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ACID TREATMENT OF OILS

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This invention relates to a process for desulfurizing oils and is particularly directed to desulfurizing such high sulfur content gasoline constituents as pressure distillate made by cracking residuum or gas oil containing a high percentage of sulfur.

It is well known to treat high sulfur content oils, such as cracked gasoline, with sulfuric acid in order to reduce the sulfur content of the oil. This method has heretofore required the use of relatively large quantities of sulfuric acid usually of at least 98% strength.

It is a principal object of my invention to provide a process which will more efficiently utilize the quantity of acid employed for removing sulfur compounds from high sulfur gasolines such as pressure distillate.

A further object of my invention is to obtain a higher yield of stable cracked gasoline containing less sulfur and having less odor than a cracked gasoline treated with the same amount of acid by previously known procedures.

Other objects, features and advantages of my invention will become apparent from the following detailed description.

As is well known, one of the conventional processes for reducing the sulfur content of cracked gasolines consists in mixing or contacting the pressure distillate with sulfuric acid, preferably of 98% strength or stronger, which reacts with impurities contained in the gasoline including the sulfur and sulfur compounds. The mixture is allowed to settle and the sulfuric acid phase containing dissolved impurities is separated in the form of a sludge from the treated pressure distillate. The latter is then washed one or more times with water and is then treated with a weak alkali solution such as caustic soda. The alkali treated pressure distillate may again be washed with water after which it is redistilled to produce a gasoline distillate of the desired boiling range. The treated and redistilled pressure distillate may be caustic washed to remove traces of acidic materials formed during the distillation, and may then be further treated with sulfur in the presence of doctor solution which consists of sodium plumbite. This final treatment sweetens the gasoline by converting mercaptans into less odorous sulfur compounds.

The present invention is directed to an improvement in acid treating sulfur containing gasoline stocks. I have discovered that when the acid treatment of the sulfur-bearing pressure distillate is carried out in the presence of a small amount of an additive consisting of a relatively high molecular weight petroleum fraction, such as residuum obtained from topping an asphalt base crude oil, a greater reduction in sulfur content is obtained than when the acid treatment is carried out in the conventional manner in the absence of such additive. For example, I have obtained a 29% greater reduction in sulfur content by the use of my process over the conventional process using no heavier petroleum fraction. To illustrate, a pressure distillate obtained from the viscosity reduction of a Los Angeles Basin crude oil residuum, which pressure distillate contained 1.35% by weight of sulfur (in the form of various organic sulfur compounds) was mixed at a temperature of about 80° F. with about 1% of an asphalt obtained by the vacuum distillation of a Santa Fe Springs crude oil, the asphalt having a melting point of 175° F. and a penetration of 6 at 77° F. The mixture was then shaken vigorously at room temperature with acid in the ratio of 10 lbs. of 98% sulfuric acid per barrel of pressure distillate. The mixture was allowed to settle in order to separate the acid and reaction products from the treated oil. The oil was decanted from the settled sludge and was then washed twice with water using 50% by volume of water in the first wash and 20% by volume in the second wash. The oil was then washed with 10% of an aqueous solution containing 2% by weight of caustic soda. This was followed by another wash with 20% by volume of water. The foregoing washes were accomplished by shaking the distillate and the aqueous solution together at room temperature and then allowing the mixture to stratify into two layers and drawing the aqueous layer from the oil.

The thus treated oil was then redistilled with steam at a maximum temperature of 450° F. to remove approximately 95% of the treated pressure distillate as an overhead fraction. The thus treated pressure distillate when tested showed a sulfur content of 0.73% by weight.

In order to compare the foregoing process with the conventional methods in which no additive is employed, the foregoing example was repeated without the use of the additive but under conditions of separation and quantities of material employed similar to those of the foregoing example. A test on the thus treated pressure distillate showed a sulfur content of 0.87% by weight.

In the conventional process, the redistillation of the acid treated pressure distillate is sometimes accomplished in the presence of a small amount of additive similar to that employed by applicant during acid treatment. Such additive

is known as "artificial bottoms" and is added purely for the purpose of assisting in the distillation as many stills require a certain volume of bottoms material to be produced in order to operate properly. In order to show that the acid treatment in the presence of the additive produces a different result from that obtained by the redistillation in the presence of the additive but without employing the additive during the acid treatment step, the foregoing process was repeated except that no additive was added during the acid treatment but was added to the acid treated pressure distillate immediately prior to the redistillation. A test on the distillate thus produced showed a sulfur content of 0.38% which is not substantially different from the 0.37% obtained in the above process when no additive was employed either during the acid treatment step or during the redistillation step. This comparison illustrates that the beneficial effect of the process forming the subject matter of my invention is due primarily to the acid treatment in the presence of the additive and is not the same as redistillation of the acid treated distillate in the presence of the additive.

In some instances the finished oils treated by the proposed process had a better odor than products from the corresponding conventional treatments. Furthermore, it was possible to take more material of acceptable quality overhead during the redistillation when using the proposed method of acid treatment rather than the conventional one.

