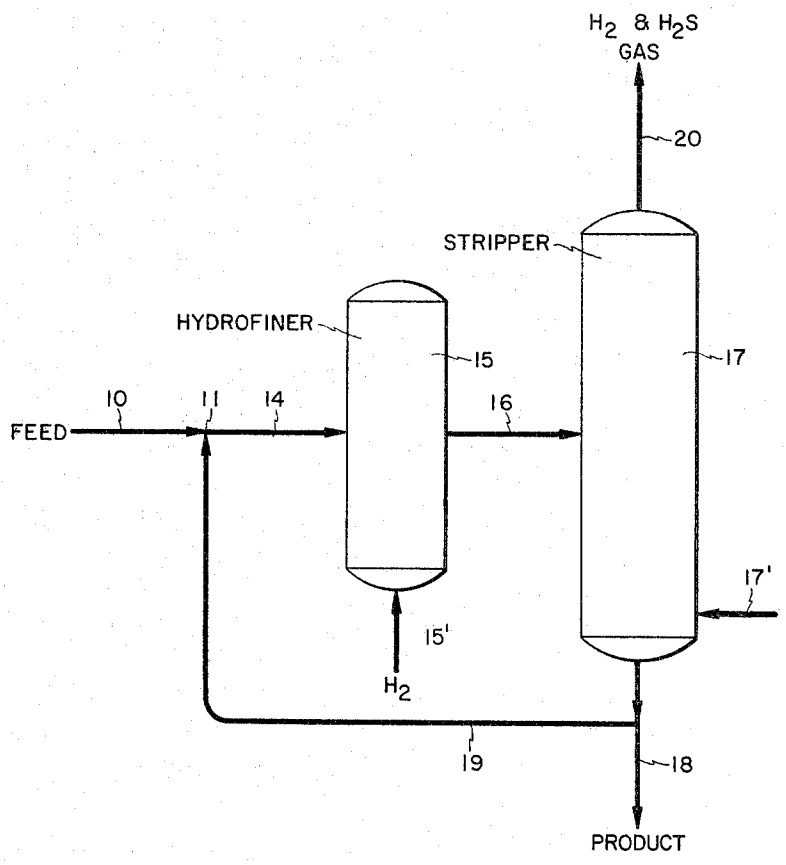
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HYDROFINING OF MICROCRYSTALLINE WAX

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HYDROFINING OF MICROCRYSTALLINE WAX

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This invention relates to a process of refining hydrocarbon waxes that are derived from petroleum. More particularly, this invention is concerned with a process of making high molecular weight wax products which have high laminating strength, excellent color, odor and stability. The present invention is concerned with high molecular weight wax recovered from residual crude oil fractions boiling above about 900° F. These waxes are known as microcrystalline waxes and are used in the manufacture of many products, such as food containers, waxed papers and coating materials where it is desired that they be impervious to moisture. Furthermore, recent uses for these devices have been found in a field of explosives and electrical devices.

Microcrystalline wax has heretofore been made by deasphalting a residual crude oil to remove substantially all of the asphaltic materials, dewaxing the deasphated oil and deoiling the wax obtained. Traditionally, this wax has been characterized by poor odor, color stability characteristics, and most important of all the fact that it quickly poisoned hydrofining catalysts. To improve these characteristics the wax was contacted with bauxite, alumina, clay or other adsorbent material. It has been recognized that these poor characteristics were generally caused by polycyclic condensed aromatic hydrocarbon oil compounds in a concentration of above about 4.0% by weight within the wax which were not completely removed during the dewaxing or deoiling steps.

Treating the wax with hydrogen by means of conventional hydrofining operations has resulted in considerable improvement in the above-mentioned wax characteristics. However, this process has presented one serious problem; catalyst life has been short and this has tended to make the process totally inexpedient. Attempts to modify the conditions of the hydrofining process so as to extend the catalyst life have resulted in products which were unsatisfactory with respect to strength and odor.

It has now been found that the most active catalyst deactivants in the feed are the multi-ring condensed aromatic hydrocarbons, including the 2 and 3 condensed ring aromatic hydrocarbons, such as naphthalene and anthracene and their derivatives, that is to say naphthalene and antharcene derivatives. If the concentration of these deactivating materials exceeds about 4% by weight, the hydrofining catalyst is rapidly deactivated. Concentrations of about 4% by weight and below are satisfactory. According to the present invention, it has been found that the concentration of 2 and 3 condensed ring aromatic hydrocarbons can be maintained at about 4% by weight or lower by diluting the wax feed to be refined with wax which has previously been hydrofined, the hydrofined product being substantially below the 4% by weight limit of 2 and 3 condensed ring aromatic hydrocarbons and their derivatives.

