the oil to be dewaxed, the better the yields and filter rates obtained.

In order to determine the effect of oil contained in this type of wax, i. e. wax separated from S. A. E. 50 vacuum distillates, two acid treated waxes and containing, respectively, 59.6% and 11.6% of oil as determined by the acetone-benzene method were separately oxidized with pure oxygen. The oxidation on the two waxes was carried under substantially identical conditions. Each wax was oxidized for 22 hours at a temperature of 450° F. The wax which contained 59.6% of oil had an acid number of 12.0 and a saponification number of 16.3 after oxidation, while the wax of low oil content had an acid number of 15.2 and a saponification number of 85.1.

When S. A. E. 20 vacuum distillates were dewaxed with 1% of the above wax separation aids and according to the procedure set forth in the first example, about 82.3% by volume of dewaxed oil having a pour point of —5° F. wax recovered when employing the oxidized wax which had the lower oil content. The wax separated from the oil had a melting point (Galician) of 129.5° F. The results obtained employing the oxidized wax of higher oil content were not quite as remarkable, the yield of oil being 70.1% by volume of a 5° F. pour point and the melting point of the wax separated was only 119° F.

The above results indicate that it is desirable to deoil the wax to at least a 40% oil content prior to oxidation with the oxidizing gas.

In another run the slack wax obtained from an S. A. E. 50 waxy distillate was deoiled by extraction with a mixture of 75% benzene and 25% acetone. The deoiled wax had a melting point (Ubbelohde) of 167° F. The deoiled wax was oxidized in a stream of air and hydrogen peroxide for 8¾ hours at a temperature of 380 to 420° F. The finished modifier had an acid number of 95, a saponification number of 238 and was quite light in color.

The potency of the above described modifier is evidenced by the fact that when the S. A. E. 20 vacuum distillates heretofore described was propane dewaxed, using 0.5% of the wax separation aid according to the procedure herein set forth, a yield of dewaxed oil of 86.9% by volume was obtained having a pour point of 0° F. The filter rate was 11.5 gal./sq. ft./hr. The wax recovered had a melting point (Ubbelohde) of 128° F.

Examples of use of oxidized S. A. E. 20 wax

A slack wax recovered from an S. A. E. 20 waxy distillate obtained by the vacuum distillation of a Santa Fe Springs crude oil by the propane dewaxing method employing asphalt as a filter aid was deoiled by the acetone-benzene method described above to an oil content of approximately 8.3%, after which it was acid treated and wet neutralized. The treated wax had a melting point (A. S. T. M. method) of 138.3° F. The material was then oxidized with pure oxygen at a temperature of 450° F. for 22 hours. The finished product had an acid number of 6.7 and a saponification number of 183.5.

Employing approximately 1% of this wax modifier as a dewaxing aid in the dewaxing of an S. A. E. 20 waxy distillate according to the propane dewaxing method described in the first ex-

ample with the exception that a higher filter pressure of 50 to 100 lbs./sq. in. was employed, a yield of 83.7% by volume of dewaxed oil having a pour point of —5° F. was obtained. The filter rate was 3.8 gal./sq. ft./hr. and the melting point (Galician) of the wax separated was 130° F.

In order to determine the effect of the oil content of oxidized S. A. E. 20 wax as a wax modifier, a mixture of 50% of the above described deoiled and acid treated wax obtained from the S. A. E. 20 waxy distillate and 50% of dewaxed S. A. E. 20 oil was oxidized with pure oxygen at 450° F. for 22 hours.

When employing 1% of the above oxidized mixture to dewax an S. A. E. 20 waxy distillate, it was observed that the yield was rather low, i. e. 70.6% by volume. The filter rate, however, was 4.2 gal. per sq. ft./hr. and the pour point of dewaxed oil was —10° F. The melting point (Galician) of the wax removed from the oil was 118° F. These figures would indicate that while the use of an oxidized S. A. E. 20 wax having a large amount of oil is not as good as a deoiled oxidized wax, it has considerable properties as a wax modifier. When employing oxidized wax modifiers of the S. A. E. 20 type, it is quite desirable to reduce the oil content to approximately 10–20% prior to oxidation.