While I prefer to employ as an additive for the acid treatment step a material containing asphalt such as a residuum obtained from topping an asphalt base crude oil, a road oil, or an asphalt-containing crude oil, I have found other petroleum fractions having a molecular weight substantially higher than that of the gasoline to be treated, to be operative in obtaining a greater sulfur reduction in the acid treatment than is obtainable without their use under similar treating conditions. Examples of such additive are lubricating oil fractions including the extracts or raffinates obtained upon extracting the lubricating oil with liquid sulfur dioxide or other selective solvents, paraffin wax, petroleum resins or plastics, oxidized petroleum fractions such as oxidized lubricating oils, paraffin wax, asphalt, etc. In addition, other high molecular weight materials of hydrocarbon character, such as coal tar, coal tar pitch, etc., may be employed as additives.

The amount of additive which is to be employed may vary with the particular additive with which the stock is to be acid treated and the strength and amount of acid employed. In general, I have found that about 0.5 to 5% by weight of the additive is sufficient for the purpose.

The strength of the acid will also vary with the stock and conditions of operation. Generally, sulfuric acid of 98% strength or greater is suitable for the purpose. The amount of acid to be employed will vary with the amount of sulfur desired to be removed, it being understood that a greater amount of the acid will remove a greater amount of sulfur. The temperature of the acid treatment will vary from the very low sub zero temperatures to the more elevated temperature of approximately 100° F. or more.

While the foregoing description of my invention has been directed to the treatment of gasoline constituents of high sulfur content, such as pressure distillate, it will be understood that the invention is applicable to the acid treatment of other petroleum or hydrocarbon fractions for sulfur removal, such as kerosene, gas oil, lubricating oil, benzene, xylene, etc., the only requirement being that the additive have a substantially higher molecular weight than the stock to be acid treated.

As is conventional in the desulfurization of oils, the acid treatment may be followed with water washing and neutralization with an aqueous solution of caustic alkali which may also be followed by a water wash and the thus treated pressure distillate may be redistilled to remove 95% or more as an overhead fraction to leave a portion of the material as bottoms which will contain sulfur compounds. Since the acid treatment is effected in the presence of a high molecular weight material, substantially all of this material will be contained in the bottoms, resulting from the redistillation. If desired, these bottoms may be recirculated; or a further quantity of the additive may be incorporated into the pressure distillate prior to the redistillation. The acid treated pressure distillate may be further treated, for example, sweetened by the doctor treatment or any other sweetening process.

The above description of my invention is not to be considered as limiting but only as illustrative of the invention as many variations may be made within the scope of the following claims.

I claim:

1. A process for treating a gasoline distillate containing sulfur-bearing compounds which comprises adding to said distillate a hydrocarbon fraction having a higher boiling point than said distillate and then treating said mixture at a temperature between about 0° F. and 100° F. with concentrated sulfuric acid.

2. A process for treating a gasoline distillate containing sulfur-bearing compounds which comprises adding a hydrocarbon fraction containing asphalt to distillate and then treating said mixture at a temperature between about 0° F. and 100° F. with concentrated sulfuric acid.

3. A process for treating a gasoline distillate containing sulfur-bearing compounds which comprises adding asphalt to said distillate and then treating said mixture at a temperature between about 0° F. and 100° F. with concentrated sulfuric acid.

4. A process for treating a gasoline distillate containing sulfur-bearing compounds which comprises adding to said distillate approximately 0.5 to 5% by weight of a distillation residue of an asphalt-containing crude oil and treating said distillate at a temperature between about 0° F. and 100° F. with concentrated sulfuric acid in the presence of said residue.

5. A process for treating a gasoline distillate containing sulfur-bearing compounds which comprises mixing said distillate with a relatively small amount of a relatively high boiling point petroleum fraction and treating said mixture at a temperature between about 0° F. and 100° F. with concentrated sulfuric acid of such concentration and quantity to reduce the sulfur content of said distillate to the desired amount.

6. An improvement in the process of acid treating cracked distillates for reduction of gum and sulfur content, which comprises mixing said cracked distillate with approximately 0.5 to 5% by weight of a distillation residue of an asphalt-containing crude oil, before contacting the said mixture at a temperature between about 0° F. and 100° F. with concentrated sulfuric acid, sep-

arating the resulting sludge from the treated oil, neutralizing the separated treated oil, and distilling it to the desired end-point.

7. A process according to claim 6 in which the distillation residue has an average boiling point approximately that of lubricating oil or higher.

8. An improvement in the process of acid treating cracked distillates for reduction of gum and sulfur content, which comprises mixing said cracked distillate with approximately 0.5 to 5% by weight of a distillation residue of an asphalt-containing crude oil, before contacting the said mixture at a temperature between about 0° F. and 100° F. with strong sulfuric acid, separating the resulting sludge from the treated oil, and distilling said oil to the desired end-point.

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