

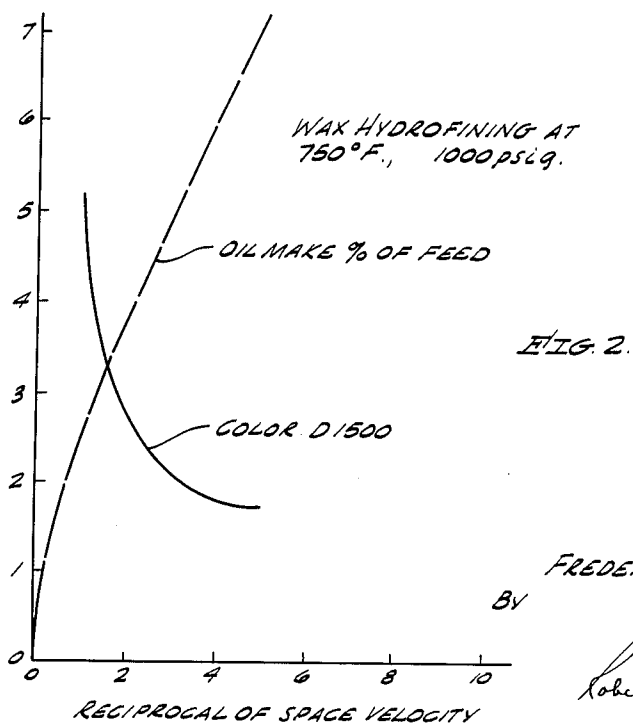
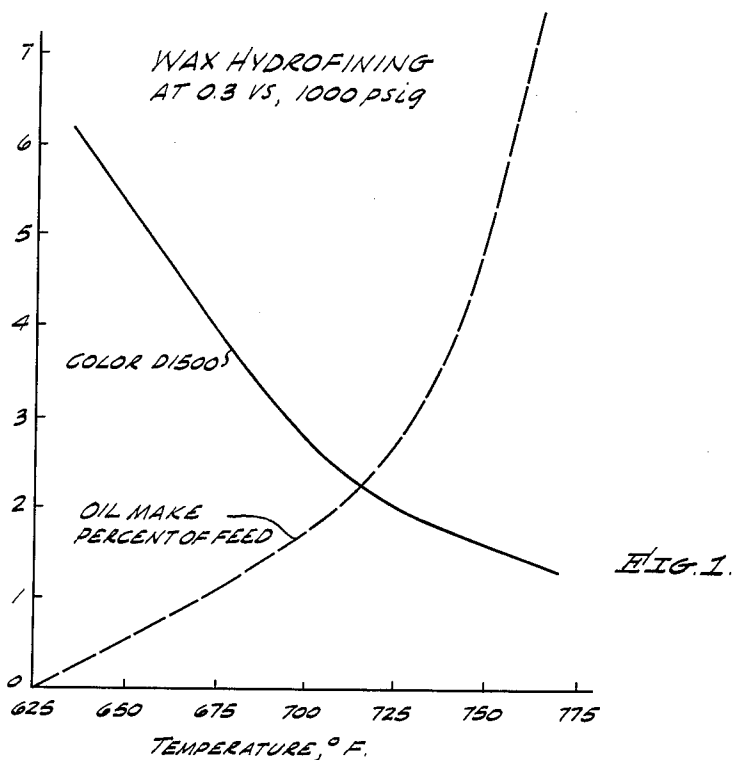
Sept. 28, 1965

F. C. WOOD

3,208,931

REFINING OF PETROLATUM

Filed Jan. 15, 1962



INVENTOR.
FREDERICK C. WOOD,
BY

Robert E. Shuman
ATTORNEY.

1

3,208,931
REFINING OF PETROLATUM
Frederick C. Wood, Fullerton, Calif., assignor to Union
Oil Company of California, Los Angeles, Calif., a cor-
poration of California
Filed Jan. 15, 1962, Ser. No. 166,261
7 Claims. (Cl. 208-27)

This invention relates to the refining of waxes includ-
ing microcrystalline waxes, petrolatums, and slack waxes.
More particularly, this invention relates to a two-stage
hydrogenation treatment of said wax fractions to achieve
a high degree of color improvement and to impart color
stability to the waxes.

