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ODOR IMPROVEMENT OF PETROLEUM OILS

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This invention relates to the refining of petroleum oils. More particularly the invention relates to the improvement of the odor of petroleum oils which are substantially mercaptan free. Still more particularly, the invention relates to the removal of "West Texas odor" from petroleum oils.

Virtually all oils obtained by the distillation of crude petroleum possess a sour odor caused by the presence of mercaptans. In addition to this sour odor, petroleum odors possess a characteristic naphtha odor. Until the discovery of the very high sulfur crudes, particularly West Texas crudes, these two odors were the only problems facing the petroleum refiner. West Texas crude, and in particular, the fraction from West Texas crude boiling in the heater oil range, i. e. about 350° to about 575° F., possesses a pungent odor distinctly different from either the sour odor of mercaptans or the naphtha-type odor normally present in petroleum oils. Since this odor was first noticed in and is most prominent in West Texas crude, this particular odor has been designated as "West Texas odor" or "W. T. odor." The sour odor of mercaptans can be eliminated by any one of the numerous sweetening processes; these processes either physically remove the mercaptans from the oil or chemically convert the mercaptans to disulfides which possess an inoffensive odor. The naphtha odor is not considered as objectionable by the consumer of petroleum products. The West Texas odor is very objectionable to the consuming public and sales of heater oils from West Texas crude have been markedly affected by the presence of West Texas odor.

An object of this invention is to eliminate West Texas odor from petroleum oils. Another object is to eliminate West Texas odor from petroleum oils that are substantially mercaptan free.

I have discovered that the so-called West Texas odor characteristic of certain high sulfur crude petroleum is caused by saturated cyclic sulfur compounds wherein the sulfur is present within the ring structure. Furthermore, I have discovered that these West Texas odor bodies combine with mercuric salts to form solid oil-insoluble complexes which can be readily separated from the oil. By contacting an oil characterized by a West Texas odor, with an effective amount of a mercuric salt, such as mercuric chloride, mercuric acetate, mercuric nitrate, etc., an oil can be obtained that has the same odor as the acceptable oils from Mid-Continent crude.

A sour oil can be sweetened by treatment with mercuric salts such as mercuric chloride, as mer-

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captans react to form generally insoluble mercaptides. However, when sweetening oils boiling above the gasoline range, such as heater oil, furnace oil, kerosene, the mercury reacts with high molecular weight mercaptans to form oil-soluble mercaptides. These oil-soluble mercury mercaptides remain in the sweet oil and very adversely affect the color stability of the sweet oil; therefore, even though the expense of sweetening with mercury salts were to be disregarded, sweetening of sour oils boiling above the gasoline range with mercury salts is not desirable.

The cyclic sulfides which cause the West Texas odor are not affected by the usual sweetening processes; neither the mercaptan removal processes nor the mercaptan conversion processes.

In the usual mercaptan removal processes I include the following: The caustic-methanol process for the extraction of mercaptans. The so-called solutizer processes wherein the mercaptans are removed from the sour oil by extraction with aqueous alkali solution containing mercaptan solubility promoters such as potassium isobutyric acid, phenolic compounds such as those derived by caustic washing from cracked oils, wood tars, etc.

In the usual mercaptan conversion processes I include the following: The so-called copper chloride sweetening process. The process wherein the sour oil is contacted with aqueous alkali at elevated temperatures in the presence of air. The process wherein sour oil is contacted with aqueous alkali at about 100° F. in the presence of an oxidation catalyst such as copper sulfate in the presence of air. The process wherein the sour oil is contacted with a very small amount of alcohol, about 1%, and a concentrated aqueous alkaline solution in the presence of air. The conventional doctor process wherein the sour oil is contacted with aqueous sodium plumbite.

Mercaptans can be removed from sour oil by sulfuric acid or phosphoric acid treating. I have found that a sour oil containing West Texas odor bodies can be sweetened by acid treating without appreciable simultaneous improvement in the West Texas odor. Thus a West Texas heater oil was treated with as much as 10 lbs. of 98% sulfuric acid per barrel of heater oil without commercially satisfactory improvement in West Texas odor characteristic; this treatment is in excess of the acid usage needed for producing a sweet oil. However, an increase in the amount of 98% sulfuric acid usage above 10 lbs. per barrel resulted in an improvement in West Texas odor properties. An oil equivalent to M. C. heater oil

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in odor quality was produced when the West Texas heater oil was treated with about 15 lbs. of sulfuric acid per barrel of oil. Thus I mean to include among my "usual sweetening processes" the treatment of a sour oil with sulfuric acid in such amounts that a sweet oil is produced with little or no improvement in West Texas odor.

