

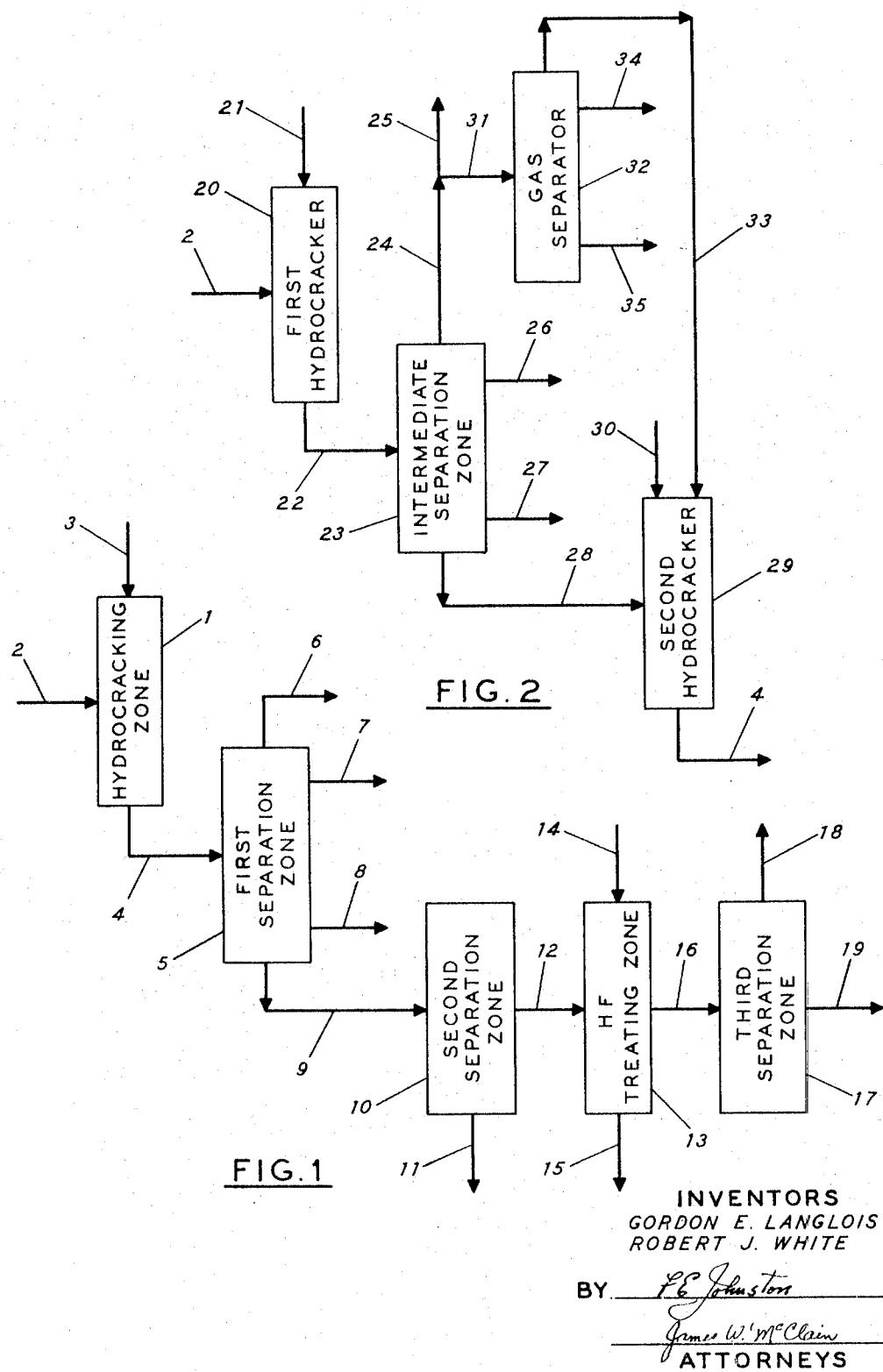
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PROCESS FOR STABILIZING LUBRICATING OIL

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3,463,724

**PROCESS FOR STABILIZING LUBRICATING OIL**  
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## ABSTRACT OF THE DISCLOSURE

A process for producing lubricating oil stable in the presence of ultraviolet light which comprises hydrocracking a hydrocarbon feedstock containing a substantial portion of components boiling above 750° F., under catalytic hydrocracking conditions, including a temperature in the range 720° to 850° F., sufficient to convert at least 15 weight percent of these components to materials boiling below 750° F., separating from the hydrocracked product a lubricating oil fraction boiling above 600° F., and treating the lubricating oil fraction with HF to improve the ultraviolet light stability of the oil.

## CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 636,345, filed May 5, 1967, now abandoned.

## BACKGROUND OF THE INVENTION

This invention relates to processes for the production of lubricating oils. More particularly, it relates to processes for the production of stable lubricating oils by hydrocracking and acid treating.

Lubricating oils, which can be defined in general as those hydrocarbon materials which boil above 600° F., are presently produced by two principal methods. The first, which produces straight-run lubricating oils, may include steps of distillation of a crude oil, solvent refining, solvent dewaxing, acid treating and clay contacting. Acid treating of straight-run lubricating oils is employed to improve the color and resistance to oxidation of the oils.

The second method is somewhat similar to the first but substitutes mild hydrorefining or hydrofinishing for one or more of the steps of solvent refining, acid treating or clay contacting. Hydrorefining or hydrofinishing is a process wherein the contaminants in the crude distillate are converted, by contacting with hydrogen in the presence of a hydrogenating catalyst, to easily removable or harmless species. Only minimal cracking occurs during hydrorefining.

Recently it has been discovered that lubricating oils may also be produced by hydrocracking. In this process, a heavy petroleum oil is contacted with hydrogen at elevated temperature and pressure in the presence of a hydrocracking catalyst; and the hydrocracked product (which is often termed the "hydrocrackate") is separated, usually by distillation, into materials boiling in different temperature ranges. One or more of these materials will boil within the lubricating oil boiling range.

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It has now been found that lubricating oils produced by hydrocracking, although having many desirable properties not otherwise obtainable by straight-run processing, also possess to a significant degree one undesirable property which had previously been noted only to an insignificant degree with straight-run lube oils. This undesirable property is the instability of hydrocracked oils when exposed to ultraviolet light in the presence of air. This instability is evidenced by the formation of a precipitate in the oil after a short period of exposure to ultraviolet light. Such a precipitate is undesirable, not only because it may prove detrimental to the lubrication function which the oil is designed to perform, particularly in high-performance oils such as turbine oils, but also because it reduces the esthetic value of what would otherwise be a clear, premium-quality oil. The latter is not a trivial consideration; refiners have learned through experience that consumers will not buy lubricating oils which contain visible precipitates even when those precipitates have no adverse effect on the performance qualities of the lubricating oil.

In the past, it has been known that certain types of lubricating oil instability, such as oxidation instability, could be prevented by treating the oil with any of a number of polar solvents, such as phenol, furfural and sulfuric acid. The acid treating of straight-run oils referred to above is such a treating process. While this treatment tends to remove the ultraviolet instability-causing components, it has the disadvantage that it also removes a considerable portion of the desirable lubricating oil components along with the undesirable components. Such indiscriminate removal occurs by either or both solvent extraction or chemical reaction with certain components of the oil (e.g., when sulfuric acid treating results in sulfonation of the oil components). Until now, it has been believed that treatment of any oil with any of the polar solvents produced approximately equivalent results; i.e., low yield of a moderately stable oil. Indeed, in many such treatments it has usually been found that the results obtained with HF are less than equivalent, and that the products obtained by HF treating are inferior to those obtained by the treating of the oils with other polar solvents. Further, since ultraviolet instability was an insignificant problem with straight-run oils, acid treating was only sparingly used in order to avoid the problem of resulting low yields. Such a solution is not satisfactory, however, for hydrocracked oils where the problem of ultraviolet instability is a very significant one.

