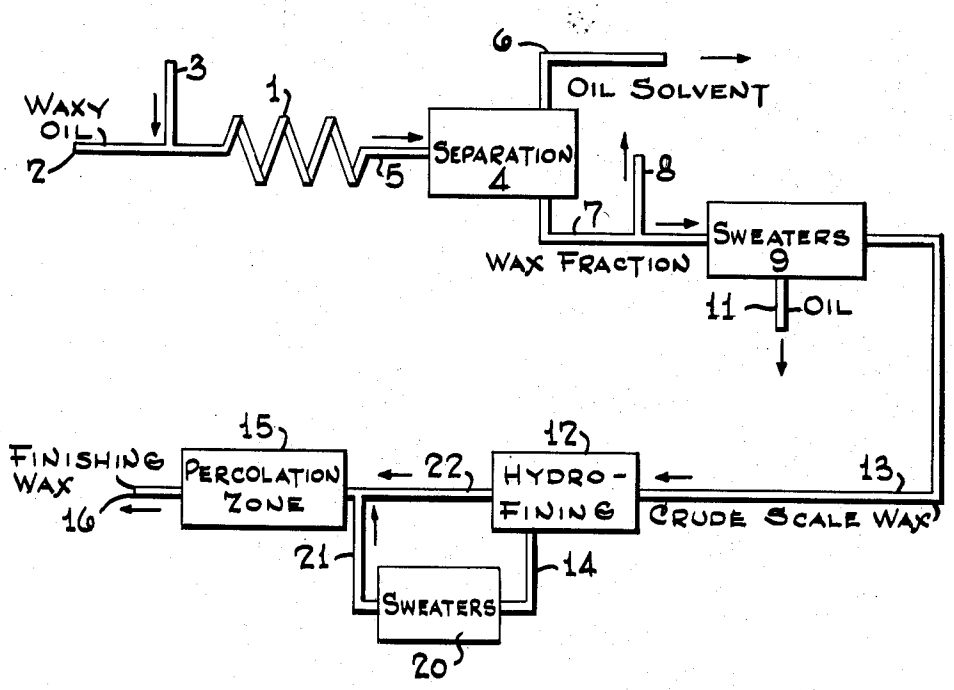
Nov. 10, 1953 S. F. PERRY ET AL 2,658,856

PROCESS OF REFINING AND STABILIZING WAXES

Filed July 27, 1951



Stephen F. Perry Inventors
Randolph M. Bailly
By W. O. Hilman Attorney

Patented Nov. 10, 1953

2,658,856

UNITED STATES PATENT OFFICE

2,658,856

PROCESS OF REFINING AND STABILIZING WAXES

Stephen F. Perry, Westfield, and Randolph M. Bailly, Little Silver, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

Application July 27, 1951, Serial No. 238,818

8 Claims. (Cl. 196—21)

1

The present invention is concerned with the production of high quality waxes. The invention is more particularly concerned with a hydrotreatment or hydro-desulfurization operation wherein an alumina base catalyst is utilized. In accordance with the present invention the catalyst employed in the hydrofining treatment of the waxes is treated in a manner to reduce the volatile content below a critical limit whereby unexpected desirable results are secured in the wax hydrofining operation.

The problem of satisfactory refining and stabilizing petroleum waxes has long been recognized, and is particularly acute when these waxes are utilized in the preservation of foods. One conventional process sequence for refining crude petroleum waxes is illustrated by the accompanying drawing.

Referring specifically to the drawing a wax containing a relatively small quantity of oil is introduced into chilling zone 1 by means of feed line 2. A dewaxing solvent, which for the purpose of illustration is assumed to be a benzol-methyl ethyl ketone mixture, is introduced by means of line 3. The amount of benzol may vary from about 20–50% by volume, whereas the methyl ethyl ketone may vary from about 80–50% by volume. Usually from about 1½ to 5 volumes of solvent are utilized based upon the volume of waxy oil being processed.

The chilled mixture is introduced into separation zone 4 by means of line 5 which for the purpose of illustration is assumed to be a filtering zone. The oil-solvent is removed from zone 4 by means of line 6 while the wax fraction is removed by means of line 7. Solvent may be removed from the wax fraction by any suitable means as illustrated by line 8. The solvent-free wax fraction is then introduced into a sweating zone 9 wherein the wax is held in perforated sweating pans and is exposed in solid form to gradually rising temperatures. As the temperature is increased, the oily constituents of the waxes tend to separate leaving crude scale wax in the sweating pans. The oil is removed from the sweaters by means of line 11.

