United States Patent Office 2,927,077 Patented Mar. 1, 1960

2,927,077

REFINING OF MINERAL OIL

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No Drawing. Application June 21, 1957
Serial No. 667,278

11 Claims. (Cl. 208—282)

This invention relates to the refining of mineral oil, and more particularly to the improvement of color stability and other properties of mineral oil fractions.

Mineral oil fractions, e.g. gasoline, fuel oil, lubricating oil, wax, etc., as ordinarily produced from petroleum, frequently have unsatisfactory color stability, as a result of the presence in the fraction of constituents which are unstable and tend with the passage of time to be converted into materials which impart a dark color to the petroleum fraction. It is often difficult by ordinary refining procedures to remove these constituents from petroleum. Often the conventional refining procedures will produce a petroleum fraction which has good color initially, but because of the presence of these constituents discolors with the passage of time.

The present invention provides a novel manner of converting constituents responsible for poor color stability, thereby to produce a petroleum fraction which has good color stability. This is accomplished according to the invention by contacting the petroleum fraction with an acylating agent at a temperature of at least 200° F., and preferably within the approximate range from 250 to 500° F., thereby to react the acylating agent with acylatable materials in the fraction. The fraction is then separated from the reaction products of the acylating agent with the unstable, acylatable constituents of the fraction.

In one embodiment of the invention, an acylating agent is added to the petroleum fraction and the latter subjected to the elevated temperature specified previously. In another embodiment of the invention, an added acylating agent is not employed, the petroleum fraction normally containing a material capable of acting as an acylating agent. Thus petroleum fractions frequently contain naphthenic acids naturally occurring in petroleum, and these acids are capable of functioning as an acylating agent. In this embodiment, the treating agent employed according to the invention comprises an acylating catalyst, which is effective to promote the reaction of naphthenic acids with acylatable constituents of the petroleum fraction. The temperature employed in this embodiment is at least 250° F., since it has been found that such elevated temperatures are required for optimum refining in the case where naphthenic acids naturally occurring in the fraction are employed as the acylating agent.

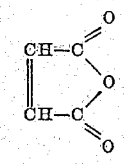
Generally speaking, the acylating conditions which are employed according to the invention may be any conditions suitable for the acylation of organic hydroxy compounds generally. When naphthenic acids in the oil are the only acylating agent, an acylating catalyst is used, e.g. sulfuric acid, hydrochloric acid, phosphoric acid, toluene sulfonic acid, acetic acid, sulfonic acids, chlorinated acetic acid, ethyl sulfuric acid, ethyl sulfonic acid, boron fluorides, silicon fluorides, monosodium sulfate, zinc chloride, calcium chloride, zinc sulfate, nickel sulfate, copper sulfate, powdered metals, metal carboxylates, alumina, silica gel, etc. Instead of or in addition to an acylating catalyst, ultraviolet light, sonic or ultrasonic

waves, or electrical vibrations may be employed. When an acid anhydride is used as acylating agent, an added acylation catalyst is not necessary, though it may be used if desired. Generally suitable acylation temperatures are those in the range from 200° F. to 500° F., preferably 250° F. to 400° F. A solvent such as xylene may be used if desired, in which case the acylation is preferably carried out under refluxing conditions. Generally the acylation will be satisfactorily effected in 0.5 to 32 hours, most usually in 3 to 12 hours.

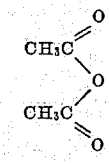
When an added acylating agent is used, the amount employed is generally a minor amount relative to the amount of oil. Most frequently, 0.1 to 10 parts of added acylating agent per 100 parts of oil will be employed. When an esterification catalyst is employed, the amount is generally in the range from 0.05 to 5 parts by weight per 100 parts of oil and is generally less than the amount of acylating agent present, if any.

