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PROCESS FOR STABILIZING FURNACE OIL

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This invention relates to a stabilized hydrocarbon oil boiling in the heavier-than-gasoline range, which oil has been derived from a catalytic cracking operation. More particularly, the invention relates to a furnace oil which contains a catalytically cracked oil which has been stabilized by the process of the invention.

Oils boiling in the heavier-than-gasoline range, i. e., between about 350° F. and about 600° F. which have been obtained from the liquid product of the catalytic cracking of hydrocarbon oils, are of unsatisfactory storage stability as determined by deterioration in color formation of gums and sediments. When catalytically cracked oils boiling in this distillate fuel range are mixed with virgin oils which boil in the distillate fuel range, which virgin oils have been sweetened by the Doctor method, the resulting blend is much less stable than either of the components alone. This characteristic is known as incompatibility of stocks. The demnad for hydrocarbon oils for use in domestic furnaces has increased so markedly in recent years that the demand cannot be supplied by a 100% virgin gas oil material. Therefore, it is necessary that a stable blended furnace oil be producible by the refiner.

An object of the invention is a method for stabilizing oils boiling in the heavier-than-gasoline range which have been derived from catalytic cracking operations. Another object is a catalytically cracked gas oil boiling in the heavier-than-gasoline range which has satisfactory storage stability with respect to gum, sediment and color. Still another object is a method of producing a furnace oil of good storage stability, which furnace oil is made by blending a Doctor sweentened virgin gas oil and a catalytically cracked cycle oil. A particular object is a furnace oil of satisfactory storage stability with respect to color, gum and sediment, which furnaces oil is made by blending a Doctor sweetened virgin gas oil and a catalyically cracked cycle oil.

A raw sour oil derived from a catalytic cracking operation, which oil boils in the heavier-than-gasoline range, is stabilized with respect to the color, gum and sediment by adding to the raw oil between about 0.001 and about 0.004 weight percent of an alkali-metal hydroxide and between about 0.0005 and about 0.002 weight percent of free iodine. A furnace oil of improved stability with respect to color, gum and sediment is produced by blending a catalytically cracked oil treated by the above process and a virgin gas oil which has been sweetened by the Doctor method.

The catalytically cracked oil charged to the treating process boils in the range of about 350° F. and 650° F. This oil has been derived from the conversion products of the catalytic cracking of heavier hydrocarbon oils, such as gas oils and reduced crudes. In the refining operation, these catalytically cracked oils are known as "catalytic cycle stocks." The catalytic cracking operation which produces the catalytically cracked oil charged to the treating process of the invention may be any one of the well-known processes now in use in the petroleum industry,

for example, the fluidized catalytic cracking process, the thermofor catalytic cracking process, the Houdriflow cracking process, the Houdry catalytic cracking process, or the cycloversion process.

The catalytically cracked oil should be treated immediately after it is withdrawn from the fractionator or stored in intermediate storage which is equipped to prevent contact of air of free-oxygen with the raw oil. Hereinafter the term "raw oil" means the sour catalytically cracked oil as it has been withdrawn from the fractionator without immediate storage to the treating process or has been stored without contact with atmospheric oxygen. Frequently the raw oil as produced contains entrained water as is evidenced by the presence of a haze. The presence of entrained water as evidenced by a heavy haze has an adverse effect on the quality of the treated oil and therefore it is preferred that the raw oil be freed of entrained water, if any is present. This may be done by prolonged settling in the absence of oxygen, or passing the oil through a coalescer such as a fibre glass packed vessel or through a salt drum.

The raw oil is treated to render it more stable by adding to the raw oil between about 0.001 and about 0.004 weight percent of an alkali-metal hydroxide, such as sodium hydroxide or potassium hydroxide. It has also been found that alkali-metal phenolates may be added to the oil to obtain the desired result. The amount of sodium or potassium phenolate which is added should be substantially equivalent to the above defined amounts of metal hydroxide. Addition of appreciably less than 0.001 weight percent of alkali-metal hydroxide is relatively ineffective for stabilizing the oil and the addition of appreciably more than 0.004 weight percent of alkali-metal hydroxide results in the formation of a separate phase of alkali-metal hydroxide. The alkali-metal hydroxide is preferably added to the oil in the form of a concentrated solution in a substantially anhydrous alcohol. For example, methanol, ethanol and isopropanol. The alkali-metal hydroxide may be added to the raw oil in the form of a saturated aqueous solution; this is particularly so when the addition is carried out at a relatively high temperature, such as 150–200° F.

The treating process includes not only the addition of the above-defined amounts of alkali-metal hydroxide but also the addition of between about 0.0005 and about 0.002 weight percent of free-iodine. (A compound which readily decomposes to produce free-iodine, such as sodium iodate, may be used.) The iodine is preferably added in the form of an alcoholic solution. Use of appreciably less than 0.0005 weight percent of free-iodine is relatively ineffective and the use of appreciably more than about 0.002 weight percent may have a deleterious effect on the stability of the treated oil.

The treating operation may be carried out at ordinary temperatures or even at moderately elevated temperatures. Thus the process may be carried out between about 30° F. and 250° F., or even somewhat higher. Normally, the treating operation will be carried out at the temperature at which the catalytically cracked oil is produced from the fractionator. Typically, this is on the order of 150° F.

It has been found that the treated oil which is very sour, as determined by the Doctor test, as produced, and immediately after having been treated, gradually becomes sweet with open exposure to free-oxygen. When adequate storage space is available, the sweetening may be obtained by simply allowing the treated oil to remain in a tank which is vented to the atmosphere for 2 to 4 days. More rapid sweetening can be obtained by adding free-oxygen to the treated oil, for example, by injecting cylinder oxygen into the stream of treated oil as it passes to the storage tank.