In a conventional operation the wax fraction prepared by solvent dewaxing usually contains from about 2–12% of oil by volume. This fraction is generally sweated in one or more stages with recycle of intermediate cuts to produce final fractions having oil contents less than about 0.5% and preferably less than about 0.25% of oil. However, it should be recognized that solvent de-oiling techniques may be used interchangeably as a substitute for part or all of the sweating technique. Thus, under certain operations the oil content of the wax fraction introduced into the hydrofining step may be as high as 3% by volume.

2

In accordance with the present invention, the wax fraction containing less than about 3.0% of oil is introduced into hydrofining zone 12 by means of line 13 wherein it is handled as hereinafter described. The hydrofined wax is withdrawn from zone 12 by means of line 14 and if the oil content is relatively high, this fraction may be sweated in sweating zone 20 and then introduced into percolation zone 15 by means of line 21. On the other hand, if the oil content is relatively low, that is, below about .25%, the hydrofined wax fraction may be introduced directly into zone 15 by means of line 22. The hydrofined wax is percolated through an adsorbent material such as bauxite in percolation zone 15. A finished high quality wax is withdrawn from zone 15 by means of line 16.

As pointed out heretofore, refined waxes produced by conventional refining operations tend to darken when exposed to elevated temperatures for extended periods of time. Exposure to light over a period of time also causes discoloration. Furthermore, as a result of this inherent instability, the wax will in many instances also develop objectionable odor and taste. As it has long been appreciated that waxes refined by conventional sweating processes are not entirely satisfactory in these regards, numerous processes have been suggested to improve the quality of the wax. For example, various caustic and acid treating processes have been developed.

In a typical process of this character, the crude scale wax is acid treated and then neutralized with an aqueous caustic solution. The treated and neutralized wax is distilled in the presence of excess alkali, in the approximate amount of 0.1% by weight, and the distilled wax is sweated to refined wax in the conventional manner. Waxes produced by this method are color stable when exposed to heat or light.

The acid treating sequence as applied in the above operation may be carried out either batchwise or continuously. The crude scale wax, in a molten state, is agitated with about 15 to 30 pounds of 98% sulfuric acid or fuming sulfuric acid per 100 gallons of wax at temperatures slightly above the melting point of the wax, that is, at about 150° to 180° F. Sludge is separated out after settling and the acidic wax is neutralized with a weak solution of sodium hydroxide at

150° to 190° F. The wax is then washed with water. However, a process of this character is not entirely satisfactory for producing high quality stable waxes, suitable for contact with food.

Consequently, it has been proposed to stabilize waxes by hydrogenation using a "Raney nickel catalyst" or equivalent at pressures of approximately 1000 lbs. per square inch and at a temperature of about 400° F. Such a catalyst is a pyrophoric form of elementary nickel. It is prepared from a nickel-aluminum alloy by dissolving the aluminum with sodium hydroxide solution and washing first with water and finally with alcohol. However, the cost of such a high pressure hydrogenation process is excessive. A further difficulty of this process is that the Raney nickel catalyst is easily poisoned by sulfur compounds. This is a serious disadvantage as waxes of the type specified, that is, Panhandle and Salt Flat waxes, have a relatively high content of sulfur compounds. It is apparent, therefore, that this process is not an effective procedure for stabilizing these types of waxes.

One method that has shown considerable promise has been to hydrofine a crude scale wax containing less than about 3.0% of oil, preferably less than about 0.25% of oil. In this operation a molybdenum oxide catalyst based upon a carrier, preferably alumina, is utilized. The amount of molybdenum oxide is about 5 to 13% by weight based upon the weight of the alumina. The catalyst is prepared by known methods, such as by impregnation of the alumina with a water-soluble molybdenum salt, followed by heating to convert this salt to molybdenum oxide, or by co-precipitation of aluminum and molybdenum hydroxides by addition of caustic to an acid solution of aluminum and molybdenum nitrates or other salts, followed by water washing and by heating to convert to oxides.

