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**SWEETENING PETROLEUM HYDROCARBONS
WITH A N,N'-DIALKYL-PHENYLENE DI-
AMINE AND OXYGEN IN THE PRESENCE OF
REFINERY SLOP OIL**

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This invention relates to the sweetening of saturated petroleum hydrocarbons by means of catalytic oxidation of mercaptans employing phenylene diamines as catalysts.

"Inhibitor sweetening" of petroleum fractions by means of phenylene diamines has become an important process in petroleum refining, but saturated petroleum hydrocarbons, e. g. straight run gasoline, have shown poor susceptibility to such sweetening processes. Although some reduction of mercaptan content of straight run gasoline, for example, can be accomplished, the results are not satisfactory, since the product still contains too much mercaptan to justify the treatment.

It has been proposed to subject saturated petroleum fractions to inhibitor sweetening with phenylene diamines in the presence of added olefins, e. g. in the presence of added cracked gasoline. In some instances, however, such operation is not feasible or desirable.

The present invention provides a process whereby saturated petroleum hydrocarbons can be substantially completely sweetened by means of catalytic oxidation using phenylene diamines. The process of the invention involves subjecting straight run petroleum hydrocarbons to inhibitor sweetening in the presence of constituents of petroleum "slop oil," as subsequently more fully described.

The process of the invention involves catalytic oxidation of mercaptans contained in petroleum hydrocarbons by means of an oil-soluble mononuclear N,N'-dialkyl-p-phenylene diamine in the presence of free-oxygen containing gas and slop oil constituents. Generally, the process is carried out in the presence of water and either ammonia or an alkali metal hydroxide, e. g. sodium or potassium hydroxide.

Advantageously, the process can be performed by adding a phenylene diamine to the hydrocarbons to be treated, then bubbling ammonia gas and steam through the hydrocarbons until the proper amounts, as subsequently more fully described, have been added, then allowing the hydrocarbons to stand, in the presence of air for a sufficient time to accomplish the sweetening operation.

Suitable saturated hydrocarbons to be treated include for example liquefied petroleum gases, straight run gasoline, hydrogenated polymer gasoline, mixtures of such gasolines, straight run naphtha, straight run kerosene, blends of such fractions with other fractions, etc. Saturated petroleum hydrocarbons, as the term is used herein, refer to petroleum charges substantially free of olefinic constituents, though aromatic constituents may be present. Distillates having boiling points up to 750° F. are preferred charge stocks, and distillates having boiling points up to 430° F. are more preferred charge stocks.

Suitable phenylene diamines for use according to the invention include N,N'-dialkyl-p-phenylene diamines wherein the alkyl groups are the same or different. Preferably, the total number of carbon atoms in both alkyl groups is not greater than 12. Examples of suitable

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alkyl groups are methyl, isopropyl, secondary butyl, secondary amyl, secondary hexyl, etc.

Generally, the amount of phenylene diamine used is within the approximate range from 1 to 20 pounds per 1000 barrels of hydrocarbons treated, and preferably the amount is within the approximate range from 2.5 to 10 pounds per 1000 barrels. The amount used depends on the reaction time available, lesser amounts being satisfactory when longer reaction times are available. Generally, the reaction time will be within the approximate range from a few minutes to four weeks.

The amount of ammonia used is preferably within the approximate range from 3 to 50 pounds per 1000 barrels of hydrocarbons treated. Greater amounts can be used, e. g. up to 3500 pounds per barrel, but recovery and recycle of ammonia is generally necessary when such greater amounts are used. The amount of water used is preferably within the range from 20 to 500 weight percent based on the amount of ammonia used.

When alkali metal hydroxide is employed instead of ammonia, the amount is preferably within the approximate range from 0.02 to 5 volume percent based on the hydrocarbons treated, and 25 to 50 percent aqueous solutions are preferably employed.

Any suitable manner may be employed to provide oxygen for the treatment. Free-oxygen containing gas such as air can be bubbled through the hydrocarbons during the treatment, or such gas can be dissolved in the hydrocarbons prior to the treatment, or the treatment can be carried out in an oxygen-containing atmosphere; any other suitable manner of operation can be used.

Preferably, the phenylene diamine is added to the hydrocarbons and slop oil constituents before contacting the latter with the other materials involved, but the order of contacting is not critical.

The temperature of the treatment is usually within the approximate range from 50° F. to 200° F. Preferred temperatures are those in the range from 70° F. to 100° F. Where ammonia is used, sufficient pressure should be employed to avoid excessive vapor pressure of the ammonia from the hydrocarbon phase at the temperature employed.

According to the present invention, inhibitor sweetening is carried out in the presence of constituents of petroleum slop oil recovered from petroleum refinery "waste water" streams. Such recovery of slop oil and means for accomplishing such recovery are well known in the field of petroleum refining. A good description is found in an article by Roy F. Weston, "Separation of oil refinery waste waters," Industrial and Engineering Chemistry, volume 42, pages 607-612 (April 1950).

The waste water streams referred to are not necessarily streams which are discarded after removal of oil therefrom. Rather, they are streams obtained in the refinery which are treated for oil removal, and in some instances subjected to other treatment, prior to re-use or to discarding as the case may be.