In addition to the foregoing oxidized waxes as dewaxing aids, we have observed that oxidized petrolatum which is a wax recovered from wax containing residues and oxidized waxes obtained from S. A. E. 70 waxy oil distillates possess remarkable potency in the dewaxing of petroleum oils. These waxes may or may not be deoiled prior to oxidation to render them active as wax modifiers. However, it has been found that the lower the oil content of the wax, the more active will be the wax as a dewaxing aid after oxidation.

We have also discovered that oxidized waxes of the natural type are also effective in improving the dewaxing characteristics of wax-containing oils. Wax separation aids of this type include oxidized Montan wax, carnauba wax and beeswax.

We have also discovered that oxidized oils are also active in aiding dewaxing of petroleum wax containing fractions. An S. A. E. 70 dewaxed oil produced from a Pennsylvania type crude oil by blending bright stock and neutrals was partially oxidized by being exposed to the atmosphere for three months to a nearly continuous temperature of 340° F. under conditions of considerable agitation. The oxidized oil had an acid number of 1.40 and a saponification number of 19.

A propane dewaxing run, employing 1% of the oxidized material with S. A. E. 20 vacuum distillate was carried out according to the propane dewaxing method described in the first example. A yield of 79.6% by volume of dewaxed oil having a pour point of —5° F. was obtained. The filter rate was 7.3 gal./sq. ft./hr. The melting point (Galician) of the separated wax was 125° F.

While the above experiment was carried out with an oil oxidized for a long period of time, it is obvious that the material may be duplicated or improved by oxidizing the bright stock for a short time under more drastic conditions of oxidation. Also, similar results may be obtained by employing the oxidized petroleum fractions after solvent extraction with a selective solvent such as sulfur dioxide, phenol, nitrobenzol and the like.

In one case a 650° F. fire point (Cleveland open cup method) steam refined oil obtained from a Pennsylvania crude oil residuum from which wax was separated was oxidized for 22 hours at 450° F. with pure oxygen. The acid number of the oxidized oil was 5.3 and the saponification number was 73.0.

When 1% of the above oxidized material was employed as a wax separation aid in propane dewaxing an S. A. E. 20 vacuum distillate in accordance to the procedure outlined under the first example, a yield of dewaxed oil was obtained of approximately 80.8% by volume having a pour point of —10° F. The filter rate was 8.2 gal./sq. ft./hr. The melting point (Galician) of the wax separated was 128° F.

In another case, a Santa Fe Springs residual oil which was deasphalted by commingling the oil with 5 volumes of propane at 70° F. to precipitate the asphalt was oxidized after removal of propane with pure oxygen at a temperature of 450° F. for 22 hours. When employing 1% of this material as an aid in propane dewaxing an S. A. E. 20 vacuum distillate, excellent results were obtained with respect to yields of oil of desired pour point, filter rates and melting point of the separated wax.

We have also obtained improved filter rates by first oxidizing the wax containing oil to be dewaxed, that is, instead of adding oxidized wax to the oil to be dewaxed, the latter is subjected to an oxidation reaction and is subsequently dewaxed by chilling and filter. In one case, a wax containing lubricating distillate of S. A. E. 20 grade (from Santa Fe Springs crude) was air blown at a temperature of 300° F. for approximately 22 hours. The rate of air introduction was 6 liters per minute for a 7 liter charge, the air being first passed through a sulfuric acid trap to remove moisture contained in the air. The oil was then mixed at a temperature of 250° F. with liquid propane at a volumetric ratio of 8 volumes of propane to one of the oil. The mixture was then chilled to —35° F. by vaporizing propane under gradually reducing pressure until a pressure of 10 lbs. per square inch existed in the chilling vessel. The chilled mixture was then filtered under a pressure of less than 25 lbs. per square inch at —30° F. It was found that a filter rate of approximately 3.7 gal./sq. ft./hr. was obtained and a yield of dewaxed oil of 70.7% by volume having a pour point of 5° F. These figures indicate that by oxidizing the oil to be dewaxed superior results may be obtained over dewaxing oils without prior oxidation.