Recently, hydrofining has been suggested as a method
for refining of petroleum waxes. In such hydrofining,
relatively mild conditions are prescribed to prevent any
possible isomerization or cracking of the wax fraction.
Thus, low temperatures, i.e., about 400° to 700° F., and
high pressures, i.e., about 1000 to 3000 p.s.i. are pre-
scribed. Because of the low temperatures employed,
relatively low space velocities, i.e., about 0.1 to about 1
are necessary to effect the refining. Contrary to the re-
sults described by the prior art for such hydrofining, I
have found that in many instances, a satisfactorily de-
colorized wax product cannot be obtained with the sug-
gested hydrofining treatment. I have also discovered that
the wax product so obtained, even when decolorized to an
initially satisfactory color, darkens upon storage to an
unmarketable product.

It is an object of this invention to prescribe a hydro-
fining method which will achieve a satisfactory decolor-
ization of crude waxes.

It is also an object of this invention to prescribe a
hydrofining method which will impart a high degree of
color stability to the wax product.

Other and related objects will be apparent from the
following discussion of the invention.

Briefly, the invention prescribes a two-stage hydro-
fining of waxes wherein the first stage is performed under
sufficiently severe conditions to remove the major por-
tions of color bodies and the subsequent stage is per-
formed under mild conditions to impart a color stability
to the product.

In a preferred embodiment, the second stage simply
comprises a continuation of the first stage wherein the
reactants are quenched by the introduction of a cool re-

2

tially improved contacting efficiency. Preferred solvents
are those boiling in the kerosene range; however, naph-
tha, light mineral oils, jet fuel fractions, etc., can also be
used, in amounts between 0 and about 80 volume percent
solvent, preferably between about 10 and about 50 volume
percent. The slack wax, slack wax distillates and petro-
latums are mixtures of a heavy oil and microcrystalline
wax and generally contain between about 50 and 95 per-
cent of the latter. The wax feedstocks used herein ordi-
narily have an initial boiling point above about 1000° F.
and are dark brown to black in color as determined by
the standard ASTM test method, D-1500. This test
method provides a classification from 0.5 to 8.0, 0.5 cor-
responding to a pale yellow and 8 corresponding to a
dark brown coloration. Commonly, the wax feedstocks
are darker than 8 when measured by this test method.
The principal objective of the hydrofining treatment is
to reduce the color to a maximum of about 1.5 to 2.0
to meet the anticipated requirements of the Food and
Drug Administration for waxes used in food packaging
containers.

The micro wax feedstocks are commonly derived from
a crude oil residuum by conventional deasphalting and
propane dewaxing of the deasphalted material. The
propane dewaxing yields a crude slack wax which is sub-
jected to a vacuum distillation to recover the high grade
paraffin waxes as wax distillate stocks. The vacuum dis-
tillation bottoms commonly contain between about 30 to
about 90 percent microcrystalline waxes and are referred
to as petrolatums. As previously mentioned, the wax dis-
tillates and slack wax bottoms (petrolatums) can be ad-
vantageously refined by my invention. The wax distil-
lates can be be hydrofined prior to or after the deoiling
step as desired. It is also within the scope of my inven-
tion to hydrofine the foots oil product from the deoiler
as this hydrocarbon oil frequently contains color bodies
which prevent its use as a paraffinic blending stock, base
stock for halogenation, etc., in the production of halo-
genated, particularly chlorinated hydrocarbons.

The hydrofining operation is carried out in a conven-
tional reactor with a fixed bed of granular catalyst. The
feed-stock and recycle gas streams are preheated to the
desired hydrofining temperature and then introduced into
the reactor in a downflow concurrent or countercurrent
technique.

The following table summarizes the reaction conditions
in the first and second stages of the treatment.