The exact composition of slop oil cannot be stated, since it depends on the source and composition of the various waste water streams which are charged to the separating apparatus. Typically, however, some of the waste water streams contain straight run hydrocarbon contaminants; others, cracked hydrocarbon contaminants; some contain wide boiling range contaminants such as crude oil, others narrower fractions such as gasoline, furnace oil, etc. The nature of the contaminants depends of course on the nature of the organic materials, etc. with which the water has been in contact, and this in turn depends on what part of the refinery the various waste water streams come from. Generally, the streams come

from a wide variety of sources and are commingled in the separating apparatus.

The effluent oil from the separating apparatus usually has undergone substantial partial oxidation, particularly where the separation process involves the accumulation of an upper layer of oil in contact with an oxygen-containing atmosphere. Typically, the separated oil has an A. P. I. gravity within the range from 20 to 45, and contains substantial amounts of material boiling within the boiling ranges of each of the common petroleum fractions; in this respect it resembles crude petroleum.

In one embodiment of the process according to the invention, slop oil is charged, together with crude oil, to a distillation operation from which straight run distillates are recovered, and one or more of the straight run distillates thus obtained is subjected to inhibitor sweetening. The distillate thus obtained contains those constituents of the slop oil which boil in the range of the distillate, and those constituents provide increased reduction of mercaptan content in accordance with the invention.

In another embodiment, the slop oil is separately distilled, and a distillate or distillates therefrom is blended with the corresponding straight run distillate from crude oil prior to subjecting such distillate to inhibitor sweetening.

Any other manner of operation may be employed whereby the inhibitor sweetening is carried out in the presence of constituents of the slop oil.

The amount of slop oil constituents required to obtain a satisfactory reduction in mercaptan content is surprisingly small. Amounts from 0.1 to 10 volume percent based on the saturated petroleum can be employed for example, but generally amounts less than 1 percent, e. g. up to 0.9 percent give satisfactory results, making it unnecessary or undesirable to use greater amounts. The indicated ranges apply, in the case where slop oil and crude are distilled together, to the amount of slop oil in the distillation charge, but the preferred ranges are generally the same for the amount of slop oil constituents in the charge to the sweetening operation.

The following example illustrates the invention:

Straight run gasoline was sweetened by contact with 5 pounds per 1000 barrels of "Tenamene 2," a commercial inhibitor of which the active ingredient is N,N'-disubstituted butyl-p-phenylene diamine, in the presence of oxygen and 1 ml. of concentrated aqueous ammonium hydroxide per 800 ml. of gasoline. The gasoline, inhibitor, and ammonium hydroxide were mixed and allowed to stand in an oxygen atmosphere for three weeks at a temperature of about 70° F.

The straight run gasoline was obtained from a distillation to which crude petroleum and slop oil were charged, the amount of slop oil being about 0.25-0.6 barrel per 100 barrels of crude petroleum. The slop oil was obtained from an A. P. I. gravity separator for recovery of oil from petroleum refinery waste water streams. The sources of these streams were typical for A. P. I. separators in petroleum refineries wherein distillation and catalytic cracking, in addition to other processes, are carried out. The water streams contained both straight run and cracked hydrocarbon contaminants having a wide

range of boiling points, from those of the heaviest portions of crude petroleum to those of the lowest boiling liquid fractions. Typical A. P. I. gravity for the slop oil is within the range from 30 to 45.

For purpose of comparison, another run was made in which the straight run gasoline which was used was obtained from a distillation of similar crude petroleum in the absence of slop oil. The following table shows the results obtained:

Run No.	Slop Oil	Mercaptan Contents—Weight Percent			
		Initial	After 1 Week	After 2 Weeks	After 3 Weeks
1	Absent	0.0055	0.0054	0.0038	0.0026.
2	Present	0.0062	0.0053	0.0009	Too small to measure.

This example shows that inhibitor sweetening in the presence of a very small amount of slop oil constituents greatly increases the sweetening of straight run gasoline obtainable in two or three weeks. In the case where slop oil was not used (run 1) the gasoline had a mercaptan content of 0.0026% after three weeks, indicating that the mercaptan content of the gasoline cannot be reduced to a satisfactory level by ordinary inhibitor sweetening. Where slop oil was used (run 2), however, substantially sweet gasoline was obtained in three weeks. Even after only two weeks, in run 2, though the gasoline contained 0.0009% mercaptan, it was nearly doctor sweet. A more rapid sweetening can be obtained by using larger quantities of sweetening agents, more mixing, etc.

The invention claimed is:

1. Process for sweetening saturated petroleum hydrocarbons which comprises: contacting saturated petroleum hydrocarbons under sweetening conditions with a small amount of an N,N'-dialkyl-p-phenylene diamine in the presence of oxygen and 0.1 to 10 volume percent based on said hydrocarbons of constituents of slop oil recovered from petroleum refinery waste water streams.

2. Process for preparing straight run gasoline having low mercaptan content which comprises: distilling crude petroleum and 0.1 to 0.9 volume percent based on crude of slop oil recovered from petroleum refinery waste water streams; and contacting straight run gasoline recovered from such distillation with a small amount of an N,N'-dialkyl-p-phenylene diamine in the presence of oxygen, said gasoline being the sole charge to said contacting.

3. Process for sweetening saturated petroleum hydrocarbons which comprises: contacting saturated petroleum hydrocarbons under sweetening conditions with a small amount of an N,N'-dialkyl-p-phenylene diamine in the presence of oxygen and 0.1 to 0.9 volume percent based on said hydrocarbons of constituents of slop oil recovered from petroleum refinery waste water streams.

References Cited in the file of this patent

UNITED STATES PATENTS

2,694,034 Moriarty Nov. 9, 1954