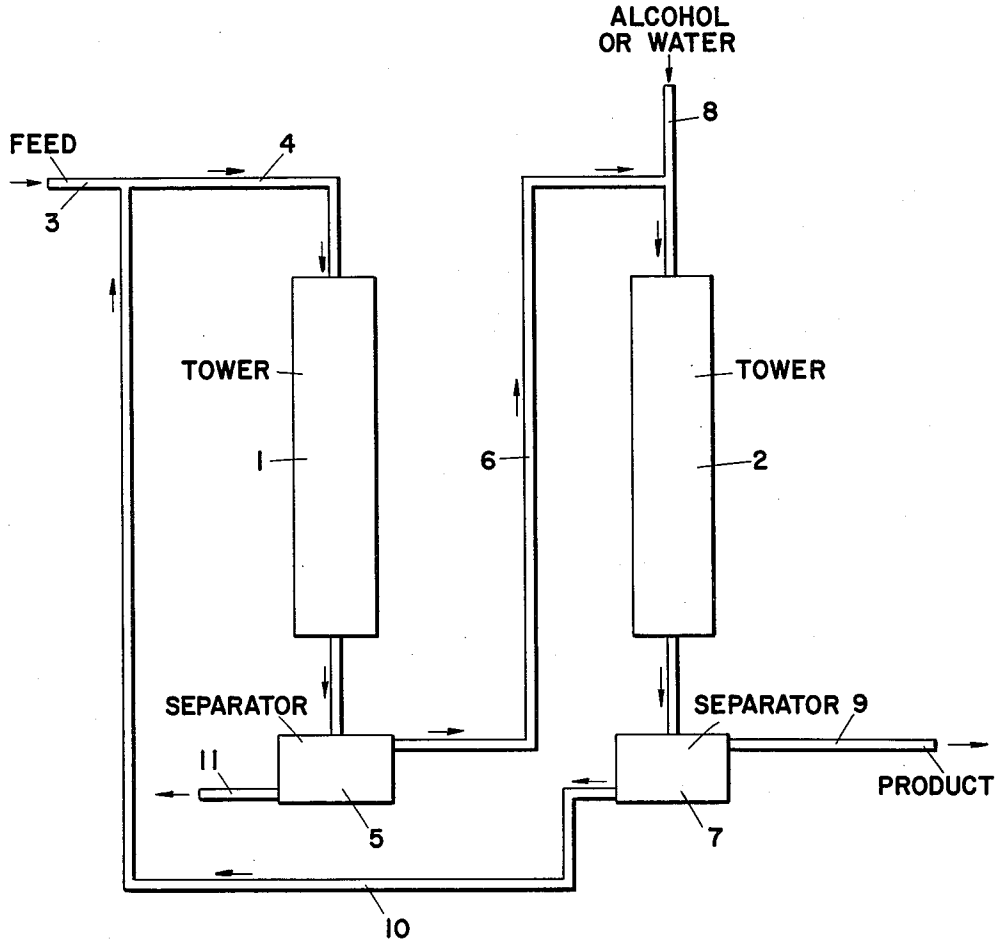
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METHOD OF SWEETENING PETROLEUM DISTILLATE

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# 3,000,817
# METHOD OF SWEETENING PETROLEUM DISTILLATE

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The present invention relates to a process of sweetening petroleum distillates and particularly to light petroleum distillates that are refined by distillation at atmospheric pressure.

The sulfur compounds present in crude petroleum are the most objectionable and harmful impurities. These sulfur compounds contribute to the objectionable smell and corrosive properties of many distillates as well as for example in the case of the gasoline fractions decreasing the lead response. Sulfur exists in petroleum as a wide variety of compounds but in the petroleum distillates the sulfur exists in relatively simple compounds, such as mercaptans, sulfides, disulfides, and heterocyclic compounds such as thiophenes. It should also be remembered that sulfur exists in many distillates as free elemental sulfur. If the petroleum refiner is to produce a vendable product it is essential that the sulfur impurities in the products are reduced below certain critical limits.

Over the past 50 years, considerable efforts have been expended on devising methods of sweetening petroleum products. Extraction of the petroleum product with aqueous solutions of alkali has become an established extractive sweetening process used in the art. This process involves intimately contacting the petroleum product with an aqueous solution of sodium hydroxide.

By virtue of their acidic properties mercaptans tend to form the sodium salt and pass into the aqueous phase. Even though this process, often referred to as the slurry process, has been in operation for many years, it is associated with several disadvantages. The mercaptan removal is incomplete since the sodium mercaptides of the higher mercaptans are extensively hydrolysed in water. Also the utilisation of the caustic is low and the utilisation is often of the order of 40 to 60%, i.e. to say unused caustic is rejected with the spent liquor. Furthermore the process will only remove acidic sulfur bodies and would not remove significant amounts of sulfur from a sulfur-containing feed at ambient temperatures. As an example of the excessive caustic utilisation of the slurry process the applicants investigated the sweetening of a light virgin naphtha by a conventional caustic soda wash and by the process of this invention. By the process of the present invention the mercaptan number was reduced to 0.4 corresponding to an efficiency of 44%. By means of the slurry process using 15 Bé. sodium hydroxide the mercaptan number was reduced to 13, corresponding to an efficiency of 4.6%. The light virgin naphtha had a mercaptan number of 16.

By means of the present invention as hereinbefore described efficient use of caustic alkali is obtained, furthermore the process provides a means for decreasing the sulfur content of feeds.