The mercuric salt can be added to the West Texas odor body containing substantially mercaptan-free oil in various ways. For example, in the form of mercuric salt-feed oil slurry; in the form of a concentrated mercuric salt-water solution; in the form of a mercuric salt-alcohol solution, aqueous alcohol can also be used. The solid mercuric salt can be dispersed into the feed oil directly. I prefer to use a saturated aqueous solution of the mercuric salt.

Contacting can be carried out in any of the numerous ways known to the art. Some of these methods are agitation in a tank, injection of the treating agent into a line and passing the material through an orifice mixer or a centrifugal pump.

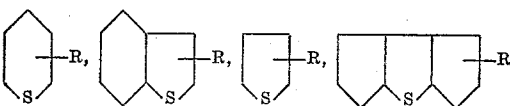
The mercuric salt-odor-body complex is a pasty solid of very low solubility in oil. This solid can be removed from the oil by a settling period or by filtration.

I have found that, in order to obtain substantially complete removal of the West Texas odor bodies, it is necessary to add from about 1 mol to about 3 mols of mercuric salt per mol of the cyclic sulfide compound present in the oil. A trace of the mercuric salt remains in the treated oil even after prolonged settling. This trace of mercuric salt can be removed from the oil by washing with an aqueous sodium sulfide solution. However, this washing procedure may be dispensed with if a metal deactivator is added to the oil in order to counteract the deleterious effect of the mercury on the color stability of the oil. A suitable metal deactivator is *N,N'*-disalicylidine-1,2-diaminopropane. In general between about 0.0002-0.01 wt. per cent of the metal deactivator should be added. A preferred amount is 2 lbs. per 1,000 barrels of oil, i. e. about 0.001 wt. per cent.

The West Texas odor bodies removed by the treatment of the West Texas oil with mercuric chloride are liquids with an extremely disagreeable odor and have the following characteristics:

ASTM distillation, °F.....	330-565
Specific gravity.....	0.93
Refractive index, n_D^{20}	1.4886
Mol. wt.....	170
Ultimate analysis (weight per cent):	
Carbon	69.3
Hydrogen	11.4
Sulfur	19.3
Hydrogen/carbon atomic ratio.....	1.96

A study of these West Texas odor bodies indicates that the structural formula for the individual compounds falls into one of the types listed below, where R can be either an alkyl radical or hydrogen.



ODOR EVALUATION PROCEDURE

The first step in the attack on the West Texas odor problem was the development of a standard odor evaluation (level) procedure. A set of standards was prepared as follows: A repre-

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sentative sample of a West Texas heater oil which had been sweetened by the doctor process was obtained. Various amounts of the standard West Texas heater oil were added to a medicinal white oil (U. S. P. grade). It was found that a small quantity of odoriferous oil added to a large quantity of virtually odorless medicinal white oil permitted fine distinctions to be made between different samples of oils containing West Texas odor bodies. The West Texas odor value and the composition of the standard are given below:

West Texas Odor Value	Sweet West Texas Heater Oil (ml.)	Medicinal White Oil (ml.)
15.....	8.6	491.4
20.....	11.5	488.7
25.....	14.2	485.8
30.....	17.1	482.9
35.....	20.0	480.0
40.....	22.9	477.1
45.....	25.8	474.2

The odor evaluation procedure is as follows: 20 ml. of the unknown oil are added to 480 ml. of the standard medicinal white oil. This diluted unknown oil is then compared with the odor standards by each of twelve sensitive and experienced individuals and assigned a West Texas odor number by each of them. It has been found that quite accurate reproducibility is obtainable. The average of the twelve odor values is taken as the West Texas odor value of the particular unknown oil. After a little practice, the odor panel can check an unknown within ± 1 odor number.

Run 1

An M. C. heater oil with a boiling range of 350° F. to 575° F. was doctor sweetened to produce a substantially mercaptan-free oil. This sweet M. C. heater oil had a West Texas odor number of 16 and is not objectionable in odor to consumers. A 250 ml. portion of this oil was contacted for 2 hours with 25 ml. of saturated aqueous mercuric chloride solution (about 7 grams of mercuric chloride per 100 ml. of water). The water layer was withdrawn and the treated oil was washed with a sodium sulfide solution to remove entrained mercuric chloride. The mercuric chloride treated oil had a West Texas odor number of 16, showing no improvement with mercuric chloride treatment.