A molybdenum-oxide-alumina base catalyst as described above is known in the art as a satisfactory hydrofining catalyst. This catalyst has been used successfully for the hydrofining of naphtha fractions boiling in the gasoline boiling range and other fractions such as kerosene and heating oil. However, the molybdenum-oxide-alumina base catalyst as prepared in the manner described normally contains from about 1 to 2% volatile matter and has a calculated average pore diameter normally less than about 90 Angstrom units. This is the result of calcining the catalyst for a relatively short period of time of from about 1–2 hours at a temperature in the range from about 1100 to 1200° F.

However, it has now been discovered that while the conventional molybdenum-oxide-alumina base catalyst of a relatively high volatile content is entirely satisfactory for hydrofining naphtha fractions and other relatively low molecular weight hydrocarbon fractions, this conventional catalyst as such is not satisfactory for hydrofining fractions having large organic molecules such as waxy fractions. It has been discovered that if the conventional catalyst is further calcined or heat treated to produce a catalyst having less than about .5% volatile matter at 1200° F., preferably having a volatile content of between .3 and .4%, unexpectedly desirable results will be secured in the hydrofining of high molecular weight wax fractions. A catalyst of this character is further characterized by having a calculated average pore diameter greater than about 100 Angstrom units. The fundamental reason for the improved results achieved with the more severely recalcined catalyst, having a volatile content below about 0.5%, has not been definitely ascertained. The improvement is not necessarily due to further dehydration, per se, but the extent of dehydration may be used as a convenient measure of calcination severity. Further calcination of the molybdenum oxide on alumina catalyst also increased average pore diameter, reduced total surface area, reduced the molybdenum content slightly and caused the molybdenum oxide to assume a more crystalline form as evidenced by X-ray diffraction. It is possible that the additional heating caused the molybdenum oxide to migrate by sublimation to parts of the surface more readily available to the large wax and oil molecules. The volatile matter as used in this specification is determined by measuring the weight loss when a sample is heated to 1200° F. until no further loss occurs.

Pore diameter is calculated from nitrogen absorption data in the classic manner. This involves measurement of surface area by determining the nitrogen adsorption corresponding to a monolayer, measurement of pore volume by total nitrogen adsorption, and calculation of average pore diameter from the surface area and pore volume by assuming that the pores are perfect cylinders.

The present invention may be further understood by the following example illustrating the same.

Example

Various portions of a wax fraction containing 3% of oil were hydrofined in different operations. In Operation 1 the molybdenum-oxide aluminum-oxide catalyst contained about 1–2% volatile matter, whereas in the remaining operations the catalyst was recalcined to secure a volatile content in the range from about 0.3 to 0.4%. In Operation 1, the catalyst had a pore diameter of 83, whereas in the remaining operations the pore diameters were in the range from 110 to 125 Angstrom units. After hydrofining the wax was sweated to approximately 0.2% oil content and percolated through bauxite at a temperature in the range from 150 to 200° F. About 25 tons of wax was percolated per ton of bauxite. A rating of 5 or lower in the National Formulary test is satisfactory. The results of these operations are as follows:

Operation	Recalcination of Catalyst Used for Scale Wax Hydrotreating	Vol. Matter, percent	N. F. Acid Test* of Hydrotreated, Refined Wax
1	None	1–2	[1] 20
2	2 Hrs. at 1200° F	.3–.4	5
3	4 Hrs. at 1200° F	.3–.4	3
4	8 Hrs. at 1200° F	.3–.4	2
5	4 Hrs. at 1400° F	.3–.4	3

*The N. F. (National Formulary) acid test is a test for "carbonaceous material" in which a sample of molten wax is agitated under specified conditions at 158° F. with an equal volume of concentrated sulfuric acid. The color of the acid layer is then compared visually with standard color solutions. If the acid is darker than the No. 5 standard, the wax does not pass; if lighter, the wax passes.

[1] N. F. acid test without hydrotreatment was also 20.

From the above it is apparent that the molybdenum-oxide-alumina catalyst when containing less than about 0.5% volatile matter is much superior to a molybdenum-oxide-alumina catalyst containing 1–2% volatile matter. As a matter of fact, the data indicates that when the volatile matter is above 1%, no improvement is

secured by hydrofining plus percolation over percolation alone.

