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REDUCING THE MERCAPTAN CONTENT OF PETROLEUM DISTILLATES WITH A HYDROPEROXIDE

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This invention relates to a process for sweetening sour petroleum distillates and particularly for sweetening sour gasoline.

An object of this invention is to reduce the mercaptan content of a petroleum distillate containing such organic sulfur compounds.

A further object of this invention is to reduce the mercaptan content of a sour gasoline.

It is well known that the presence of organic sulfur compounds in gasoline lowers its lead susceptibility. That is, the introduction of lead tetraethyl causes a smaller improvement in the octane number of sour gasoline than would be obtained if the gasoline were free from organic sulfur compounds. Accordingly, from the standpoint of lead susceptibility and sulfur reduction, it is usually considered best practice to extract mercaptans from gasoline rather than to convert them into the less-reactive disulfides by oxidation treatment. However, except in those distillates which contain mercaptans of very low molecular weights, it becomes costly or uneconomical to extract all of the mercaptans. Accordingly, it is advantageous to operate an extraction process so as to remove from about 50 to about 99% of the mercaptans present and then to oxidize the remaining mercaptans to disulfides. According to this invention, organic peroxy compounds, particularly organic peroxides and organic hydroperoxides are utilized to oxidize these residual mercaptans or to convert them into compounds that do not give a positive reaction by the "doctor test," that is, they do not give a precipitate of lead sulfide upon being treated with doctor solution which contains sodium plumbite, Na_2PbO_2 dissolved in caustic soda solution.

One embodiment of this invention relates to a process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate with an organic peroxy compound.

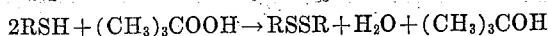
Another embodiment of this invention relates to a process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate with an organic hydroperoxide.

A further embodiment of this invention relates to a process which comprises extracting from about 50 to about 99% of the mercaptans from a sour petroleum distillate, oxidizing substantially all of the remaining mercaptans by treatment with an organic hydroperoxide, and recovering a substantially mercaptan-free petroleum distillate.

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A still further embodiment of this invention relates to a process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate with an organic peroxy compound and a catalyst comprising essentially a salt of an organic acid and of a metal selected from the group consisting of copper, cobalt, nickel, chromium, manganese, and iron.

This process may be used for reducing the mercaptan sulfur content of straight-run petroleum distillates including gasoline, kerosene, range oil, heater oil, and the like. The process is also applicable to cracked gasoline and naphtha. As the oxidation of the mercaptans results in the production of disulfides which are generally left in the gasoline or other petroleum distillate being treated, the sulfur content of this hydrocarbon material remains substantially unchanged after oxidation. As the lead susceptibility is improved by reducing the total sulfur content as well as by reducing the mercaptan content of the hydrocarbon distillate, it is desirable to extract the hydrocarbon material with caustic soda solution and preferably with caustic methanol solution to remove from about 50 to about 99% of the mercaptans. The remaining hydrocarbon material or raffinate containing from about 1 to about 50% of the original mercaptans is then treated by this process to oxidize mercaptans to disulfides as illustrated by the following equation:



Alkyl mer- captan	t-butylhydro- peroxide	Alkyl disulfide	t-butyl alcohol
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The organic peroxy compounds used as treating agents in this process contain the bivalent radical $-\text{O}-\text{O}-$. Examples of such compounds are peracetic acid, persuccinic acid, dimethyl peroxide, diethyl peroxide, methyl ethyl peroxide, ditertiary butyl peroxide, dipropyl peroxide, acetyl benzoyl peroxide, acetyl peroxide, propionyl peroxide, butyryl peroxide, lauroyl peroxide, benzoyl peroxide, tetralin peroxide, urea peroxide, tertiary butyl perbenzoate, tertiary butyl hydroperoxide, cumene hydroperoxide, methylcyclohexyl hydroperoxide, and the like. The organic peroxy compounds constitute a preferred class of treating agents for use in this invention. Mixtures of peroxy compounds also may be employed.

The extraction of mercaptans from sour petroleum distillates is carried out by treating the hydrocarbon material with from about 5 to about 50% of its volume of caustic soda solution containing from about 5 to about 50 percent by

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weight of NaOH. Also an alcoholic solution of caustic soda is sometimes used to extract mercaptans from sour hydrocarbon oils. Thus a sour petroleum distillate is treated with from about 2 to about 5 percent by volume of a caustic-methanol solution formed by mixing 25 volumes of methanol with 75 volumes of aqueous sodium hydroxide solution of 48° Bé. gravity. The extraction with caustic soda solution is made at a temperature of from about 60° to about 110° F. and with caustic methanol solution at a temperature of from about 80° to about 110° F.