The preferred acylating agents used according to the invention are certain carboxylic acids and the corresponding anhydrides and acid halides, the anhydrides being preferred. Anhydride, as the term is used here, refers to a carboxylic acid derivative having one molecule of water eliminated between two carboxyl groups. The preferred carboxylic acids which can be used as such or in the form of the corresponding anhydride or acid halide are the following: aliphatic acids, including saturated and unsaturated acids, preferably having not more than 20 carbon atoms, e.g. acetic, propionic, butyric, caprylic, pelargonic, lauric, myristic, oleic, etc.; petroleum naphthenic acids; maleic acid; saturated acyclic dicarboxylic acids having at least 3 carbon atoms and preferably having not more than 10 carbon atoms, e.g. malonic, succinic, glutaric, adipic, azelaic, sebacic, etc.; phthalic acids, i.e. homophthalic, isophthalic and terephthalic; tetrahydrophthalic acids; hexahydrophthalic acids; etc.

The term, acid acylating agent, as used herein, refers to the acid in question, its anhydride, or acid halide; thus, for example phthalic acid acylating agents include phthalic acid, phthalic anhydride and phthalic acid chloride. Acid anhydrides, as contemplated here, include both internal anhydrides such as



and external anhydrides such as



In the treatment of petroleum fractions according to the invention, amines, phenols, pyrroles, indoles, mercaptans, etc. are converted by acylation to amides, esters, thioesters, ketones, etc. Reactions of acylating agent with thiophenes may also occur in the case of maleic anhydride for example. After the acylation step, unreacted acylating agent and the acylation products may be separated by distillation, contact with adsorbent, caustic washing, etc. For example, when acetic anhydride is used as acylating agent, the acetic acid formed may be removed as an azeotrope with an added hydrocarbon, e.g. 2,2,4-trimethyl pentane (commercial isooctane) or other hydrocarbon boiling between 70° C. and 105° C. The amount of hydrocarbon employed may be for ex-

ample about 5% based on the petroleum fraction to be refined. Any suitable minor amount, determinable by a person skilled in the art in the light of the present specification can be employed. When the acylation step is complete, unreacted acetic anhydride may be distilled out as a forecut or washed out with caustic soda, and the acylation products may be left in the oil, or separated as a distillation residue, or removed with clay or other adsorbent. When a dibasic acid anhydride is used as acylating agent, those acylation products which contain a free carboxyl group can be washed out with caustic, or removed as a distillation residue, or removed by clay treating. When acid halides are used as acylating agents, halogen acids which are formed in the reaction may be washed out with caustic.

The following examples illustrate the invention:

Example I

A lubricating oil distillate having S.U. viscosity at 100° F. of about 200 seconds was prepared by saponifying a topped naphthenic crude and vacuum distilling to obtain the distillate. This distillate had N.P.A. color of 1¾. In a color stability test, wherein the oil was maintained at 220° F. for 16 hours, the N.P.A. color was 3 at the end of the test.

The distillate was contacted with stirring at 300° F. for 3 hours with 4 parts by weight of acetic anhydride per 100 parts of oil. Unreacted acetic anhydride was stripped from the oil, and the latter was distilled under vacuum to obtain a 0–92% distillate having N.P.A. color of 1½+. After 16 hours at 220° F., the oil had N.P.A. color of 1½, indicating very good color stability. The cast, or bloom, of the oil was also improved over the original distillate, and the stability of the bloom was also improved.

This example shows that the color stability and other properties of a straight run lubricating oil are considerably improved by treatment with acetic anhydride followed by distillation of the oil.

Generally similar results are obtained employing other acid anhydrides such as those disclosed previously.

Example II

Operation generally similar to that described in Example I is carried out, employing 2% of phthalic acid as an acylating agent and 1% of toluene sulfonic acid as acylation catalyst. The treatment is performed at 300° F. for 4 hours, and the products of the treatment are distilled under vacuum to obtain a 0–94% distillate. The color stability of this distillate is substantially improved over that of the original lubricating oil.

Generally similar results are obtained employing other carboxylic acids and other catalysts such as those disclosed previously.

Example III

Operation generally similar to that described in Example I is carried out, employing as acylating agent, naphthenic acid halides having the formula RCOCl where R is a hydrocarbon radical having molecular weight ranging from about 180–220 and containing a plurality of cycloaliphatic rings including at least one 5-membered ring, as normally contained in petroleum naphthenic acids, RCOOH. The refining is performed at 300° F. for 3 hours, and a 0–90% distillate is obtained from the reaction products. This distillate has superior color stability to that of the original lubricating oil.