TABLE 1

Condition	First Stage			Second Stage		
	Broad	Preferred	Most Preferred	Broad	Preferred	Most Preferred
Temperature, ° F.	600-800	675-775	725-755	400-700	450-600	500-550
Space Rate, v./v./hr.	0.1-1.5	0.2-0.5	0.25-0.5	0.2-10	0.5-5	1-4
Pressure, p.s.i.g.	500-1,500	800-1,200	800-1,200	500-1,500	800-1,200	800-1,200
Gas Rate, s.c.f./bbl.	500-10,000	1,000-2,000	1,000-2,000	500-10,000	3,000-7,000	3,000-7,000

cycle gas stream. Conventional downflow contacting
techniques with concurrent or countercurrent gas contact-
ing can be employed.

The waxes which are treated in accordance with this
invention include the various deoiled microcrystalline
waxes, slack waxes, slack wax distillates, and petrolatums.
The deoiled microcrystalline waxes can be directly pro-
cessed, or processed in dilution with a suitable solvent
to lower the viscosity of the feed and thereby improve
diffusion rates. Solubility of hydrogen in the feed is
also increased and vaporization of the diluent may assist
in additional agitation in the reactor with consequen-

It is understood of course that selection of the neces-
sary conditions to obtain the desired severity in each of
the hydrofining stages is within the skill of the art. Vari-
ous processing techniques can greatly affect such selec-
tion, e.g., use of a flooded bed technique generally will
provide more severe processing than conventional down-
flow because of the greater residence time of the feed-
stock in the reactor. With such flooded bed techniques,
it is within the scope of the invention to employ slightly
milder conditions than set forth in Table 1.

Conventional hydrofining catalysts are used herein,
including in general any of the Group VIB and/or Group

VIII metals, their oxides or sulfides, either as such or preferably distributed upon an absorbent oxide carrier such as alumina, titania, zirconia, silica, aluminum silicates, clays, etc. Particularly suitable catalysts for the first stage are the various sulfur resistant catalysts which comprise a combination of an iron group metal, oxide or sulfide with a Group VIB metal oxide or sulfide supported upon activated alumina, or activated alumina stabilized by the addition of a small proportion (3–15%) of silica gel.

The total hydrogenating components of the catalyst can comprise between about 4 and about 25 percent by weight of the finished catalyst. Preferred catalysts are the cobalt molybdate type, which contain between about 1 and about 5 percent cobalt oxide or sulfide and between about 5 and about 20 percent molybdenum oxide or sulfide. Preferably, the catalyst is subject to a presulfiding technique in order to convert the active hydrogenating components substantially completely to the sulfide form. The catalyst is employed in subdividing form, e.g., pellets between about $\frac{1}{16}$ and $\frac{1}{4}$ inch or as 8 to about 20 mesh granules.

The catalyst for the second stage treatment preferably is the same sulfur-resistant type as disclosed for the first stage of hydrofining; however, if desired, catalysts having a higher hydrogenation activity can be used in the second stage such as the various Group VIII metals, e.g., nickel, particularly the noble metals, e.g., platinum, palladium, rhodium, etc. The active metals are distributed on various supports, preferably those supports which are finely divided and have a high surface area, e.g., silica gel, alumina gel, titania, zirconia, activated clays, various crystalline metalo aluminosilica zeolites such as the H, X, Y type molecular sieves, etc.

In the preferred downflow processing, the second stage of hydrofining merely comprises a quenched extension of the first stage. In this embodiment, the second stage catalyst preferably is the same sulfur resistant type as employed in the first stage. In concurrent downflow processing, this is achieved by introducing the preheated feed and recycle gas into the top of the reactor and permitting it to flow downwardly through the catalyst bed. Cool recycle gas is introduced near the exit portion of the bed so as to quench the wax to the desired low temperature severity conditions necessary to impart the color stability to the product. In general, the cool recycle quench gas can be introduced at the midportion of the catalyst bed, at the last 5 percent of the bed, or at any increment therebetween. Preferably the exit 10 to about 40 percent of the bed is quenched.

In downflow countercurrent contacting, the hot recycle gas stream is introduced at the base of the reactor and the feed flows downwardly, countercurrent to this gas stream. The invention as applied to this processing technique comprises the introduction of the main hot recycle gas stream at the midportion of the catalyst bed, at the last 5 percent increment of catalyst bed, or at any increment therebetween including the preferred 10 to 40 exit portion. The cool quench gas is introduced at the base of the reactor and permitted to flow through the entire catalyst bed.