## SUMMARY OF THE INVENTION

It has now been discovered that, when lubricating oils produced by hydrocracking under certain specific conditions are treated with HF, there is obtained an unexpectedly high yield of significantly more stable premium-grade oil. It appears that HF selectively removes the instability-causing compounds from hydrocrackates but does not affect the desirable lubricating oil components.

Broadly stated, this invention comprises contacting a liquid hydrocarbon feedstock containing a substantial portion of components boiling above 750° F. with hydrogen in the presence of a hydrocracking catalyst at a temperature in the range 720° to 850° F. and an elevated pressure in order to convert at least 15 weight percent of

said feedstock components boiling above 750° F. to materials boiling below 750° F., recovering from the hydrocrackate a lubricating oil fraction boiling above 600° F., treating the said lubricating oil fraction with a treating agent comprising a major portion of concentrated HF, and recovering a lubricating oil with an improved ultraviolet light stability.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, FIGURE 1 illustrates schematically flow paths which appear in one specific embodiment of the process of this invention. FIGURE 2 illustrates schematically a preferred embodiment of the hydrotreating part of the process.

#### DETAILED DESCRIPTION OF THE INVENTION

Broadly stated, this invention comprises contacting a liquid hydrocarbon feedstock containing a substantial portion of components boiling above 750° F. with hydrogen in the presence of a hydrocracking catalyst at a temperature in the range 720° to 850° F. and an elevated pressure in order to convert at least 15 weight percent of said feedstock components boiling above 750° F. to materials boiling below 750° F., recovering from the hydrocrackate a lubricating oil fraction boiling above 600° F., treating the said lubricating oil fraction with a treating agent comprising a major portion of concentrated HF, and recovering a lubricating oil with an improved ultraviolet light stability.

In a more preferred embodiment, the temperature at which the oil is hydrocracked is maintained in the range of 750°-830° F.

The hydrocracking step in this process is operated at a pressure in the range of from about 500 to about 5,000 p.s.i.g., a liquid hourly space velocity in the range of from about 0.2 to about 10.0 volumes of liquid hydrocarbon feed per volume of catalyst per hour (v./v./hr.), and a hydrogen throughput rate in the range of from about 1,000 to about 20,000 s.c.f./bbl. More preferred conditions are 1,500-3,000 p.s.i.g., 0.5-2.0 LHSV and 5,000-10,000 s.c.f./bbl. of hydrogen.

The contacting of the oil and the treating agent comprising a major portion of concentrated HF occurs in what, for convenience, will herein be termed the "HF treating step." The HF treating step, as defined in this process, may be a single contacting step; but, more preferably, it comprises a plurality of sequential contacting steps; and, still more preferably, comprises two or three contacting steps in series. The "treating agent comprising a major portion of concentrated HF" is preferably entirely "concentrated HF," as the latter term is defined below, for it is use of the HF which is one of the key elements of the present invention. However, in some cases other components may be present in minor amounts with the HF in the treating agent which contacts the oil without reducing the effectiveness of the HF. A nonlimiting example is boron trifluoride. A typical HF-BF<sub>3</sub> combination is described in U.S. Patent 2,343,841. The methods of contacting the oil with the treating agent during the HF treating step are well known in the art. Any conventional contacting method is suitable for use in this process if it provides for substantially complete contacting of the oil and the HF portion of the treating agent. Each contacting step should be operated at a temperature in the range of from about 0° F. to about 250° F. and a pressure sufficiently high to maintain the oil, HF, and other components in the liquid phase. Where the oil is relatively heavy and viscous, it is desirable to add a hydrocarbon diluent to thin the oil and improve the degree of HF-oil contacting. Suitable diluents are the C<sub>4</sub>-C<sub>8</sub> paraffins, especially pentane.

The HF used in the process is "concentrated HF," which is defined in this process to mean anhydrous HF or an aqueous solution containing at least 50 weight percent HF.

Preferred are anhydrous HF or an aqueous solution containing at least 90 weight percent HF. Less preferred are aqueous solutions containing from 70 up to 90 weight percent HF.