Reference to the hereinbefore mentioned Galician and Ubbelohde methods for determining the melting points of wax may be found in the book by Holde entitled "Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes", 1922, 2nd English Edition.

It will be observed that the foregoing description of our invention is not to be considered as limiting as many variations thereof may be made by those skilled in the art within the scope of the following claims.

We claim:

1. An oxidized wax produced from a wax-oil mixture containing less than approximately 40% oil, said oxidized wax having an acid number of about 15 and a saponification number of about 85.

2. An oxidized wax produced from a wax-oil mixture containing approximately 11.6% oil, said oxidized wax having an acid number of approximately 15 and a saponification number of approximately 85.

3. An oxidized wax produced from a wax hav-

ing a melting point of approximately 150° F., said oxidized wax having an acid number of approximately 15 and a saponification number of approximately 85.

4. An oxidized wax produced from a wax which has been separated from an S. A. E. 50 waxy lubricating oil distillate, said wax having a melting point of approximately 150° F. and said oxidized wax having an acid number of approximately 16 and a saponification number of approximately 82.

5. An oxidized wax produced from a wax which has been separated from an S. A. E. 50 waxy lubricating oil distillate by chilling said waxy lubricating oil distillate in the presence of a diluent and removing the wax from the chilled diluted oil, said separated wax having a melting point of approximately 150° F. after it has been deoiled and said oxidized wax having an acid number of about 16 and a saponification number of about 82.

6. A process for the production of oxidized wax from a wax-oil mixture containing a substantial amount of oil which comprises deoiling said wax to produce a wax of high melting point, treating said deoiled wax with acid, treating said acid treated wax with caustic alkali and subsequently oxidizing said treated wax with an oxygen-containing gas at a temperature of approximately 450° F.

7. A process for the production of oxidized wax from a wax-oil mixture containing a substantial amount of oil which comprises deoiling said wax to produce a wax of high melting point, treating said deoiled wax with acid, treating said acid treated wax with caustic alkali and without separation of all of the alkali from the wax oxidizing said treated wax with an oxygen-containing gas at a temperature of approximately 450° F.

8. A process for the production of oxidized wax from slack wax which comprises deoiling said slack wax to produce a wax of high melting point, treating said deoiled wax with sulfuric acid, washing said acid treated wax, treating said acid treated wax with caustic soda and subsequently oxidizing said treated wax with air at a temperature of approximately 450° F. to 500° F.

9. A process for the production of oxidized wax from a wax-oil mixture containing a substantial amount of oil which comprises extracting said wax-oil mixture with a solvent under conditions such that the oil is soluble but the wax is insoluble, separating the solution of oil and solvent from the wax, treating the solvent treated wax with acid and alkali and subsequently oxidizing said treated wax with an oxygen-containing-gas at a temperature of approximately 450° F.

10. A process for the production of oxidized wax from a wax-oil mixture containing a substantial amount of oil which comprises treating said wax oil mixture with acid and thereby removing a substantial amount of oil from said wax-oil mixture, treating said acid treated oil with an alkali to neutralize the acidity of said acid treated wax-oil mixture and subsequently oxidizing said treated wax with an oxygen-containing-gas at a temperature of approximately 450° F.

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CERTIFICATE OF CORRECTION.

Patent No. 2,119,940. June 7, 1938.

DONALD E. CARR, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 51, for the numeral "31.1" read 3.1; line 54, for "Example" read Examples; page 6, second column, line 42, for "reducing" read reduced; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of August, A. D. 1938.

Henry Van Arsdale

(Seal)

Acting Commissioner of Patents.

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