A third processing technique comprises concurrent flow in the first stage and countercurrent flow in the quenched zone. In this embodiment, the preheated hydrocarbon feed and hot hydrogen or recycle gas stream are introduced at the top of the reactor and flow downwardly therethrough. Intermediate the hydrocarbon's travel through the reactor, the hot gas stream is withdrawn. The liquid hydrocarbons continue their downward flow countercurrent to the upward flow of a cool quench, hydrogen-rich, gas stream which is introduced at the base of the reactor. The quench gas joins the hot recycle gas at the intermediate point and is withdrawn from the reactor therewith. As with the previously described techniques, the quench zone can comprise the exit 5 to

about 50 percent of the catalyst bed, preferably between about the exit 10 to about 40 percent.

It is, of course, apparent that in either upflow or downflow processing, separate reactors can be used for the two hydrofining steps. The use of separate reactors, while increasing the capital investment, provides a flexible process which permits a wide variance of space rates and recycle gas rates in each of the contacting zones. When separate reactors are employed, the intermediate effluent from the first reactor can be processed directly into the second reactor or, preferably, the effluent is separated into the vapor and liquid phases and the liquid phase is introduced into the second stage reactor together with the desired amount of cool recycle hydrogen.

The following examples are presented to illustrate my invention.

Example 1

In this and subsequent examples a 28-foot reactor, 2 inches in diameter, was employed in a downflow technique. The refined product removed from the bottom of the reactor was passed to a vapor liquid separator from which a liquid product was removed and passed to a stripping vessel for the removal of hydrogen sulfide. The liquid product was passed downwardly through a packed stripping tower countercurrent to the flow of nitrogen.

A cobalt molybdate catalyst, $\frac{1}{8}$ inch pellet size, was placed in the reactor and presulfided by passing hydrogen over the catalyst at 100 p.s.i.g. while slowly adding hydrogen sulfide to the hydrogen gas to obtain a 3 percent hydrogen sulfide concentration at the reactor inlet. Throughout the presulfiding procedure the catalyst temperature was maintained below 400° F. When the temperature wave passed through the catalyst bed, the reactor was heated to the desired temperature while maintaining the hydrogen sulfide-hydrogen circulation. The hydrogen sulfide addition was continued until no further adsorption of hydrogen sulfide was observed.

Thereafter, the reactor was employed for the hydrofining of a wax by introducing a petrolatum containing about 11.3 weight percent oil into the top of the reactor with a hydrogen containing recycle gas in the desired quantities. The feedstreams were preheated to the desired reaction temperature. The initial series of runs were made to determine the required severity of hydrofining to obtain a satisfactorily decolorized product. The reactor pressure was maintained through the series of runs at 1000 p.s.i.g.; the hydrogen rate was maintained at about 2000 standard cubic feet per barrel of feed and the liquid hourly space velocity was maintained at about 0.3 volume per volume per hour. The decolorization results are illustrated by FIGURE 1 which is a plot of the product colors so obtained as a function of the reactor temperature. At the preferred temperature, about 750° F., the sulfur content was reduced from about 0.21 to about 0.04 weight percent; the nitrogen content from about 980 to about 160 parts per million.

The preceding demonstrates that relatively severe hydrofining temperatures are necessary to obtain a product having a color less than about 3 on the ASTM scale and that the art recommended range of about 400°–600° F. is insufficient to effect a satisfactory decolorization. While FIGURE 1 illustrates that temperatures in excess of about 775° F. can be expected to further improve the color of the product, such temperatures are generally prohibited by the degree of isomerization and cracking of the wax. The extent of this secondary reaction is indicated by the percent conversion of the feed to oil and is depicted by the dashed line in FIGURE 1. Generally, conversions greater than about 10 weight percent of the feed are to be avoided because of the loss of wax and greater deoiling capacity which will be needed to deoil the wax stock. Accordingly, temperatures less than about 775° F., preferably less than about 755° F., are to be employed.