The hydrofining operation may be varied appreciably but the reaction temperature is generally in the range from about 400° F. to 700° F., preferably at about 600° F. A pressure of atmosphere to 400 pounds per square inch may be employed; however, the preferred pressure is about 200 pounds per square inch. The hydrogen feed rate is in the range from about 100 to 500 cubic feet per barrel. A hydrogen rate of about 200 cubic feet per barrel of feed is suitable from a practical standpoint. The wax feed rate may range from 0.5 to 4.0 v./v./hr. (volume of wax per volume of reactor per hour). It is preferred that a wax feed rate of 1 v./v./hr. feed rate be used.

In operation a mixture of melted wax and hydrogen gas is fed to the hydrogenation unit. This mixture is preheated to the reaction temperature and is passed over the catalytic material in a liquid phase operation. Unconsumed hydrogen may be recycled through the hydrogenation chamber. It is apparent that the condition and manner of hydrogenation may be greatly varied.

The present invention is concerned with the use of a molybdenum-oxide-alumina catalyst containing less than 1%, preferably less than 0.5% of volatile matter for the production of high quality waxes utilizing a hydrofining step.

Having described the invention it is claimed:

1. Process for the production of high quality petroleum waxes which comprises subjecting a wax fraction containing less than about 3% of oil to contact with a catalyst comprising 5 to 13% by weight of molybdenum oxide on alumina at a temperature in the range from about 400–700° F., and at a pressure in the range from about 0–400 lbs. per sq. in. wherein a quantity of hydrogen in the range from about 100–500 cu. ft. per barrel of wax is utilized, said catalyst being characterized by containing less than about 0.5% volatile matter and which is further characterized by having a pore diameter greater than 100 Angstrom units, said catalyst being prepared by recalcination at a temperature of about 1200° F. of a catalyst comprising molybdenum oxide on alumina.

2. Process as defined by claim 1 wherein the temperature of contacting is about 600° F., wherein the pressure is about 200 lbs. per sq. in. and wherein the hydrogen employed per barrel of wax is in the range from about 100–300 cu. ft.

3. Process for the production of high quality petroleum waxes which comprises sweating a wax fraction to an oil content of less than about 0.3% of oil, then contacting said wax fraction with a catalyst comprising 5 to 13% by weight of molybdenum oxide on alumina at a temperature in the range from about 400–700° F. and at a pressure in the range from about 0–400 lbs. per sq. in., and wherein a quantity of hydrogen in the range from about 100–500 cu. ft. per barrel of wax is utilized, said catalyst being characterized by containing less than about 0.5% of volatile matter and being further characterized by having a pore diameter in the range from 110 to 125 Angstrom units, said catalyst being prepared by recalcining at about 1200° F. a catalyst comprising molybdenum oxide on alumina.

4. Process as defined by claim 3 wherein the temperature of contacting is about 600° F., wherein the pressure is about 200 lbs. per sq. in., and wherein the hydrogen employed per barrel of wax is in the range from about 100–300 cu. ft.

5. Process as defined by claim 3 wherein the hydrofined wax is percolated through bauxite.

6. Process for the production of high quality petroleum waxes which comprises subjecting a wax fraction containing less than about 3% of oil to contact with a catalyst comprising 5 to 13% by weight of molybdenum oxide on alumina at a temperature in the range from about 400–700° F., and at a pressure in the range from about 0–400 lbs. per sq. in., wherein a quantity of hydrogen in the range from about 100–500 cu. ft. per barrel of wax is utilized, withdrawing the wax from contact with said catalyst and sweating the same in a sweating zone to an oil content of less than about .25% of oil, said catalyst being characterized by containing less than about 0.5% volatile matter and being further characterized by having a pore diameter greater than about 100 Angstrom units, said catalyst being prepared by recalcining at about 1200° F. molydenum oxide on alumina.

7. Process as defined by claim 6 wherein the temperature of contacting is about 600° F., wherein the pressure is about 200 lbs. per sq. in., and wherein the hydrogen employed per barrel of wax is in the range from about 100–300 cu. ft.

8. Process as defined by claim 6 wherein the wax subsequent to sweating is percolated through bauxite.

STEPHEN F. PERRY.
RANDOLPH M. BAILLY.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,973,833	Wietzel et al.	Sept. 18, 1934
2,487,466	Nahin	Nov. 8, 1949
2,554,244	Dole	May 22, 1951
2,574,331	Knox	Nov. 6, 1951
2,577,823	Stine	Dec. 11, 1951

FOREIGN PATENTS

Number	Country	Date
416,711	Great Britain	Sept. 13, 1934