Multi-ring or condensed ring aromatics are partially converted, during hydrofining, to aliphatic compounds. These aliphatics do not have a deleterious effect on hydrofining catalysts and, therefore, their presence is not undesirable. Consequently, the hydrofined product itself may be used as a diluent. Product which has been passed through a hydrofiner and is low in 2 and 3 condensed ring aromatic hydrocarbon concentration is recycled back into the wax feed stream and serves to dilute the stream so that the concentration of 2 and 3 condensed ring aromatics and their derivatives in the stream never reaches above about 4% by weight of the entire stream.

It is, therefore, the primary object of this invention to produce a microcrystalline wax product which has high laminating strength, good color and odor by a process of making said wax which does not poison the hydrofining catalyst. It is also the object of this invention to provide an improved hydrofining process in which the catalyst is maintained at a high level of activity for a heretofore unattainable length of time.

These and other related objects are attained in accordance with the present invention by subjecting a microcrystalline wax petrolatum, which has been recovered from crude oil boiling above about 900° F. in a conventional dewaxing step, to a hydrofining operation. Part of the product obtained from the hydrofining is recycled in order to keep the 2 and 3 condensed ring aromatic hydrocarbon concentration in the oil feed below about 4% by weight.

The catalyst of the present invention consists essentially of cobalt oxide and molybdenum oxide possibly combined as cobalt molybdate on a solid adsorbent carrier. However, other catalysts such as the nickel molybdate family may be used. The catalyst is a well-known hydrofining catalyst and can be purchased commercially. The carrier may be selected from the many materials, such as adsorptive alumina, bauxite, promoted alumina and the like, which are usually employed for this general purpose. A material which is particularly effective is alumina. It is preferred that this catalyst contain about 2 to 5 wt. percent cobalt oxide and 8 to 15 wt. percent molybdenum oxide. About 3.6 wt. percent cobalt oxide and 12.5 wt. percent molybdenum oxide have been found to be especially effective.

The catalyst, as it is employed in the present invention, may be in the form of a fixed bed, a fluidized bed or a moving bed. It is contemplated that the process is best carried out by utilizing it in the form of a fixed bed. In this case it is desired that the catlyst have a particle size of from about 1/16" to 1/2" and preferably about 1/16" to 1/4". Particles of this nature may be prepared by conventional crushing, pilling and extruding processes or by other well-known techniques. It has been found that a catalyst in the form of 1/16" extrudates affords particularly satisfactory operation.

The feed to be treated according to the present invention is commonly referred to as soft microcrystalline wax petrolatum. This feed is a black to brown colored gelatinous, oily, translucent, semisolid, amorphous mass whose consistency varies with the temperature. It has a specific gravity of 0.815 to 0.880 at 60° C. and a melting point of 38–60° C. Its chief constituents are hydrocarbons of the methane series and of the olefin series. It is soluble in a variety of organic solvents including ether and carbon disulfide and is totally insoluble in water. Derivation is from the fractional distillation of still residues from the steam distillation of paraffin-base petroleum, or from steam-reduced amber crude oils.

It should be noted that, although this invention will produce satisfactory results with raw microcrystalline wax, it may be utilized where one wishes to first subject the microwax to a mild deasphalting. By mild deasphalting is meant deasphalting to produce a wax of 90–100% yield. The deasphalting solvent that is used is propane. Ratios of propane to wax feed of 10/1 to 15/1 may be used. Deasphalting temperatures between 130° and 180° F. may be utilized. In this manner deasphalted wax yields of 90 to 99% are obtained.

Before entering into a more detailed description of the present invention, it is well to have in mind the procedures that are usually employed for evaluating a hydrocarbon wax insofar as its color, odor, stability and carbonizable

matter content are concerned. Thus, the color of a wax is generally evaluated by either the Saybolt or Tag-Robinson method of color determination both of which are standard tests in the petroleum industry. Descriptions of these methods can be found in the "New and Revised Tag Manual for Inspectors of Petroleum" published by the C. J. Tagliabue Manufacturing Company.

The odor characteristics of such waxes are determined in various ways. In general, either wax shavings or vapors from the wax are sniffed by a committee composed of a minimum of three persons. The wax is then rated by each committeeman using a number system. The wax is rated on both odor type and intensity of the odor.