5

Although FIGURE 1 illustrates that the initial color of the wax effluent from the reactor is below about 3 and can be obtained below about 2, a satisfactorily decolorized material, the sample rapidly darkens upon storage to an unmarketable material.

Example 2

In the reactor previously described, a petrolatum stock containing about 11.3 weight percent oil with a color greater than about 8.0 on the ASTM scale was hydrofined at a temperature of 750° F. and at 1000 p.s.i.g. pressure. The recycled gas rate was about 2000 s.c.f. per bbl. of feed. The space rate of the feed through the reactor was varied from about 0.2 to about 0.5 volumes per volume per hour. The product collected from the hydrogen sulfide stripper was analyzed for color and the results obtained are depicted in FIGURE 2. These results indicate that decreasing the space rate from about 1 to about 0.5 greatly improves the decolorizing efficiency of the process. Preferably, space rates between about 0.5 and about 0.25 are employed.

The reactor effluent was also analyzed for oil content and the conversion to oil is depicted by the dashed line of FIGURE 2. The results indicate that the conversion to oil is greatly affected by space rates and that any decrease in space velocity substantially increases the conversion of wax to oil. Accordingly, it is preferred to employ no lower space rates than are necessary to obtain the desired color improvement, i.e., no less than about 0.25 volumes per volume per hour. As with temperature, no improvement in color stability was observed throughout the range of space velocities investigated.

Example 3

The preceding examples amply demonstrate the need for improvement on wax hydrofining treatments. Specifically, a need exists to provide an improvement in the initial color of the reactor effluent and to impart a color stability to such effluent. The following examples demonstrate how my invention achieves these goals.

The aforescribed reactor was modified so as to permit the introduction of a quench stream of recycle gas into the lower (exit) 10 percent portion of the bed. The remainder of the bed was maintained at 750° F. and 1000 p.s.i.g. pressure.

The petrolatum was passed downwardly through the reaction vessel at an overall space velocity of 0.3 volumes per volume per hour. Quench gas was introduced at the lower 10 percent portion of the catalyst bed to quench the reactants to 650°, 600° and 500° F. in successive experiments. The following table summarizes the results:

TABLE 2

Temperature, Second Stage	Color		Sulfur	Nitrogen
	Initial	Final ^b		
750 ^a -----	2.3	3.5-4.5	0.04	160
650-----	1.5	1.9	-----	65
600-----	1.3	1.8-1.9	-----	-----
500-----	1.3	1.8-1.9	-----	104

^a Single stage hydrofining at 750° F. (no quench).

^b After 84 hours' storage at 185°-200° F.

The results presented in Table 2 illustrate that the initial color of the petrolatum is reduced 0.8 to 1.0 units below the best heretofore obtained by single stage hydrofining. The results also demonstrate that the color of the product is more stable than that obtained from single stage operation. Thus, the samples from single stage hydrofining increase between about 1 and about 2 color units upon storage, whereas the samples obtained by the 2-stage hydrofining of this invention increase in color no more than about 0.5 color units. In all cases the

6

samples were stable in color after the 84-hour storage period.

To demonstrate that the color improvement and stability improvement of the product was indeed a catalytic hydrofining effect, the point of quench gas introduction was moved to the exit of the catalyst bed. Quench gas was introduced into the reactor effluent immediately upon its exit from the catalyst bed in sufficient quantities to lower the temperature to about 650° F. The color of the sample so obtained was 2.0 and upon storage the color degraded to 3.2 units within 48 hours at 185°-200° F.

Example 4

The point of quench gas introduction was moved upwardly to provide a second stage catalyst bed which comprised about 40 percent of the total catalyst. Table 3 summarizes the reaction conditions in each of the hydrofining stages and the results obtained thereby.

