

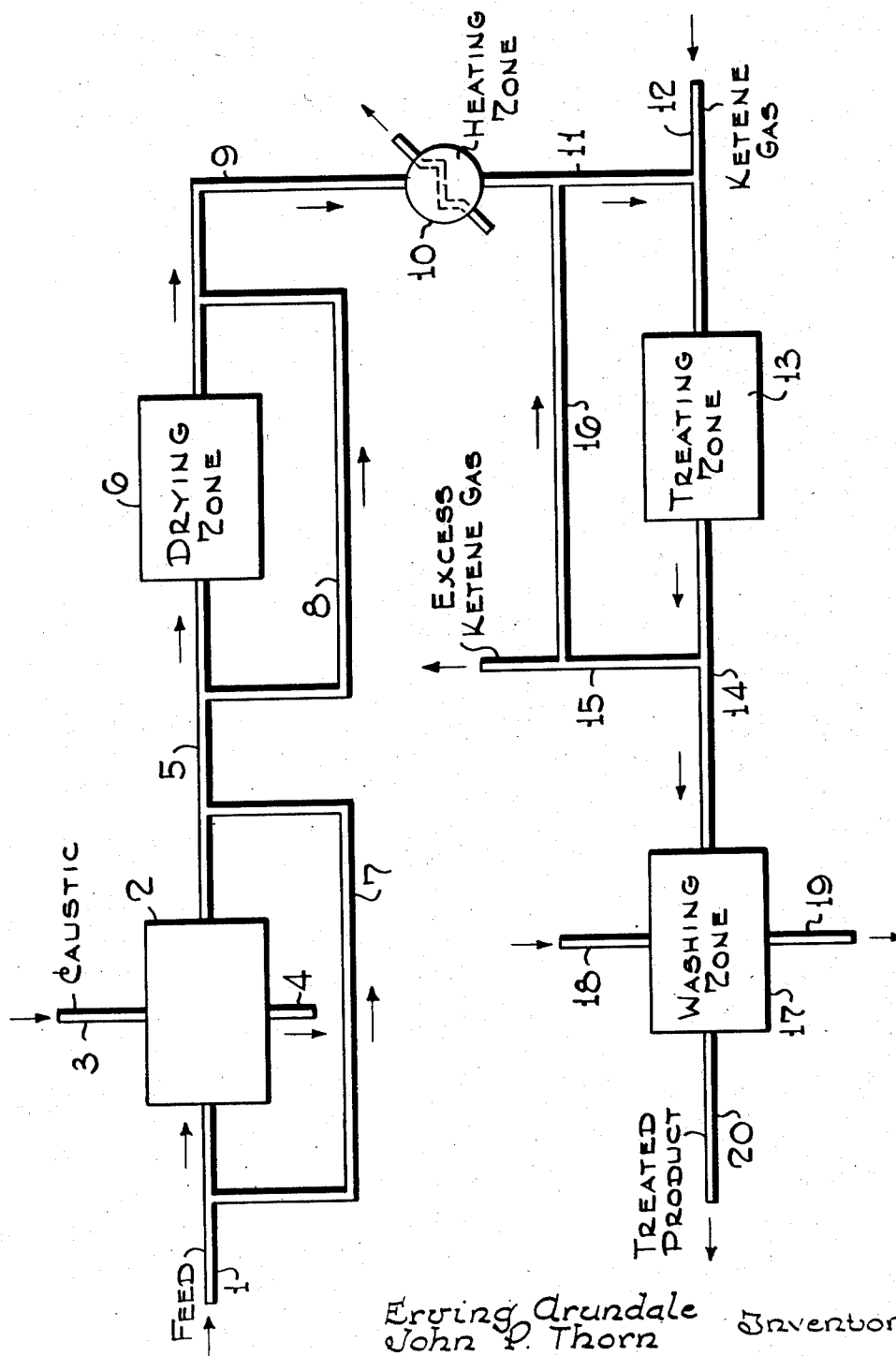
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SWEETENING PROCESS

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SWEETENING PROCESS

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The present invention is concerned with an improved sweetening process and is more particularly concerned with the removal of objectionable mercaptan compounds from oils containing the same. The invention is especially directed toward the removal of these mercaptan compounds from hydrocarbon fractions boiling in the motor fuel, kerosene, diesel oil and heating oil boiling ranges. The invention is particularly concerned with the removal of these mercaptan compounds utilizing a ketene as the treating agent.

It is well known in the art to treat petroleum oils by various procedures in order to remove objectionable constituents, as for example sulfur compounds therefrom. For example, it is known to treat petroleum fractions boiling in the motor fuel boiling range and in the general range below about 700° F. with various chemical agents, such as sodium or potassium hydroxide solutions. It is also known to treat mineral oil distillates, as for example petroleum oil distillates boiling in these ranges with an alkali metal plumbite solution such as a sodium plumbite solution which is prepared by dissolving lead oxide in an excess of sodium hydroxide. The petroleum oil and plumbite solution are mixed and a chemical reaction occurs, resulting in the conversion of mercaptans to the corresponding lead mercaptides. These mercaptides are then decomposed usually by the addition of free sulfur resulting in the lead being precipitated as an insoluble lead sulfide and in the formation of odorless organic disulfide compounds.