The FIGURE is a schematic representation of a preferred embodiment of apparatus adapted to practice the instant invention.

Turning to the figure, the reference numeral **10** represents a line through which a raw or crude microcrystalline wax feed is passed. The wax may be light yellow to amber colored. It is gelatinous, oily, translucent, semisolid, amorphous mass. The wax has a specific gravity between 0.815 and 0.880 at 60° C. and a melting point of 38–60° C. It is comprised mainly of hydrocarbons of the methane and olefin series having more than 16 carbon atoms per molecule. At reference point **11**, this line **10** is joined by a second stream from line **19** which contains hydrofined microcrystalline wax product. The two streams together are directed into line **14** which leads into hydrofiner **15**.

Within hydrofiner **15** is a solid catalyst consisting of cobalt oxide and molybdenum oxide either as a mixture or combined as cobalt molybdate on a solid adsorbent carrier which may be adsorptive alumina, bauxite or any of a variety of well-known carriers employed for this general purpose. The catalyst contains about 2 to 5 wt. percent cobalt oxide and 8 to 15 wt. percent molybdenum oxide, about 3 to 6 wt. percent cobalt oxide and 12.5 wt. percent molybdenum oxide is particularly effective.

Temperatures within the hydrofiner may be in the range of 400–700° F.; preferably a temperature of about 600° F. is utilized. Pressures of 400–3000 p.s.i.g. may be utilized; a preferred pressure would be in the range of 500–1000 p.s.i.g. Wax feed rate may vary between 0.5–2.0 v./hr./v., depending on operating conditions. Hydrogen is introduced into hydrofiner **15** through line **15'** at the rate of 50–5000 s.c.f./b. of wax feed with 500 s.c.f./b. of feed being preferred. Effluent from hydrofiner **15** containing hydrogen, hydroformed wax and hydrogen sulfide is passed through line **16** into stripping tower **17**. Stripping gas such as steam is passed into the lower portion of stripping tower **17** through line **17'** for upward flow countercurrent to the wax to strip out hydrogen and hydrogen sulfide.

The hydrofined wax is removed from stripping tower **17** through line **18**. A portion of the wax is removed from line **18** as product and another portion is passed through line **19** to point **11** where it is joined with the crude microcrystalline wax feed in line **10**. Hydrogen sulfide gas and excess hydrogen are removed overhead through line **20**.

The amount of hydrofined wax product which is to be recycled may be calculated from the following formula and solving for R:

$$Z=\frac{(X)(F)+(Y)(R)}{F+R}$$

Z=wt. percent of 2 and 3 condensed ring aromatic hydrocarbons in the total wax feed

F=bbl. of raw wax feed

X=wt. percent 2 and 3 condensed ring aromatic hydrocarbons in the raw wax feed

R=bbl. of recycle (hydrofined wax product)

Y=wt. percent 2 and 3 condensed ring aromatic hydrocarbons in the recycle stream

Thus, in the case of a deasphalted wax feed containing 7.6 wt. percent of 2 and 3 condensed ring aromatic hydrocarbons in the raw wax feed and 1.8 wt. percent of 2 and 3 condensed ring aromatic hydrocarbons in the hydrofined wax product, 164 barrels of hydrofined wax product as recycle would be needed to maintain a level of about 4% by weight of 2 and 3 condensed ring aromatic hydrocarbons. The recycle percentage would be

$$\frac{164}{100}\times 100 \text{ or } 164\%$$

Utilizing a 94% yield deasphalted feed, X or the wt. percent of 2 and 3 condensed ring aromatic hydrocarbons in the raw deasphalted wax feed would equal 5.2%. This would reduce the recycle percentage to 55%.

The present invention may be used in liquid phase hydrofining where a flooded bed of catalyst is used and the hydrogen absorbed by the feed is the hydrogen used as in Berlin et al. Serial No. 25,716, filed April 29, 1960, as then the recycled hydrofined wax product provides additional absorbent for absorbing more hydrogen per unit amount of raw wax feed impurities.

One obvious advantage to be gained from this method is that since product is being used as a diluent no separate step is required to remove the diluting material.

