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SULFURIC ACID SWEETENING OF STRAIGHT RUN PETROLEUM DISTILLATES

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This invention relates to a method for refining hydrocarbon oils, particularly petroleum distillates, by treatment with sulfuric acid.

It is known that sulfur compounds, particularly mercaptans, can be removed from petroleum hydrocarbon oils by contacting the oil with concentrated sulfuric acid. The mercaptans contained in these oils are extracted by the sulfuric acid and react therewith to form disulfides. The latter are soluble in sulfuric acid, but still more soluble in oil, and can only be extracted and removed from the hydrocarbon oil in the presence of a considerable amount of acid, as is the case with the alkyl monosulfides which are frequently present. If it is desired only to sweeten an oil, i.e., to remove the mercaptans from the oil so that it gives a negative reaction to the doctor test, the treatment requires relatively little acid. In this case most of the disulfides and other sulfur compounds remain in the oil. The sulfuric acid treatment is of particular advantage in desulfurizing or sweetening hydrocarbon oils obtained by straight-run distillation of crude oil and boiling below the lubricating oil boiling range as these distillates contain no or virtually no olefinic hydrocarbons which under the influence of concentrated sulfuric acid rapidly form polymers which have to be removed by a separate treatment.

However, sulfuric acid sweetening of even straight-run petroleum distillates has often been precluded in commercial practice because of still another difficulty. This is that such distillates often contain tertiary mercaptans and, when these compounds are present in concentrations even as low as about 0.0004% by weight mercaptan sulfur, contacting the distillate with sulfuric acid heretofore has resulted in the formation of free sulfur and other highly corrosive forms of sulfur which remain in the product. Besides making the product corrosive, this is especially deleterious in the case of gasoline because it greatly reduces tetraethyl lead anti-knock effectiveness, i.e., the "lead susceptibilty" of the product. Any after-treatment of the product to remove this type of sulfur is too complicated and expensive to be commercially feasible.

It is accordingly a principal object of this invention to provide an improved process for the refining of hydrocarbon oils by treatment thereof with sulfuric acid. A more particular object is to provide an improved process for the sulfuric acid sweetening of petroleum straight-run distillates boiling below the lubricating oil boiling range. Still another object is to provide a process for sweetening such distillates which contain tertiary mercaptans, wherein the formation of free sulfur and other highly corrosive forms of sulfur is lesssened or avoided, and other advantages are obtained. Other objects will be apparent in the description of the invention.

It has now been found that these and other objects are accomplished by treating a petroleum straight-run distillate hydrocarbon oil which boils below the lubricating oil boiling range and which contains tertiary mercaptans by adding thereto a small amount of a bromine-reactive unsaturated hydrocarbon material, to be described below in more particularity, and thereafter contacting the oil with a relatively small amount of sulfuric acid.

The petroleum hydrocarbon distillate oils treated by the process of the invention are tertiary mercaptan-containing fractions obtained by straight-run distillation of petroleum crude oil. These fractions are essentially free from aliphatic unsaturation such as is present in olefinic and acetylenic compounds or either acyclic or alicyclic structure. Any bromine absorption by such fractions in a bromine number determination, above an amount equivalent to a bromine number of about 1, is due to non-addition type of reaction such as is obtained with certain higher boiling aromatics. Cracked hydrocarbons, or other fractions containing aliphatic unsaturation equivalent to a bromine number above about 1, cannot be suitably treated by this process because such oils contain large quantities of olefins which form gums, polymers, resins, and the like in the presence of sulfuric acid. Thus, the yield of treated product from cracked oils would be low and the product would be contaminated with undesirable material. The suitable distillates are also normally liquid fractions which boil below the boiling range of lubricating oil, that is, those which have end boiling points (ASTM method D–86) not greater than about 400° C. Best results are obtained when the end boiling point is not over about 315° C. Such suitable distillates include gasoline, special boiling range solvents, white spirit (mineral spirits), V. M. and P. naphtha, kerosene, aviation turbine fuels, and the various grades of distillate heating oils. The process is especially advantageous in the sweetening of the middle range distillates such as white spirit or mineral spirits, kerosene, and aviation turbine fuels, i.e., those which boil within the range of about 150° C. to about 315° C. Treatment of such distillates according to the invention results in greatly reduced total sulfur content of the product as compared to conventional sulfuric acid treatment of such distillates without the prior addition of bromine-reactive unsaturated hydrocarbon material.