It has now been discovered that objectionable mercaptan compounds can be removed in a sweetening operation utilizing ketene as a treating agent and the quality of the petroleum oils improved. The present invention may be readily understood by reference to the drawing illustrating one embodiment of the same.

Referring specifically to the drawing, a hydrocarbon feed fraction boiling in the heating oil boiling range (350-650° F.) and containing mercaptans is introduced into the system by means of line 1. If the fraction contains hydrogen sulfide, it is preferably passed into alkali treating zone 2 where it is contacted with a caustic solution, as for example, sodium hydroxide solution introduced by means of line 3. The spent caustic solution is withdrawn by means of line 4. The treated fraction is withdrawn from zone 2 by means of line 5 and preferably introduced into a drying zone 6 wherein substantially all water is removed therefrom. If the feed fraction com-

example, a fraction boiling in the heating oil boiling range, and is substantially free of hydrogen sulfide, the fraction may bypass treating zone 2 by means of line 7. Also, if the fraction is substantially completely free of water, it may bypass drying zone 6 by means of line 8. The fraction is then introduced into heating zone 10 by means of line 9 wherein the temperature is raised to the desired degree. The heated feed fraction is withdrawn from zone 10 by means of line 11 and mixed with ketene gas which is introduced by means of line 12. The mixture is passed to treating zone 13 wherein the ketene gas and the feed fraction are contacted for the desired time period. The mixture is withdrawn from treating zone 13 by means of line 14. Excess ketene gas may be removed from the system by means of line 15 but is preferably recycled by means of line 16.

The treated fraction is introduced into washing zone 17 wherein it is contacted with a washing solution introduced by means of line 18 which is withdrawn by means of line 19. The treated product is withdrawn from washing zone 17 by means of line 20 and further handled or refined as desired.

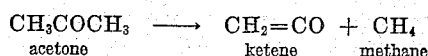
The invention is broadly concerned with the removal of objectionable mercaptan and thiophenol compounds from virgin or cracked mineral oil fractions boiling in the range from about 75-700° F. such as gasoline, kerosene, diesel fuel heating oil and the like; utilizing ketene as the treating agent. The invention is particularly adapted for the treatment of petroleum fractions boiling in the heating oil boiling range, which fractions boil in the range from about 350-650° F. If lower boiling fractions are treated, it is preferred to pretreat these fractions in order to remove hydrogen sulfide and the relatively low boiling mercaptans therefrom. The pretreating agent preferably comprises an alkali metal hydroxide solution; as for example, sodium hydroxide solution. A very desirable treating agent comprises a sodium hydroxide solution having a concentration in the range from about 5-20% B_e.

As pointed out above, it is very desirable to completely remove water from the feed fraction. This is accomplished in a drying zone employing drying agents as for example, silica gel, bauxite, alumina and the like, by filtration, or by heating and removing the water by distillation or stripping.

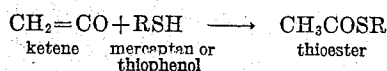
The fraction to be treated is heated to a temperature in the range from about 100-300° F.,

preferably to a temperature in the range from about 125°–150° F. Ketene gas is introduced in the desired amount and the ketene gas and feed fraction thoroughly mixed by any suitable mixing means. The amount of ketene gas added will depend on the concentration of the mercaptans present in the feed fraction. Usually, the amount of ketene gas added will be in the range from about .05 to 1.5%, preferably in the range from 0.1 to 0.5% by weight based upon the feed fraction. Just sufficient ketene is added to sweeten the hydrocarbon distillate.

The ketene gas may be secured by any suitable means. A very desirable method of securing the ketene gas for use in accordance with the present invention is from acetone utilizing a simple pyrolysis process. In this operation acetone is pyrolyzed in a hot tube at a temperature of 1100–1400° F. with a short contact time in order to decompose the acetone in accordance with the following equation:



Methyl ketene can be made in a similar manner from methyl ethyl ketone. The methane may be removed and the ketene then contacted with the feed fraction wherein it is believed that the following reaction occurs:



The time of contact between the ketene gas and the feed fraction may vary appreciably, and is dependent on the treating temperature but is generally in the range from about 2 to 30 minutes. A preferred time of contact is in the range from about 10 to 30 minutes. Mineral acid catalysts such as sulfuric acid, phosphoric acid and the like can also be used in catalytic amounts (less than 2%) to improve the ketene sweetening operation.

The mixture, after a sufficient time of contact, is handled in a manner to remove excess ketene gas which is preferably recycled. The

treated fraction is washed, preferably at an elevated temperature with a satisfactory washing solution, preferably selected from the class consisting of water and alkali metal hydroxide solutions. If an alkali solution is employed, it is preferred to use a sodium hydroxide solution having a concentration in the range from about 3–5% sodium hydroxide. A very satisfactory solution comprises a sodium hydroxide solution having a concentration of 5% by weight.