Any hydrocarbon oil having a substantial portion boiling above 750° F. may be converted in this process to lubricating oils. Preferred feeds are lubricating oil stocks boiling above 900° F., although crude oils, reduced crudes, residua, and deasphalted oils, among others, may also be used.

While HF treating can be used to moderately improve the properties of oils produced by methods other than hydrocracking, HF treating of such other oils is not significantly better than other known treating agents which are used to improve oil stability; and, in fact, in many cases is decidedly inferior. However, when the treated oils have been produced by hydrocracking, HF is markedly and unexpectedly superior to these other-known treating agents; for, as illustrated in Table I, it is the only one which produces a high yield (greater than 95 weight percent) of a highly stable oil (one which will withstand more than ten hours' exposure under the test described below without forming a precipitate). The data in the following table were derived by treating a hydrocracked light neutral oil produced from California deasphalted oil. The ultraviolet light stability of the untreated oil was 2 hours to precipitate.

TABLE I

Treating agent	Volume used per vol. of feed	Oil yield wt. (percent)	Oil neutral oil (hrs. to ppt.)	Ultraviolet light stability of treated light neutral oil (hrs. to ppt.)
HF (anhydrous)	0.5	98	20	20
H <sub>2</sub> SO <sub>4</sub> (20% fuming)	(1)	60	20	20
Phenol	2	50	20	20
Furfural	1	80	30	30
Dimethyl formamide	1	80	15	15
Nitrobenzene	2	54	40	40
Clay contracting	(2)	96	5	5
Dimethyl sulfoxide	1	93	8	8
Benzonitrile	2	46	40	40
Sulfur dioxide	1	85	4	4

<sup>1</sup> 1 lb./gal.

<sup>2</sup> 0.25 lb./gal.

It is apparent from the above table that if any treating agent other than HF is used yield must be sacrificed if a stable product is to be obtained; or, conversely, a high yield can be obtained only by accepting an unstable and inferior product. With HF, however, one unexpectedly obtains both a high yield and a stable product.

A critical element in the invention is the conversion of at least 15 weight percent of the materials boiling above 750° F. to materials boiling below 750° F. by hydrocracking at elevated temperatures in the range of 720°-850° F., and preferably 750°-830° F. The reduced effectiveness of HF treating of oils hydrocracked at temperatures below 720° F. is believed to be due to the nature of the instability-causing components, which are believed to be polynuclear aromatic compounds. At the lower temperatures, one or more rings of each of the polynuclear molecules will become saturated; and it is believed that in this partially or fully saturated form the compounds are less susceptible to extraction by HF. Conversely, if the temperature of conversion is too high, catalytic hydrocracking is minimized and the predominant reaction is thermal cracking. The actual operating temperature will depend on the type of feed processed and its viscosity index, the viscosity index of the lubricating oil product desired, and the degree of conversion required to produce the desired viscosity index increase. It is usually found that feedstocks which contain higher proportions of aromatics require higher degrees of conversion, which may be accomplished by hydrocracking at a high temperature, low space velocity or any combination of relatively more

severe conditions within the acceptable ranges described above. The following table indicates several typical processing conditions and conversions which are to be expected when processing different feedstocks.

passed into the hydrocracking zone through line 2 to first hydrocracker 20. Hydrogen enters first hydrocracker 20 through line 21. Conversion in hydrocracker 20 is generally 40-70 percent. The partially hydrocracked oil is

TABLE II

Hydrocarbon feedstock			Boiling range (° F.)	Nitrogen content (p.p.m.)	Sulfur content (wt. percent)	Hydrocracking conditions to produce lube oil		
Source	Characteristic	Gravity (° API)				Temp. (° F.)	Conv. (wt. percent)	LHSV
So. American residuum	Paraffinic	20.4	910	1,400	0.5	780	50	0.7
California vacuum gas oil	Aromatic	16.0	640-1,000	4,300	0.9	800	80	1.0
California cracked gas oil	do	17.0	600-1,050	4,650	1.1	800	80	1.0
Sumatran residuum	Paraffinic	28.7	900+	800	0.1	780	50	0.7
California deasphalted oil	Aromatic	15.0	900+	5,600	2.0	810	80	0.7