The bromine-reactive unsaturated material which, according to the invention, is added to the hydrocarbon dis-

tillate before the sulfuric acid contacting step can be a single unsaturated hydrocarbon compound or a mixture of a number of such compounds and may or may not contain other hydrocarbons. It should not contain any significant amount of non-hydrocarbon material. Especially useful are catalytically or thermally cracked petroleum fractions, such as light and heavy normally liquid cracked distillates and the normally gaseous olefinic petroleum fractions such as ethene, propene, butenes, and mixtures thereof with saturated hydrocarbons of the same average carbon number such as cracked petroleum gas. Acetylene and other acetylenic hydrocarbons containing triple bonds are also suitable. In this connection, the term "bromine-reactive unsaturated hydrocarbon material" is used herein to include hydrocarbon material which contains one or more compounds which have at least one bromine-reactive (i.e., by addition) double or triple bond and may have a plurality of such bonds in either conjugated or non-conjugated positions, in addition to any non-bromine-reactive, resonating type of unsaturation such as that typified by the benzene ring. They are thus materials which contain aliphatic unsaturation, including olefinic and acetylenic compounds which can be either acyclic or alicyclic.

The suitable unsaturated materials have bromine numbers of at least 10 and preferably at least 30, corrected for any bromine absorption not due to aliphatic unsaturation. In the case of normally gaseous unsaturated material such as acetylene, propene, etc., the calculated bromine number is adequate for this criterion. For example, since acetylene has one triple bond and can therefore theoretically add two moles of bromine, the calculated bromine number (grams of bromine per 100 grams of acetylene) is 1230. As long as the bromine number is at least as indicated above, the unsaturated material will contain a sufficient concentration of unsaturation to bring about the advantages of the invention. The unsaturated material must have a boiling point or boiling range which does not exceed 400° C., and preferably does not exceed 315° F. Light cracked distillates having end boiling points (ASTM D–86) not greater than about 225° C. give especially good results.

The amount of bromine-reactive unsaturated material added to the tertiary mercaptan-containing oil to be sweetened must be at least 0.1% by weight of the oil. Less than this amount, especially in the case of unsaturated material having bromine numbers in the lower part of the operable range described above, will not adequately reduce the formation of free sulfur and other highly corrosive forms of sulfur. An amount of at least about 0.5% by weight is preferred. On the other hand, the amount of the unsaturated material added must not be greater than 4% by weight, and preferably not greater than 3% by weight, of the oil to be treated since greater amounts than this give rise to the formation of gums, polymers, resins and the like to an extent that would significantly contaminate the treated product. In the case of light cracked distillates, 1% by weight is ordinarily the most that need be used. Heavy cracked distillates and normally gaseous fractions or compounds containing bromine-reactive unsaturation are generally used in amounts above 1% by weight of the oil to be treated.

The addition of normally gaseous unsaturated material can be accomplished merely by dissolving it in the oil to be treated. The use of pressure is not necessary.

The sulfuric acid suitably used in the present process has a concentration of at least 85% by weight, and preferably at least 93% by weight. The amount of acid used is from about 0.1 to about 10% by weight of the oil to be treated. Within this range, it is preferred to use at least 1% by weight, and best results are usually obtained when no more than 5% by weight, especially no more than about 3.5% by weight, is used.

The technique used in contacting the oil and acid is not critical to the invention. In general, techniques heretofore used in conventional sulfuric acid treatment are equally applicable in the present process. Thus the total required amount of acid can be applied to the oil in a single step, or fractions of the total required amount can be successively added until the total is supplied, with or without intermediate oil and acid phase separation steps. The type of mixing can be either mechanical, such as with a paddle or propeller mixer or a turbo-mixer or a circulating pump, or it can be by air or inert gas agitation. A mechanical method or agitation with a non-oxidizing gas is preferred, however, since this will result in a product which has better color and odor stability. The contacting can be either batch or continuous. The time of contact between the oil and acid should be sufficient for the sweetening process to be completed, i.e., for the product to be negative to the doctor test, but it should not be extended substantially beyond this since needlessly prolonged contact results in poor product color and odor. Generally, the sweetening reaction is complete within 15 minutes to 2 hours, depending upon the particular oil being treated.