The resulting raffinate which contains from about 1 to about 50% of the mercaptans generally present in the sour distillate is then washed with water to remove residual caustic soda solution and the water-washed raffinate is then mixed with an organic peroxy compound in an amount sufficient to convert the remaining mercaptans into disulfides and the mixture is maintained at a temperature of from about 20° to about 350° F. and at sufficient pressure to keep the hydrocarbon material in liquid phase. This heating with an organic peroxide or preferably an organic hydroperoxide may be carried out under reflux, it may be effected also under pressure in an autoclave, or it may be carried out in a tubular reactor in which the hydrocarbon-peroxide mixture is passed over heated quartz chips.

The hydrocarbon distillate which has been so treated with an organic peroxide or hydroperoxide to reduce the mercaptan content by converting or oxidizing mercaptans into disulfides, is then subjected to a further heat treatment or extraction, for example, with caustic to decompose or to extract the excess of the organic peroxides remaining after the previous treating. This removal of residual peroxides is necessary in order to avoid loss of octane number over that of the hydrocarbon material which is free from organic sulfur compounds and peroxides.

This process for sweetening a sour petroleum distillate by treating with an organic peroxy compound and particularly with an organic hydroperoxide is also speeded up or accelerated by the presence of a salt of an organic acid and of a metal and particularly the naphthenates and oleates of copper, cobalt, nickel, chromium, manganese and iron. The metallic salt is used in an amount of from about 0.01 to 1.0 weight percent based on the organic peroxide used. The copper salts are preferred in this process. However, when such metallic salts are used, it is also generally necessary to add a metal deactivator to the hydrocarbon oil at the conclusion of the sweetening reaction in order to prevent the metal salt from catalyzing further oxidation reactions, said further oxidation reactions being objectionable. Metal deactivators which are suitable for such use include the condensation products of salicylaldehyde with propylene diamine, ortho-aminophenol and the like and also tetra-acetic acid derivatives of ethylene diamine.

The nature of the present invention and types of results obtained thereby are also illustrated by the following examples which should not be misconstrued as imposing undue limitations upon the generally broad scope of the invention.

EXAMPLE I

A thermally cracked gasoline was treated with aqueous caustic soda solution of 20° Bé. gravity in three stages to reduce the mercaptan sulfur content to 0.032% by weight. Then tertiary

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butylhydroperoxide was added to the caustic treated gasoline in ten-fold excess of that calculated as necessary on the basis of one mole of hydroperoxide reacting with two moles of mercaptan, as indicated in the foregoing equation. This gasoline was then passed through a bed of quartz chips at a temperature of 260° F. and a liquid hourly space velocity of one and five. The resultant hydrocarbon product was sweet, that is, it was free from mercaptan sulfur as shown both by the doctor test with sodium plumbite and by potentiometric titration with silver nitrate. The peroxide number of the treated hydrocarbon product was from 0.5 to 0.9 as compared with 36.5 for the charging stock. A blank run which was also made showed that the same gasoline did not undergo sweetening reaction under the same conditions but in the absence of tertiary butylhydroperoxide. Further work, however, indicated that the gasoline to which tertiary butylhydroperoxide was added would undergo sweetening when merely stored at room temperature (about 20° C.) for 24 hours. The large amount of peroxides remaining in the gasoline was undesirable and accordingly further work was carried out to determine the minimum amount of tertiary butylhydroperoxide required to effect complete sweetening when gasoline was passed over quartz chips at a temperature of approximately 265° F. at atmospheric pressure and using a hydrocarbon charging rate corresponding to a liquid hourly space velocity of one. The minimum amount of tertiary butylhydroperoxide was so found to be from 6.8 to 7.0 times the stoichiometric amount based upon one mole of hydroperoxide reacting with two moles of mercaptans.

EXAMPLE II

A straight-run gasoline was also sweetened by means of an organic peroxide. Preliminary tests showed that this gasoline, containing the minimum amount of tertiary butyl hydroperoxide, did not sweeten after 3 hours refluxing and after 4 hours in an autoclave at 300° F. with 100 p. s. i. nitrogen. However, it did sweeten when passed over quartz chips at 266° F. at atmospheric pressure and 1 LHSV. The product was inspected as shown below.