Referring now to FIGURE 1, a hydrocarbon feedstock is passed into hydrocracking zone 1 through line 2. In hydrocracking zone 1, the feedstock is hydrocracked to the desired degree of conversion—i.e., at least 15 weight percent—to 750° F.—material by contacting with a catalyst at conditions described hereinafter in the presence of hydrogen added to the reaction zone through line 3. The hydrocracked oil is then passed through line 4 into first separation zone 5, in which all the materials boiling below 600° F. are separated and removed through at least one line, such as lines 6, 7, and 8. The bottoms fraction, now containing only materials boiling above 600° F., is passed through line 9 into second separation zone 10 wherein a portion of the 600° F.+ material may be removed through line 11.

Zone 10 may comprise any conventional separation process or processes whereby a portion of the 600° F.+ material may be removed. Typical of such process is, among others, vacuum distillation. In a preferred embodiment of this process, zone 10 comprises a dewaxing zone, and more preferably, comprises a conventional solvent dewaxing zone.

The remaining portion of the 600° F.+ material is passed through line 12 into HF treating zone 13, where it is mixed with the HF-containing treating agent supplied through line 14. The HF layer containing the extracted instability-causing compounds is removed through line 15. The stabilized oil layer is passed through line 16 into third separation zone 17 wherein any residual HF in the oil is separated by conventional means, such as flashing, and removed through line 18. The final product lubricating oil is withdrawn through line 19.

If it is desired to HF treat the whole 600° F.+ fraction, second separation zone 10 may be eliminated, and the bottoms oil of first separation zone 5 may be passed directly into HF treating zone 13.

FIGURE 2 shows an embodiment of hydrocracking zone 1 preferred for use when a high degree of conversion (e.g., more than 60 percent) is desired. When reaction zone 1 contains only one hydrocracking reactor, that reactor must necessarily be operated at severe conditions of temperature, pressure and space velocity in order to accomplish the desired high conversion. Under such conditions, the reactor has little flexibility to process different feedstocks, for the temperature must be maintained at a level near the equipment limit. Consequently, the range over which the temperature can be varied to accommodate different feedstocks is severely limited.

It is, therefore, preferred to hydrocrack the feedstock in two stages as shown in FIGURE 2 and to separate light materials from the oil between the stages. Such a procedure permits greater catalyst life, especially in the second stage where the incoming feed is low in contaminants, as well as better control of and flexibility in the operation of the process to obtain the required high conversion of a variety of feedstocks.

Referring now to FIGURE 2, the feedstock is again

removed from hydrocracker 20 through line 22 and passed into intermediate separation zone 23. Gaseous products, including unconverted hydrogen, ammonia H<sub>2</sub>S and volatile hydrocarbons, are removed through lines 24 and 25 while liquid products boiling below 600° F. are removed through at least one line, such as lines 26 and 27. The materials boiling above 600° F. pass through line 28 into second hydrocracker 29. Hydrogen for second hydrocracker 29 may be supplied through line 30. Conversion in second hydrocracker 29 is regulated in a conventional manner to bring the total conversion of the feedstock to the desired high degree. The hydrocracked oil passes out of second hydrocracker 29 through line 4 and is thereafter processed as described in the discussion of FIGURE 1. This mode of operation of the process of this invention results in longer catalyst life in second hydrocracker 29.

A more preferred method of operation of reaction zone 1 is also shown in FIGURE 2. Hydrogen which is separated from the hydrocracked oil in intermediate separation zone 23 and removed through line 24 may, rather than being taken out of the process through line 25, be passed with all the volatile materials through line 31 into conventional gas separator 32, wherein the hydrogen is separated from the other volatile materials and passed through line 33 into second hydrocracker 29. The other volatile materials may be removed from separator 32 through lines 34 and 35 to be processed and collected by conventional methods.

HF treating has been found to be superior to other types of acid or solvent treating for the improvement of properties of lubricating oils which have been produced by hydrocracking over a wide range of temperatures. However, it has also been found, as illustrated below in Table III, that the degree of ultraviolet light stability of the HF-treated oils is dependent on the temperature at which the hydrocracking is performed. The data in Table III were derived from experiments conducted with a California deasphalted oil.