After the sweetening reaction is complete, the oil must be separated from the acid phase, which at this point is "acid sludge." This is conveniently done by settling or centrifuging, or by the addition of an absorptive solid to the mixture or by percolation of the mixture through a bed of sand or gravel or other filtering material, or by water washing. The process of the present invention results in products which ordinarily need no further treatment. However, if desired, the product can be given a finishing treatment such as distillation to recover the product as a distillate, or contacting with clay or other adsorbent.

Not only is the formation of elemental sulfur prevented in the process of the invention but also the reaction time and the amount of sulfuric acid necessary for sweetening are reduced. Irak white spirit was treated according to the invention to give a negative doctor test by means of 2.5% by weight of sulfuric acid of 96.7% by weight concentration, whereas without the addition of olefins 3 or 3.5% by weight of acid was required, the duration of treatment being identical. On the other hand with 3% by weight of sulfuric acid of 96.7% by weight by adding 0.6% by weight of a light cracked distillate an Irak white spirit was obtained which after 25 minutes gave a negative reaction to the "doctor test," a result which was only obtained after 90 minutes without the addition of light cracked distillate.

The process according to the invention is generally carried out at ambient temperature. If the temperature is increased, a negative reaction to the "doctor test" is obtained more rapidly, but there is a great risk of free sulfur formation.

Tests have also been made for treating hydrocarbon oils in several stages by mixing each time with 0.5% by weight of sulfuric acid and adding each time 0.1 to 0.2% by weight of light cracked distillate. By operating in this manner the product sometimes contained free sulfur. However, by adding the whole quantity of cracked distillate beforehand good results are obtained.

The presence of elemental sulfur and other corrosive forms of sulfur is shown by the Mercury Corrosion Test (A.S.T.M. method D–268). This test is carried out by

shaking in a closed tube 10 cc. of oil with 1 cc. of clean mercury, after which the tube is allowed to stand for 15 minutes. If the mercury does not change color as compared to a similar test in which the oil is replaced by distilled water, there is no elemental or other highly corrosive form of sulfur; i.e., the test is "negative."

In general, it is found that oils produced by the process according to the invention give a negative mercury test. There are, however, cases in which, as Example III shows, it is not possible to prevent the formation of elemental sulfur completely. In such cases it is found, however, that the result of the mercury test is considerably less positive than without the addition to the oil of unsaturated hydrocarbons.

The invention is illustrated in the following examples.

EXAMPLE I

Different quantities of cracked distillate, viz. 1% and 1.5% by weight of light cracked distillate and 1% and 1.5% by weight of heavy cracked distillate were added respectively to four samples of Irak white spirit containing tertiary mercaptans and having a boiling range of 145° C. to 183° C., a specific gravity of 0.773 and a mercaptan sulfur content of 0.038% by weight. Each sample was then mixed with 3% by weight of sulfuric acid of 96% by weight concentration. After stirring vigorously by means of a mechanical stirring device, and settling to separate the hydrocarbon from the sludge formed, the samples with respective additions of 1 and 1.5% by weight of light cracked distillate and with 1.5% of heavy cracked distillate were found to give a negative "doctor test" and a negative mercury test, as is shown by the data in Table I. The fourth sample, treated with sulfuric acid after the addition of 1.0% by weight of heavy cracked distillate, gave a positive mercury test. The control sample which was treated with sulfuric acid in a similar manner, but to which no unsaturated material had been added, gave a positive mercury test.

The data of Table I also show that the duration of the operation is considerably reduced by adding cracked distillates.