	Chg. Stk.	Product
RSH Sul, weight per cent.....	0.045	nil
Doctor test.....	Positive	Negative
Peroxide Number.....	48.3	0.11
Color, Saybolt.....	+23	-13
Vapor pressure, p. s. i.....	6.7	5.0
Specific Gravity @ 60° F.....	0.7362	0.7393
I. B. P.....	114	110
50%.....	254	256
E. P.....	379	386

¹ 9.3 times the calc. stoichiometric amount.

The above run was repeated, using a smaller amount of tertiary butyl hydroperoxide and a higher temperature (approx. 330° F.). The results shown below indicate a smaller color drop.

	Chg. Stk.	Product
RSH Sul, weight per cent.....	0.045	nil
Doctor test.....	Positive	Negative
Peroxide Number.....	33.0	nil
Color, Saybolt.....	+23	+12
Vapor pressure, p. s. i.....	7.0	6.3
Specific Gravity, @ 60° F.....	0.7374	0.7377
I. B. P.....	108	118
50%.....	254	256
E. P.....	384	387

¹ 6.5 times the calculated stoichiometric amount.

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EXAMPLE III

Another cracked gasoline was first treated with caustic methanol solution which reduced the mercaptan content to 0.01%. It was found that heating was unnecessary to cause sweetening of this gasoline with cumene hydroperoxide. At room temperature a sample of caustic-methanol treated gasoline was mixed with cumene hydroperoxide in the calculated stoichiometric amount needed to oxidize the 0.01% of mercaptan. This removal of mercaptan was found to be superior, yielding a completely sweetened hydrocarbon distillate at the end of 24 hours. When less than the calculated stoichiometric amount of peroxide was employed, the time of sweetening was increased.

EXAMPLE IV

A sour heater oil boiling from 300° to about 600° F. was mixed with 6.5 times the calculated stoichiometric quantity of tertiary butylhydroperoxide needed for reacting with the mercaptan content and the resultant mixture was heated at a temperature of 265° F. for 3.5 hours during which the mercaptan content was reduced from 0.073 weight percent in the charging stock to 0.028 weight per cent in the product. The same heater oil to which 6.5 times the calculated amount of tertiary butylhydroperoxide was added became sweet within thirteen days when stored at a temperature of 20° C. There was also a small decrease in the color of the heater oil during this treatment.

EXAMPLE V

The straight run gasoline referred to in Example II was distilled and the fraction boiling above 265° F. was sweetened when stored at room temperature with 7.9 times the calculated quantity of tertiary butylhydroperoxide.

EXAMPLE VI

This treating process was applied further to a stable sour cracked gasoline which had the inspection data shown in Table I.

Table I

INSPECTION DATA ON SOUR CRACKED GASOLINE

Analyses:

Peroxide number	0.04
Mercaptan sulfur, weight percent	0.049
Hydrogen sulfide	None
Total sulfur, weight percent	0.17
Bromine number	24
Color, Saybolt	+17
Phenols, weight percent (U. V.)	0.004
Thiophenols, weight percent (U. V.)	0.003
Total phenols, weight percent (U. V.)	0.007
A. S. T. M. gum, mg./100 ml.	2
Oxygen bomb, Ind. Per., Min.	95
Octane number, F-2 method	
clear	61.2
+ 3 cc. TEL/gal.	72.4
Reid vapor pressure, p. s. i. g.	6.3
A. P. I. gravity @ 60° F.	59.5
I.B.P. ° F.	99
5%	129
10	150
50	250
90	352
E. P.	412
Percent rec.	98.0
Percent Botts.	1.0
Percent loss	1.0

As shown in the above table, this gasoline had a low A. S. T. M. gum content but had a rather

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high mercaptan content. This gasoline was partially sweetened by a caustic-methanol treatment which reduced the mercaptan sulfur to 0.010%. This treated gasoline was then treated further with two times the stoichiometric amount of cumene hydroperoxide and stored in the dark at room temperature. The stoichiometric amount of cumene hydroperoxide was calculated on the basis of two moles of mercaptan reacting with one mole of cumene hydroperoxide to form one mole of disulfide, one mole of water, and one mole of phenyl-dimethyl carbinol. A sample of the gasoline containing no added cumene hydroperoxide was stored at the same time as a blank. After twenty-two hours the gasoline containing the cumene hydroperoxide was found to be sweet, but still contained some peroxide as measured by the UOP method No. H-33-40. The residual peroxide was substantially removed by extraction with a strong alkaline reagent.