Example 1

In a specific embodiment of this invention, a sample of Panhandle dual purpose microcrystalline wax obtained from a lube oil fraction boiling above about 1000° F. and having the following inspection:

Congealing point, ° F.	145
Oil content (approx.), weight percent	0.4
Sulphur content	0.19
Color, Tag-Robinson	3/4

was utilized. The sample was divided into two parts. One part was directed into an apparatus similar to that illustrated by the figure. 100 volumes of raw wax feed were directed through line **10** and at point **11** the raw wax feed was joined by 164 volumes of hydrofined microcrystalline wax product. The raw wax feed contained 7.6% of 2 and 3 condensed ring aromatic hydrocarbons and the hydrofined microcrystalline wax product contained 1.8% of 2 and 3 condensed ring aromatic hydrocarbons. Therefore, the combined wax feed contained about 4.0% of 2 and 3 condensed ring aromatic hydrocarbons.

The combined wax feed was hydrofined over a catalyst which consisted of 3.6 wt. percent cobalt oxide and 12.5 wt. percent molybdenum oxide supported on an alumina base at about 600° F., 900 p.s.i.g. with 500 s.c.f./b. of 100% hydrogen treat gas. Recycle hydrofined wax rate was about 164% based on fresh feed. This resulted in a wax feed which contained about 4% by weight of 2 and 3 condensed ring aromatic hydrocarbons. The wax produced had excellent odor and strength and a 16 Tag-Robinson color or better for more than 550 hours of operation with no loss in catalyst activity.

Example 2

The second portion of the Panhandle microcrystalline wax was subjected to identical conditions as in Example 1 except that no recycle was employed. Therefore, the raw wax feed entered hydrofiner **16** with 7.6% of 2 and 3 condensed ring aromatic hydrocarbons. Initially the microwax product recovered had color, odor and strength equivalent to the first portion. However, after about 70 hours the wax produced was of a vastly inferior quality. Product color dropped below the specification level of 12 TR. Thus, it was indicated that the catalyst had deactivated.

Example 3

A Panhandle wax similar to that utilized in Example 1 is subjected to identical conditions as the first example except that the percentage of 2 and 3 condensed ring aromatic hydrocarbons in the combined feed is main-

tained at a level of 4.8% by weight. Since the feed has a concentration of 7.6%, the hydrofined wax product has a concentration of 2.16% of 2 and 3 condensed ring aromatic hydrocarbons. The amount of hydrofined wax product to be recycled is 106%. For 100 hours the catalyst is sufficiently active to produce a product which is 12 TR or better. After this, the product falls below 12 TR. It should be understood that the catalyst is not rendered totally inoperative, but is not able to produce a product having a TR of 12 or better. At this point, i.e. below 12 TR, it is considered unsatisfactory for most uses and the catalyst is then considered to be essentially inoperative.

It is understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. A method of refining a raw microcrystalline wax so that is has at least a 12 TR color characteristic which comprises combining the said raw microcrystalline wax with a stream of hydrofined microcrystalline wax in such proportions that the concentration of 2 and 3 condensed ring aromatics in the combined wax is a maximum of about 4% by weight, catalytically hydrofining the said combined wax feed containing a maximum of about 4% of 2 and 3 condensed ring aromatics, dividing the hydrofined wax in two portions, recycling one portion of said hydrofined microwax into a stream of the said raw microwax in such proportion that the said combined stream contains a maximum of about 4% by weight of 2 to 3 condensed ring aromatics, and recovering the said remaining portion of hydrofined microwax as product.

2. The method of claim 1 where the said catalyst contains 2 to 5 wt. percent cobalt oxide and 8 to 15 wt. percent molybdenum oxide supported on an alumina carrier

3. The method of claim 1 where the said hydrofining takes place at a temperature of 400° to 700° F., a pressure of 400–3000 p.s.i.g., and a hydrogen feed rate of 50–5000 s.c.f./b. of wax feed.

4. The method of claim 1 where the said raw microcrystalline wax is mildly deasphalted before being combined with the said hydrofined wax.

5. A method of refining a high molecular weight microcrystalline wax which comprises combining a raw microcrystalline wax with a hydrofined microcrystalline wax in such proportions that the concentration of 2 and 3 condensed ring aromatic hydrocarbons in the combined wax feed is a maximum of about 4% by weight, catalytically hydrofining said combined wax feed which contains a maximum of 4% by weight of 2 and 3 condensed ring aromatic hydrocarbons, removing a portion of the hydrofined wax as product and recycling the other portion of said hydrofined wax for admixture with said raw microcrystalline wax.

6. The method of claim 5 where the hydrofining catalyst comprises 2 to 5 wt. percent cobalt oxide and 8 to 15 wt. percent molybdenum oxide supported on an alumina carrier.

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