Table I

Treatment with—	White spirit treated with sulfuric acid only	White spirit treated with sulfuric acid after the addition of heavy or light cracked distillate			
Light cracked distillate, percent by weight		1.0	1.5		
Heavy cracked distillate, percent by weight				1.0	1.5
Sulfuric acid, percent by weight	3.0	3.0	3.0	3.0	3.0
Mixing time in minutes	60	50	45	45	30
"Doctor test"	neg.	neg.	neg.	neg.	neg.
Mercury test, ASTM/D 268	pos.	neg.	neg.	pos.	neg.
Color Lovibond after 60 days	0.75	0.5	0.5	0.5	0.5
Odor	fairly good	fairly good	fairly good	good	fairly good

When the white spirit thus treated is stored in light for 60 days, neither its color nor its odor deteriorates.

By repeating the above tests, mixing being effected by means of air instead of by mechanical means, a white spirit is also obtained which shows a negative mercury test; the stability of the odor and color is, however, not as good.

EXAMPLE II

300 tons of a tertiary mercaptan-containing Irak white spirit with a mercaptan sulfur content of 0.0144% by weight and a total sulfur content of 0.09% by weight were treated five to seven times with 0.2 to 0.5% by weight of sulfuric acid (96% by weight) after previous addition of 0.6% by weight of cracked distillate having a boiling range of 40° C. to 183° C. and a bromine number of 56. The results are shown in Table II.

Table II

Test No.	1	2	3
Quantity of cracked distillate added, percent by weight	0.6	0.6	0.6
Number of additions of H_2SO_4	5	6	7
Total amount of sulfuric acid (96% by weight) added, percent by weight	1	3.5	3.5
Duration of treatment in hours	25	29	32
"Doctor test"	neg.	neg.	neg.
Mercury test	neg.	neg.	neg.
Total sulfur content of product, percent by weight	0.04	0.03	0.03

EXAMPLE III

In this series of experiments, tertiary mercaptan-containing hydrocarbon oils listed in Table II were contacted with sulfuric acid after addition of unsaturated material as listed in Table IV.

Table III

Petroleum Fraction	Gasoline	White spirit	Kerosene	Gas oil
Specific gravity at 15° C.	0.740	0.777	0.803	0.834
Boiling range in ° C.	100–150	150–185	200–260	200–360
Mercury test	neg.	neg.	pos.	pos.
Total sulfur content, percent by weight	0.080	0.150	0.260	0.83

Table IV

Unsaturated Hydrocarbon	Light cat. cracked distillate I	Light cat. cracked distillate II	Light cat. cracked distillate III	Light cat. cracked distillate IV	Light thermal cracked distillate
Specific gravity at 15° C.	0.731	0.637	0.719	0.738	0.749
Boiling range, ° C.	41–144	20–47	68–94	41–205	51–179
Bromine number	57	132	103	86.5	70
Maleic anhydride number	30.2	28.4	46.3	6	32
Total sulfur content, percent by weight	0.031	0.065	0.047	0.150	0.067
Mercury test	neg.	neg.	neg.	neg	neg.

Table V summarizes the results of the treatment according to the invention of the distillates referred to in Table III after addition of the light cracked distillate I shown in Table IV.

Table VII shows clearly that although the sweetening reaction proceeds more quickly at higher temperatures, the mercury test gives a positive reaction at even 30° C. Since the object in view, which is to prevent the formation of elemental sulfur, is not attained in this way, the use of a temperature which is higher than about 20 or 25° C. is usually inadvisable. While not usually necessary, the acid and oil can be contacted at a reduced temperature, e.g., —10 to +10° C., if desired.

Table V

Petroleum fraction treated	Gasoline			White spirit			Kerosene			Gas oil		
Light catalytic cracked distillate I, percent by weight	0	0.6	1.0	0	0.6	1.0	0	0.6	1.0	0	0.6	1.0
Sulfuric acid, percent by weight	3	3	3	3	3	3	3	3	3	3	3	3
Time required to obtain a negative "doctor test," in minutes	50	30	30	70	35	40	80	60	70	60	55	60
Mercury test	pos.	neg.	neg.	pos.	neg.	neg.	pos.	neg.	neg.	slightly pos.	slightly pos.	neg.
Total sulfur content	0.023	0.024	0.027	0.042	0.029	0.018	0.195	0.159	0.131	0.770	0.736	0.732
Color Lovibond	0.5	0.5	0.5	0.5—	0.5—	0.5—	0.75—	0.75—	0.75—	3.5—	3.5—	3.5—

Table VI gives the results of the treatment of the white spirit of Table III with sulfuric acid, with prior addition of the unsaturated hydrocarbons referred to in Table IV. Table VI also shows the results obtained by using as unsaturated hydrocarbons cracked gases and acetylene.