Properties of the caustic-methanol treated but still sour cracked gasoline and of this gasoline after sweetening treatment with cumene hydroperoxide are given in Table II. A hydrocarbon material which contains mercaptans as indicated by the "doctor test" is said to be "sour" whereas a hydrocarbon product which does not give the "doctor test" for mercaptans is referred to as a "sweet" product.

Table II

STABILITY DATA OF PEROXIDE SWEETENED RAW CRACKED GASOLINE ONE STAGE JET CAUSTIC-METHANOL TREATMENT

Treatment	None	2 times stoich. am't. cumene hydroperoxide added
Storage time and conditions	(3)	(4)
Peroxide Number	0.03	0.22
Mercaptan sulfur, weight per cent.	0.101	Swt.
Doctor test	Positive	Negative
Color, ° Saybolt	+11	+6
A. S. T. M. Gum, mg./100 ml.	4	7
Octane Number, F-2, clear	61.6	60.0
+ 3 cc. TEL/gal.	73.7	73.6
Cu. Dish Gum, mg./100 ml.:		
Blank	39	29
+ .010% UOP #4	13	14
+ .006% UOP #5	25	29
Oxygen Bomb, Ind. Per., Min.:		
Blank	110	95
+ .010% UOP #4	225	715
+ .006% UOP #5	190	695
Reid Vapor Pressure, p. s. i.	6.0	5.8
A. P. I. Gravity @ 60° F.	58.9	58.6
I. B. P. ° F.	110	117
5%	142	147
10	162	165
50	255	256
90	353	352
95	378	377
E. P.	410	413
Per Cent Rec.	98.0	98.5
Per Cent Botts.	1.0	1.0
Per Cent Loss	1.0	0.5

¹ N-n-butyl-p-aminophenol.

² N,N'-di-sec-butyl-p-phenylenediamine.

³ 22 hours in dark at 70° F.

⁴ 22 hours in dark at 70° F. alkali extraction of residual peroxide.

The above results show that this particular sour gasoline can be sweetened by addition of twice the calculated amount of cumene hydroperoxide followed by room temperature storage. The sweetened and alkali extracted gasoline has good antiknock and stability characteristics.

I claim as my invention:

1. A process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate with an organic peroxy compound selected from the group consisting of tertiary butyl hydroperoxide and cumene hydroperoxide.

2. A process for reducing the mercaptan con-

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tent of a sour petroleum distillate which comprises treating said distillate with tertiary butyl hydroperoxide.

3. A process which comprises extracting from about 50 to about 99% of the mercaptans from a sour petroleum distillate, oxidizing substantially all of the remaining mercaptans by treatment with an organic hydroperoxide selected from the group consisting of tertiary butyl hydroperoxide and cumene hydroperoxide, and recovering a substantially mercaptan-free petroleum distillate.

4. A process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate with an organic peroxy compound selected from the group consisting of tertiary butyl hydroperoxide and cumene hydroperoxide at a temperature of from about 20° to about 350° F.

5. A process which comprises extracting from about 50 to about 99% of the mercaptans from a sour petroleum distillate, oxidizing substantially all of the remaining mercaptans by treatment with tertiary butyl hydroperoxide at a temperature of from about 20° to about 350° F. and recovering a substantially mercaptan-free petroleum distillate.

6. A process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate with an organic peroxy compound selected from the group consisting of tertiary butyl hydroperoxide and cumene hydroperoxide and a catalyst comprising essentially a salt of an organic acid and of a metal selected from the group consisting of copper, cobalt, nickel, chromium, manganese, and iron.

7. A process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate at a temperature of from about 20° to about 350° F. with an organic

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peroxy compound selected from the group consisting of tertiary butyl hydroperoxide and cumene hydroperoxide and a catalyst comprising essentially a salt of an organic acid and of a metal selected from the group consisting of copper, cobalt, nickel, chromium, manganese, and iron.

8. A process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate with tertiary butyl hydroperoxide at a temperature of from about 20° to about 350° F.

9. A process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate with cumene hydroperoxide at a temperature of from about 20° to about 350° F.

10. A process for reducing the mercaptan content of a sour petroleum distillate which comprises treating said distillate at a temperature of from about 20° to about 350° F. with an organic hydroperoxide selected from the group consisting of tertiary butyl hydroperoxide and cumene hydroperoxide and a catalyst comprising essentially a copper naphthenate.

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