TABLE III

60	Hydrocracking temperature (° F.):	Ultraviolet Light Stability of HF-Treated Oil (hrs. to ppt.)		
		Light neutral oil	Heavy neutral oil	Bright stock
740		5	60	>100
760		10	70	>100
780		16	80	>100
815		20	100	>100

The process of the present invention is operated within the catalytic hydrocracking temperature range of 720°-850° F. If the temperature is below 720° F., the effect of HF treating is lessened. If the temperature is above 850° F., thermal cracking becomes a principal cracking reaction and hydrocracking is minimized. It should be noted, however, that HF treating of oils produced at temperatures outside the optimum range of 720°-850° F.

still produces significantly higher yields of stable oils than those produced when other treating agents, such as sulfuric acid or phenol, are used on hydrocracked oils produced under the same conditions. When only one hydrocracking reactor is used, it is preferred to operate in the temperature range of 750°-830° F. for, as indicated in Table III, stability of the HF-treated oil increases as the temperature at which the oil was produced by hydrocracking is raised. If two-stage hydrocracking is used to produce the oil, it is preferred to operate such that the temperature in the second hydrocracking zone is in the range of 740°-800° F.

Table IV below illustrates the comparison of one- and two-stage hydrocracking followed by HF treating. The feed is a California deasphalted oil.

TABLE IV

	Single Pass; or First Stage of Two-pass Operation	Second Stage of Two-pass Operation
Temperature, ° F-----	810	780
Pressure, p.s.i.g.-----	2,400	2,400
LHSV-----	0.7	4.0
Ultraviolet light stability of light neutral oil product (hrs. to ppt.):		
Before HF treating-----	2	2
After HF treating-----	30	20

The catalyst used in the hydrocracking reactors may be of the sulfactive hydrogenation type commonly used for desulfurization and denitrification. Suitable catalysts include combinations of the Group VI and Group VIII metals, oxides or sulfides associated with porous refractory oxide carriers. The most suitable metals are nickel or cobalt in combination with molybdenum or tungsten as sulfides. The refractory oxide may be alumina; but usually, to provide more hydrocracking activity, there is employed a combination of alumina with silica, magnesia, titania and other like materials or combinations of such other oxides—for example, silica-magnesia. Such catalysts can be prepared in a number of ways, including preparing the porous carrier first and then impregnating it with solutions of the metal compounds which are later converted to metal oxides by calcining. Particularly good catalysts for use in the hydrocracking step can be prepared by coprecipitation or cogelation techniques wherein all of the components are initially supplied as dissolved compounds in aqueous solutions and coprecipitated together. Zeolitic-supported hydrocracking catalysts may also be used.

As noted earlier, ultraviolet light instability is evidenced by the formation of a visible precipitate in the oil. The degree of stability possessed is determined by the relative amount of time required for the precipitate to form. One obvious way to measure this degree of stability is to expose the oil to the ultraviolet light in sunlight and observe the number of days required for the precipitate to form. This, however, is an unsatisfactory procedure for two related reasons: First, natural ultraviolet light is not concentrated, so the oils usually require several weeks or months of exposure before any precipitate forms. Secondly, over this period of time, the daily exposure is not uniform, for the amount of sunlight varies with the time of year and the weather on any particular day. Consequently, in order to measure ultraviolet stability rapidly and reliably, the following test has been developed. A 5 ml. sample of the oil in a clear glass container is exposed to a 450 watt mercury vapor ultraviolet light (type L) placed in a closed cabinet with the oil sample and with a distance of 2 inches between the oil sample and the light source. Light neutral oils which form a precipitate in less than four hours' exposure are considered to be too unstable to be commercially acceptable. Oils which form precipitates in more than four but less than ten hours are considered reasonably stable and marginally acceptable, although inferior, while those

which require more than ten hours' exposure before precipitation are considered of premium quality.

The above-described examples are given for illustrative purposes only. It is apparent that many different embodiments of this invention may be made without departing from the scope and spirit thereof, and therefore it is not intended to be limited except as indicated in the appended claims.