Generally similar results are obtained employing other acid chlorides such as those disclosed previously.

Example IV

Operation generally similar to that described in Example I is carried out, employing 1% of toluene sulfonic acid acylation catalyst as the sole treating agent. The charge stock is a lubricating oil distillate having S.U. viscosity at 100° F. of about 200 seconds and containing about 1½% of naphthenic acids. The refining operation is performed at 300° F. for 5 hours, and a 0–92% distillate is obtained from the products, the distillation residue containing reaction products of naphthenic acids and acylatable impurities in the charge stocks. The distillate has superior color stability to that of the original lubricating oil.

Generally similar results are obtained employing other acylation catalysts such as those disclosed previously.

The process of the invention is applicable generally to crude oil and to straight run petroleum fractions, e.g. gasoline, kerosene, mineral spirits, gas oil, furnace oil, stove oil, lubricating oil, transformer oil, paraffin wax, microcrystalline wax, etc.

This application is a continuation-in-part of application Serial No. 391,303, filed November 10, 1953, now U.S. Patent No. 2,868,835, issued January 13, 1959. The parent application discloses and claims refining petroleum naphthenic acids, which may contain minor amounts of oil, by means of an acylating agent, whereas the present application is directed to the refining of mineral oil, which may contain minor amounts of naphthenic acids, by means of an acylating agent.

The invention claimed is:

1. Method for refining petroleum fractions which comprises: treating a straight run petroleum fraction with treating material consisting essentially of 0.1 to 10 weight percent based on the petroleum fraction of an added organic carboxylic acid and 0.05 to 5 weight percent based on the petroleum fraction of an added organic acylation catalyst at a temperature within the approximate range from 200 to 500° F.

2. Method for refining petroleum fractions which comprises: treating at a temperature within the approximate range from 200 to 500° F. a straight run petroleum fraction with treating material consisting essentially of 0.1 to 5 weight percent based on the petroleum fraction of an added organic carboxylic acid anhydride having one molecule of water eliminated between two carboxyl groups.

3. Method for refining petroleum fractions which comprises: treating at a temperature within the approximate range from 200 to 500° F. a straight run petroleum fraction with treating material consisting essentially of an added organic carboxylic acid halide.

4. Method for refining petroleum fractions which comprises: treating at a temperature within the approximate range from 200 to 500° F. a straight run petroleum fraction with treating material consisting essentially of 0.05 to 5 weight percent based on the petroleum fraction of an added organic acylation catalyst.

5. Method for refining mineral oil which comprises treating at a temperature within the approximate range from 200 to 500° F. straight run mineral lubricating oil with treating material consisting essentially of 0.1 to 5 weight percent based on oil of an organic carboxylic acid anhydride having one molecule of water eliminated between two carboxyl groups.

6. Method for refining mineral oil which comprises treating at a temperature within the approximate range from 200 to 500° F. straight run mineral lubricating oil with treating material consisting essentially of an organic carboxylic acid anhydride; and distilling to recover a refined mineral oil distillate.

7. Method for refining mineral oil which comprises treating at a temperature within the approximate range from 250 to 500° F. straight run mineral oil containing naphthenic acids with treating material consisting essentially of 0.05 to 5 weight percent based on oil of an added organic acylation catalyst, thereby to form relatively high boiling products of acylation of naphthenic acids with acylatable materials in said oil; and separating said products from the oil.

8. Method for refining petroleum fractions which comprises treating a straight run petroleum fraction with an

organic acylating catalyst and an agent selected from the group consisting of carboxylic acids, carboxylic acid anhydrides and carboxylic acid halides at a temperature within the approximate range from 200 to 500° F.

9. Method according to claim 8 wherein said catalyst is toluene sulfonic acid.

10. Method according to claim 4 wherein said catalyst is toluene sulfonic acid.

11. Method according to claim 2 wherein said anhydride is acetic anhydride.

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