The washing step is preferably conducted at a temperature in the range from about 125–150° F. After washing, the washing solution is removed, the treated fraction is cooled and handled as desired. Although the invention has been described specifically with respect to ketene, it is to be understood that di-ketene, methyl ketene, diphenyl ketene and the like may also be used. Mixtures of ketene and di-ketene are also effective.

The present invention may be further understood by reference to the following example illustrating the same:

Sweetening runs were carried out on samples of West Texas P. C. naphtha, heavy virgin naphtha, virgin heating oil and a sour cracked naphtha. In most cases these feed stocks were washed with caustic soda solution and filtered prior to use. This pretreatment considerably reduced the ketene requirements. In the runs, 750 cc. of the sour distillate were placed in a seltzer bottle and the ketene generator product was passed in at room temperature for a period of time necessary to obtain the desired amount of ketene. The bottle was then closed and placed on a rotating wheel for one-half hour at a temperature of 135° F. The bottle was then cooled to room temperature, the contents removed, washed three minutes with 100 cc. of water and then filtered. A copper number and doctor test were then obtained on the product.

The results are presented in Table I and it will be noted that, even with high copper number stocks, contacting with 0.1–0.4 weight per cent ketene (based on feed) results in sweet products possessing copper numbers of 1.0 or below.

Table I

Operation.....	1		2		3		4	
Feed.....	Sour Cracked Naphtha, Boiling Range 160–440° F.		West Texas Virgin Heating Oil (Prewashed 2%–15° Be. caustic), Boiling Range 350–650° F.		West Texas P. C. Naphtha (Prewashed with equal vol. of 5% NaOH sol. under N ₂), ^a Boiling Range 100–275° F.		West Texas Heavy Naphtha (Prewashed with equal vol. of 5% NaOH under N ₂), ^a Boiling Range 260–430° F.	
Feed Inspections:								
Copper No.* as Rec'd.....	3.0		88.5		10		30	
Copper No. after H ₂ O wash.....	2.0		84.0		10		28	
Specific Gravity.....	0.835		0.840		0.718		0.795	
Treatment: Per Cent Ketene by weight on Feed.....	0.16	0.26	0.076	0.115	0.187	0.167	0.237	0.36
Product Inspections:								
Copper No.....	1.0	0.5	31.0	1.0	<1.0	1.0	1.0	1.0
Doctor Test ^b	DNP	Pass	DNP	DNP	Pass	DNP	Pass	Pass

* 750 cc. sample placed in seltzer bottle and ketene generator product passed in at room temperature (unless otherwise indicated) for a period of time necessary to obtain desired amount of ketene. Bottles closed and mixed for 0.5 hr. at 135° F., cooled, product washed 3 min. with 100 cc. water, separated and filtered. Inspections then obtained on product.

^b Ketene adsorbed in naphtha at alcohol-Dry Ice bath temperature.

^c 750 cc. of feed washed 3 min. with 100 cc. water, separated and filtered.

^d To remove H₂S and reduce copper number from 68 to 10.

^e To reduce copper number from 38 to 30.

^f Theoretical ketene requirement for a stock of this Cu No.=0.14%.

^g The copper number is the milligrams of mercaptan sulfur present in 100 ml. of sample under test which will react with a standard copper ammonium sulphate solution.

^h The doctor test is a means of making sure that hydrocarbon fractions are free of mercaptans which render the fraction "sour." A sample of the hydrocarbon is shaken with a sodium plumbite solution and a trace of free sulfur. If after shaking, the hydrocarbon, plumbite solution, and sulfur have not changed color, mercaptans are absent, the stock is "sweet" and the doctor test is "Pass." If discoloration occurs mercaptans are present and the test does not pass ("DNP").

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What is claimed is:

1. Process for the removal of mercaptan compounds from a petroleum oil containing the same which comprises contacting said petroleum oil with a treating agent comprising ketene.

2. Process as defined by claim 1 wherein said petroleum oil boils in the heating oil boiling range.

3. Process as defined by claim 1 wherein said oil is contacted with said ketene at a temperature in the range from about 100 to 300° F.

4. Improved process for sweetening a petroleum oil boiling in the range below about 700° F. which comprises contacting said oil in an initial stage with an alkali metal hydroxide solution, removing the treated oil from said initial stage and processing the same in a secondary stage in order to substantially completely free said oil of water, thereafter heating said oil to an elevated temperature and contacting the same in a tertiary stage with a treating agent comprising a ketene, removing said treated oil from said tertiary stage and processing the same in a final stage with a washing reagent in order to produce a treated product.

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5. Process as defined by claim 4 wherein the temperature maintained in said final stage is in the range from about 125 to 150° F. and wherein said washing agent comprises water.

6. Process as defined by claim 5 wherein said oil is heated to a temperature in the range from about 125 to 150° F. prior to contacting the same with ketene.

7. Process as defined by claim 6 wherein said oil comprises an oil boiling in the heating oil boiling range.

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