We claim:

1. A process for producing lubricating oil from a liquid hydrocarbon feedstock containing a substantial portion of components boiling above 750° F., which comprises:
  - (a) contacting said feedstock with hydrogen in a reaction zone containing at least one catalytic hydrocracking zone under catalytic hydrocracking conditions, including a temperature in the range 720° to 850° F., in the presence of a sulfactive hydrocracking catalyst to convert in said reaction zone at least 15 weight percent of said feedstock components boiling above 750° F. to materials boiling below 750° F.;
  - (b) recovering in a separation zone from the hydrocracked product of said reaction zone a lubricating oil fraction boiling above 600° F.;
  - (c) treating said lubricating oil fraction with a treating agent comprising a major portion of concentrated HF in a treating zone; and
  - (d) recovering from said treating zone a lubricating oil having improved ultraviolet light stability.
2. The process of claim 1 wherein said treating zone comprises a plurality of sequential contacting steps.
3. The process of claim 1 wherein said reaction zone comprises in series a first catalytic hydrocracking zone, a separation zone wherein materials boiling below about 600° F. are separated from the product of said first catalytic hydrocracking zone, and a second catalytic hydrocracking zone.
4. The process of claim 3 wherein said second catalytic hydrocracking zone is operated at a temperature in the range of 740°-800° F.
5. The process of claim 1 wherein the catalyst used in said reaction zone comprises a Group VI component and a Group VIII component associated with an inorganic oxide support.
6. The process of claim 1 wherein the hydrogen pressure in said reaction zone is in the range of from about 1,500 to 3,000 p.s.i.g.
7. The process of claim 1 wherein said treating agent consists essentially of anhydrous HF.
8. The process of claim 1 wherein said treating agent consists essentially of an aqueous solution containing at least 90 weight percent HF.
9. The process of claim 1 wherein said separation zone comprises a dewaxing zone.
10. A process for producing lubricating oil from a liquid hydrocarbon feedstock containing a substantial portion of components boiling above 750° F., which comprises:
  - (a) contacting said feedstock with 1,000 to 20,000 s.c.f. of hydrogen per barrel of said feedstock in a reaction zone containing in at least one catalytic hydrocracking zone a catalyst comprising a Group VI component and a Group VIII component associated with an inorganic oxide support, said reaction zone operated at a temperature in the range of 750° to 830° F., a pressure in the range of 500 to 5,000 p.s.i.g. and an LHSV in the range of 0.2 to 10, to convert in said reaction zone at least 15 percent of said feedstock components boiling above 750° F. to materials boiling below 750° F.;
  - (b) separating from the hydrocracked product of said reaction zone a lubricating oil fraction boiling above 600° F.;
  - (c) dewaxing said separated lubricating oil fraction;
  - (d) treating said dewaxed lubricating oil fraction with

a treating agent comprising a major portion of concentrated HF in a treating zone;

(e) separating HF from the effluent of said treating zone; and

(f) recovering from the effluent of said treating zone a lubricating oil having an ultraviolet light stability of at least four hours.

11. The process of claim 10 wherein said treating zone comprises a plurality of sequential contacting steps.

12. The process of claim 11 wherein each of said sequential contacting steps is operated at a temperature in the range of from about 0° to about 250° F.

13. In a process which comprises producing lubricating oil from a liquid hydrocarbon feedstock containing a substantial portion of components boiling above 750° F. by contacting said feedstock with hydrogen in a reaction zone containing at least one catalytic hydrocracking zone under catalytic hydrocracking conditions, including a temperature in the range of 720° to 850° F., to convert in said reaction zone at least 15 weight percent of said feedstock components boiling above 750° F. to materials boiling below 750° F. and recovering in a separation zone

from the hydrocracked product of said reaction zone a lubricating oil boiling above about 600° F., the improvement which comprises treating said recovered lubricating oil with a treating agent comprising a major portion of concentrated HF in a treating zone, and recovering from said treating zone a lubricating oil having improved ultraviolet light stability.

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