Table VI

Unsaturated hydrocarbon added	Unsaturated hydrocarbon, percent by wt.	Percent by wt. of sulfuric acid of 96.7% by wt. concentration	Color, Lovibond	Time required to obtain a negative "doctor test," minutes	Mercury test	Total sulfur content of white spirit after treatment
Light cat. cracked distillate I	0	3	—	70	pos	0.041
	0.3	3	0.5—	45	neg	0.022
	0.6	3	0.5—	35	neg	0.027
	1	3	0.5—	40	slightly pos	0.020
Light cat. cracked distillate II	0.6	3	0.5—	35	neg	0.021
Light cat. cracked distillate III	0.6	3	0.5—	25	slightly pos	0.024
Light cat. cracked distillate IV	0.3	3		45	pos	
	0.6	3	0.5—	45	slightly pos	0.025
Light thermal cracked distillate	0.3	3		30	pos	
	0.6	3	0.5	40	slightly pos	0.022
	1	3		50	do	
Cracked gas poor in unsaturated compounds, washed with NaOH, Schilling density=1.1.	2.2	3	0.5—	50	do	0.032
	1.2	3	0.5—	30	do	0.030
Cracked gas rich in unsaturated compounds, washed with NaOH, Schilling density=2.4, Specific gravity at 15° C.=0.584.	2.2	3	0.5—	25	neg	0.038
Acetylene	1.5% by volume.	3	0.5—	45	neg	0.039

According to the data in Table VI the hydrocarbon oils treated according to the invention do not all give a clearly negative mercury test. However, a considerable improvement is nevertheless obtained as compared to the conventional sulfuric acid treatment without prior addition of unsaturated material.

EXAMPLE IV

This example shows the effect of temperature on the treatment of tertiary mercaptan-containing Irak white spirit according to the invention. The unsaturated hydrocarbon used was the light catalytic cracked distillate I referred to in Table IV of Example III. The results of the tests are given in Table VII.

Table VII

Quantity of light cracked distillate, percent by weight	Temperature, ° C.	Sulfuric acid, percent by weight	Time required to obtain a negative "doctor test"	Mercury Test	Total sulfur content, percent by weight	Color Lovibond
0.6	20	3	35	neg	0.027	0.5—
0.6	30	3	28	pos	0.022	0.5—
0.6	40	3	30	pos	0.024	0.5—
1	20	3	40	neg	0.020	0.5—
1	30	3	27	pos	0.024	0.5—
1	40	3	30	pos	0.024	0.5—

I claim as my invention:

1. In the process of sulfuric acid sweetening of a straight run petroleum hydrocarbon distillate having an end boiling point no higher than about 400° C. and containing tertiary mercaptans which normally form free sulfur during the sulfuric acid sweetening process, the improvement which comprises reducing said free sulfur formation by adding to the untreated distillate from about 0.1 to about 4% by weight of a bromine-reactive unsaturated hydrocarbon material having a bromine number of at least 10 and boiling no higher than 400° C., and thereafter contacting the distillate with from 0.1 to 10% by weight of sulfuric acid having a concentration of at least 85% by weight.

2. A process according to claim 1, wherein the bromine number of the unsaturated hydrocarbon material is at least 30.

3. A process according to claim 1, wherein the bromine-reactive unsaturated hydrocarbon material is a cracked petroleum fraction having an end boiling point no higher than 225° C., and the amount of unsaturated hydrocarbon material added is no greater than 1% by weight of the distillate.

4. A process according to claim 1, wherein the bromine-reactive unsaturated material is cracked petroleum gas.

5. A process according to claim 1, wherein the distillate boils within the range 150° C. to 315° C.

6. A process according to claim 5, wherein the distillate is an aviation turbine fuel fraction.

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