Presently the higher quality distillate fuels used in do-

mestic furnaces, i. e., furnace oils, are blends of cracked oils and virgin oils. Typically the virgin oil component is a gas oil boiling in the range of about 350° F. and 650° F. The virgin gas oil component has been made sweet to the Doctor test usually by the well-known Doctor method. In this method, the sour oil is contacted with an aqueous plumbite solution in the presence of free-sulfur and air until the oil is sweet as determined by the Doctor test. Usually the refiner uses as the virgin component 2, or even more, different virgin gas oils, different in the sense of boiling range primarily.

Generally the furnace oil consists of not more than about 70 parts of catalytically cracked oil and about 30 parts of the Doctor-sweetened virgin gas oil. Generally the furnace oil consists of at least about 20 parts of catalytically cracked oil and about 80 parts of Doctor-sweetened virgin gas oil.

The effectiveness of the treating process of this invention in stabilizing catalytically cracked oils and overcoming incompatibility with Doctor-sweetened virgin oils, is illustrated by the following tests. In these tests, the catalyically cracked oil was a light catalytically cracked oil (LCCO) which boiled over the range of 350° F. to 550° F. This oil had been produced by the fluidized catalytic cracking, using a silica alumina catalyst, of high sulfur virgin gas oils. The virgin gas oil component of the furnace oil tested was derived from two sources. The virgin component boiled over the range of 350° to 650° F. The virgin component had been sweetened by contacting it with 4 volume percent of Doctor solution and 150% of the theoretical of free-sulfur. The Doctor solution contained water, sodium hydroxide, and sodium plumbite; the lead content was about 1.7 grams, as PbO, per 100 ml. of solution. The furnace oil consisted of a blend of 32 volumes of LCCO and 68 volumes of Doctor-sweetened virgin oil. Four furnace oils were made up wherein the LCCO portion was given either no treatment or treated as follows: The raw, sour oil obtained directly from the fractionator had added to it 0.002 weight percent of sodium hydroxide as a concentrated solution in anhydrous methanol; another portion of raw, sour oil had added to it 0.001 weight percent of free-iodine as an alcohol solution; another portion of the raw oil had added to it both sodium hydroxide and free-iodine—0.002 weight percent of sodium hydroxide and 0.001 weight percent of free-iodine. Two different batches of each furnace oil were produced in order to enable testing of the different furnace oils after 3 months and 6 months, respectively, of storage in vented bottles. The storage was at about 90° F.

The comparisons between the furnace oils were made on the basis of the NPA color of the oil, the acid floc gum and sediment. Both gum and sediment were determined as mg. per 100 ml. of oil by the technique of Proell and Bolt, Oil and Gas Journal, March 30, 1946.

TEST 1

The four different oils were inspected after 3 months of storage in vented bottles and the results of these tests are set out in Table I below.

Table I

Treatment of LCCO Component	NPA Color	Gum	Sediment
None	2−	7.0	1.8
0.002% NaOH	1.5−	3.0	1.0
0.001% I_2	3−	5.9	0.5
0.002% NaOH and 0.001% I_2	1−	1.9	0.5

TEST 2

The oils were again inspected after 6 months of storage. The results of these tests are set out in Table II below.

Table II

Treatment of LCCO Component	NPA Color	Gum	Sediment
None	2	7.9	2.5
0.002% NaOH	2+	10.9	1.4
0.001% I_2	3+	8.3	1.9
0.002% NaOH and 0.001% I_2	1+	2.4	1.2

The above data show that a remarkable improvement in stability with respect to color, gum and sediment is obtained by treating the catalytically cracked portion of the furnace oil according to the process of this invention. In every respect the oil containing LCCO treated with both sodium hydroxide and free-iodine was better than the furnace oils which had been treated with only one of the two components of the treating processes. It is submitted that these data show that the objects of the invention have been attained.

Thus having described the invention, what is claimed is:

1. A process for producing a sweet, storage-stable furnace oil which process comprises (A) (i) removing entrained water, immediately subsequent to the production thereof and before any contact with atmospheric oxygen, from a liquid sour oil boiling in the range of about 350° F. and about 650° F., which oil has been produced by the catalytic cracking of a petroleum oil and (ii) dissolving in said dewatered oil between about 0.001 and about 0.004 weight percent of alkali-metal hydroxide, and between about 0.0005 and about 0.002 weight percent of free-iodine, based on said dewatered oil, respectively, (B) contacting a sour virgin gas oil obtained by distillation of petroleum, which oil boils in the range of about 350° F. and about 650° F., with aqueous plumbite in the Doctor method and separating a sweet gas oil from aqueous solution, (C) blending said alkali-metal hydroxide and free-iodine containing-oil and said sweet gas oil in a volume ratio of said oil and said sweet gas oil between about 20:80 and 70:30, said blend being sour to the Doctor test, and (D) exposing said blend to free-oxygen for a time sufficient to produce a sweet furnace oil which is storage-stable.

2. The process of claim 1 wherein said alkali-metal hydroxide is added to said dewatered oil in the form of a saturated aqueous solution.

3. The process of claim 1 wherein said alkali-metal hydroxide is added to said dewatered oil in the form of a solution in anhydrous methanol.

4. The process of claim 1 wherein said free-iodine is added to said dewatered oil in the form of an alcohol solution.

5. The process of claim 1 wherein said blend is composed of about 32 volumes of said oil and about 68 volumes of said sweet gas oil.

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