TABLE 3

Run-----	1	2	3
First Stage:			
Temperature, ° F-----	750	750	750
Space Rate, v./v./hr-----	0.3	0.48	0.48
Pressure, p.s.i.g-----	1,000	1,000	1,000
Gas Rate, s.c.f./bbl-----	2,000	2,000	2,000
Color, D-1500-----	2.6	-----	2.9
Second Stage:			
Temperature, ° F-----	600	600	500
Space Rate, v./v./hr-----	0.49	0.81	0.81
Pressure, p.s.i.g-----	1,000	1,000	1,000
Gas Rate, s.c.f./bbl-----	8,500	8,500	12,000
Color D-1500-----			
Initial-----	1.5	1.8	1.6
After 2 days at 185°-200° F-----	1.8	2.7	2.0
After 30 days at 185°-200° F-----	2.0	3.1	2.9

The results demonstrate that a marked color improvement and increased color stability can be achieved by employing a second stage low temperature hydrofining treatment of a severely hydrofined wax stock.

As apparent to those skilled in the art, various modifications of the invention can be employed without departing therefrom. Thus, separate reactors and distinct catalyst beds can be employed for each of the hydrofining stages. My invention is intended to be covered by the method series of steps and their obvious equivalents set forth in the following claims.

I claim:

1. A method for obtaining a decolorized wax product having a high degree of color stability which comprises: subjecting a wax stock selected from the class consisting of slack wax bottoms and petrolatum and characterized by color instability on storage to catalytic hydrofining with added hydrogen in contact with a hydrofining catalyst at a temperature between about 700° and about 775° F., a liquid hourly space rate between about 0.1 and about 1.0 and a pressure between about 500 and about 1500 p.s.i.g. to obtain a substantially decolorized wax stock in a first stage, withdrawing said wax stock from said first stage, admixing said wax stock with a cold hydrogen gas in a quantity sufficient to reduce the temperature of said wax stock to about 450° and 600° F. and thereafter subjecting said substantially decolorized wax stock to mild hydrogenation with a hydrogenation catalyst a second stage at a temperature between about 450° and 600° F. to obtain said product.

2. In a method for decolorization of a wax stock selected from the class consisting of slack wax bottoms and petrolatum and characterized by color instability on storage wherein said wax stock is subjected to hydrofining conditions with hydrogen and a bed of hydrofining catalyst at a temperature between about 675° and about 775° F., the improved method of improving the decolorization and the color stability of said stock which comprises quenching said wax stock by introducing a cold hydrogen-containing gas stream in quantity sufficient to reduce the temperature of said stock to between about

7

400° and about 600° F., said introduction of said cold gas being at a point intermediate of the travel of said stock through said bed to provide a mild catalytic hydrogenation of said wax.

3. The method for obtaining a decolorized microcrystalline wax having a high degree of color stability which comprises subjecting a reactant stream comprising a wax containing stock characterized by color instability on storage and hydrogen to hydrofining conditions with a bed of hydrofining catalyst at a temperature of 675° to about 775° F., quenching said reactant stream at a point intermediate its travel through said bed of catalyst by introducing a cold recycle gas stream into said bed at said point in a quantity sufficient to provide a final hydrogenation zone having a temperature between about 400° and about 600° F. and a space velocity between about 0.1 and about 1.0 liquid volumes per volume per hour to impart a color stability to said wax and thereafter deoiling the decolorized wax stock to obtain said microcrystalline wax.

4. The method of claim 3 wherein said space velocity in said final hydrogenation zone is between about 0.25 and about 0.5.

5. The method of claim 3 wherein said catalyst is a

8

sulfided composite of cobalt oxide and molybdenum oxide supported on a carrier which is essentially activated alumina.

6. The method of claim 3 wherein said reactant stream comprises said wax stock and a light petroleum distillate diluent.

7. The method of claim 3 wherein said stock is petrolatum.

References Cited by the Examiner

UNITED STATES PATENTS

2,587,149	2/52	Gwynn	208—303
2,846,356	8/58	Mills et al.	208—27
2,985,579	5/61	Heinemann et al.	208—27
2,998,377	8/61	Beuther et al.	208—27
3,022,245	2/62	Spars et al.	208—26
3,052,622	9/62	Johnson et al.	208—27
3,089,841	5/63	Berkowitz et al.	208—27

FOREIGN PATENTS

851,969	10/60	Great Britain.
797,744	7/58	Great Britain.

ALPHONSO D. SULLIVAN, *Primary Examiner.*