Run 2

A West Texas heater oil of about 350 to 575° F. boiling range was doctor sweetened to produce a substantially mercaptan-free sweet oil. The sweet West Texas oil had a total sulfur content of 0.70 wt. per cent and a West Texas odor number of 36. A 250 ml. sample of this oil was treated with mercuric chloride as shown in Run 1. The treated oil had a West Texas odor number of 14. The loss of material in this treatment was slightly less than 0.1 volume per cent. The sulfur content of the West Texas odor-free sweet oil was 0.68. Thus by removing only 0.1 volume per cent of the feed oil, a heater oil having an odor better than the generally acceptable M. C. oil was obtained.

Run 3

The experiment of Run 2 was repeated using aqueous mercuric chloride and a 30-minute contact time. The treated oil had a West Texas odor number of 16.

A 250 ml. portion of doctor sweet West Texas heater oil was treated with 25 ml. of a solution of mercuric chloride in aqueous methanol; the contacting time was $\frac{1}{2}$ hour. The treated oil from this run had a West Texas odor number of 15.

I have found that my process is not appreciably affected by the temperature of contacting. I prefer to operate at temperatures lower than the decomposition temperature of the disulfides present in the sweet oil, about 350 to 400° F. My preferred operating temperature is at ambient temperatures, i. e. between about 60 and about 100° F.

Briefly, my process comprises the treatment of a petroleum oil which is substantially mercaptan-free and contains West Texas odor bodies, with a mercuric salt in an amount sufficient to produce a final oil of the desired West Texas odor level, separating the oil-insoluble odor-body-mercuric salt complex from the treated oil and, if desired, adding an effective amount of a metal deactivator to the treated oil.

I claim:

1. A combination process for the elimination of mercaptans and cyclic-sulfides from a petroleum oil containing appreciable amounts of these organic-sulfur compounds, which process comprises (1) treating said oil under conditions wherein essentially only mercaptans are eliminated from said oil, (2) contacting said treated oil from (1) with a mercuric salt, in an amount of between about 1 and about 3 mols per mol of cyclic-sulfides in said treated oil, and (3) separating an oil-insoluble mercury salt-cyclic-sulfide complex from an essentially cyclic-sulfide-free oil.

2. The process of claim 1 wherein said oil is a high sulfur heater oil boiling between about 350° and 650° F.

3. The process of claim 1 wherein said mercuric salt is mercuric chloride.

4. A combination process for the removal of odors from petroleum oils boiling between about

350° and 650° F. caused by the presence of mercaptans and cyclic-sulfides, which process comprises (1) doctor sweetening said oil to produce a sweet oil containing cyclic-sulfides, (2) contacting said sweet oil with an aqueous mercuric salt solution in an amount of between about 1 and about 3 mols of salt per mol of cyclic sulfide in said sweet oil, (3) separating a cyclic-sulfide containing solid from an essentially cyclic-sulfide-free oil and (4) stabilizing the oil from (3) by dissolving therein an effective amount of a metal deactivator.

5. A combination process for the removal of odors from high sulfur petroleum oils boiling between about 350° and 650° F., which odors are caused by the presence of mercaptans and cyclic-sulfides, which process comprises (1) treating said oil with about 10 lbs. of about 98% sulfuric acid per barrel of said oil, (2) separating acid sludge from treated oil, (3) contacting said treated oil with aqueous alkali metal hydroxide solution, (4) separating a sweet oil containing cyclic-sulfides from aqueous solution, (5) contacting said sweet oil with an aqueous mercuric chloride solution containing between about 1 and about 3 mols of mercuric chloride per mol of cyclic-sulfide in said sweet oil, (6) separating a cyclic-sulfide-free oil from a cyclic-sulfide containing complex, and (7) adding an effective amount of a metal deactivator to the oil of (6).

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References Cited in the file of this patent UNITED STATES PATENTS

Number	Name	Date
1,771,350	Ramage	July 22, 1930
1,954,887	Morrell	Apr. 7, 1934
1,963,556	Morrell	June 19, 1934
1,980,555	Schulze	Nov. 13, 1934
2,221,183	Dolbear	Nov. 12, 1940

OTHER REFERENCES

U. S. Bureau of Mines—Report of Investigations 4060, December 1946.