During investigations on methods of sweetening petroleum products the applicants investigated a process in which the sour feed was passed over a fixed bed of sodium or potassium hydroxide. The applicants discovered that when the feed contained certain added concentrations of free sulfur and mercaptans a reaction took place in the bed which resulted in the removal of mercaptan and sulfur from the feed. It was discovered that sulfur could be removed from feeds by adding specified amounts of mercaptan and percolation over solid sodium or potassium



hydroxide and that it was preferably to add $C_4+$ mercaptans.

The process of the present invention comprises a process for desulfurizing a mercaptan-containing petroleum distillate which comprises adjusting the water or $C_1$ to $C_4$ alcohol content of the distillate to a value between 0.01 to 5 wt. percent, percolating the distillate so obtained over a fixed bed of solid sodium hydroxide or potassium hydroxide and isolating the desulfurized distillate so obtained.

The process is preferably carried out by determining the water or $C_1$ to $C_4$ alcohol content of the distillate. If this content is not within the defined range then additional water or $C_1$ to $C_4$ alcohol is added. Many of the distillates to be desulfurized may be wet and contain water. Provided that the water content is within the defined range additional $C_1$ to $C_4$ alcohol within the defined range may be added to the wet distillates before percolation over the solid sodium or potassium hydroxide.

In a further preferred embodiment of the present invention soluble mercaptans or free sulfur are dissolved in the distillate so that the ratio of free sulfur to mercaptan sulfur is greater than 2.

An unexpected advantage derived from the use of the process with light petroleum gas and potassium hydroxide is that the product is dry and a further drying stage is not required.

The preferred ratio of free sulfur to mercaptan sulfur is from 2½ to 4½. Within reasonable limits the process of the invention may be carried out when the aforementioned ratio is greater than 4½, but it will be understood that excess mercaptans present in the feed will utilise further caustic alkali. In the main therefore it is desirable to adjust the aforementioned ratio to within the range of 2½ to 4½. The applicants have discovered that for the maximum efficiency with light petroleum gas the ratio of 2.9 to 3.5 was preferred and that with a light virgin naphtha or cracked stocks a ratio of 2.8 to 3.6 was preferred.

The process may be applied to mercaptan-containing or free sulfur-containing petroleum distillates such as light petroleum gas, light virgin naphtha, cracked stocks and distillate heating oils and fuels, such as diesel fuels. The process is most advantageously applied to distillates which contain from 5 to 35 p.p.m. of free sulfur and/or have a mercaptan number less than 30, preferably less than 25.

The size of the solid caustic used in the fixed bed, is not critical since the size of the particles is decreasing during the operation of the process. The applicants have used fixed beds made up of lumps from 1/16" in diameter up to 3" in diameter. During the operation of the process the alcohol or water is adsorbed on to the solid surface and a solution comprising caustic alkali and sulfur bodies trickles down the column. This solution may be removed from the process as a lower layer. It is therefore preferred that the feed descends from the fixed bed.

While our process is operable with sodium hydroxide or with potassium hydroxide, we have found that potassium hydroxide is to be preferred. It has been observed that potassium hydroxide has a greater tendency to absorb either alcohol or water from the distillate. As previously explained this absorbed water or alcohol tends to keep the surface of the alkali clean. We have found that our process may be advantageously operated when the fixed bed consists of an intimate mixture of potassium hydroxide and sodium hydroxide. By "an intimate mixture" we mean an intimate mixture of finely divided solid alkalies or a mixture obtained by fusing the two alkali together and then grinding or pelleting the solidified mixture. It is preferred that the mixture consists of 1 part of potassium hydroxide to 1 to 4.3 parts of sodium hydroxide.

The process is conveniently operated under ambient conditions namely from 15 to 25° C. However, a faster reaction will take place at higher temperatures and column temperatures up to 60° C. may be used. Under ambient temperature conditions from ½ to 1½ b./d. is a suitable rate of passing a feed having a mercaptan number from 4 to 20 or containing 1 to 5 mgs. of free sulfur per 100 cc. over 1 kg. of sodium hydroxide or potassium hydroxide. Therefore the linear velocity of the feed through the column may well depend on the quantity of caustic alkali present in the column. Linear velocities from 0.2 to 2 ft. per minute may be used, and linear velocities from 0.05 to 1.5 ft. per minute are preferred. According to the process of the present invention the water or $C_1$ to $C_4$ monohydric alcohol content of the feed, is adjusted to a particular value before passage over the fixed bed of caustic alkali. The desired amount of water may be introduced by passing steam into the distillate. It will be realised that in many cases the water will exist in the distillate in the form of a haze. Methanol is the preferred alcohol for inclusion in the feed. The water and/or alcohol adjustment may be carried out before the adjustment of the free sulfur to mercaptan sulfur ratio.

Without wishing to restrict the invention the following theoretical explanation is included since this explanation may help to describe the best method of performing the present invention.

The free sulfur removal process is probably based on an oxidation reaction of the mercaptans by free sulfur according to a scheme of the following type:

$$2RSH+S\rightarrow R2S2+H_2S \quad (1)$$

$$\left.\begin{array}{l}2KOH+H_2S\rightarrow K2S+2H2O\\ 2NaOH+H_2S\rightarrow Na2S+2H2O\end{array}\right\} \quad (2)$$

It will also be realised that the mercaptan will react with the solid sodium or potassium hydroxide according to Equation 3.

$$RSH+KOH\rightarrow RSK+H_2O \quad (3)$$

We have shown that the reaction undergone by the mercaptan is dependent on its molecular weight.

It is preferred to add $C_4$ to $C_{12}$ mercaptan since with these mercaptans the Reaction 3 is slow so that the added mercaptan will not be utilised before Reactions 1 and 2 have gone to completion. Furthermore the corrosion danger of permitting an excess of mercaptan to remain in the feed is not so great since the applicants have shown that the corrosivity of $C_4+$ mercaptans is less than for lower mercaptans. If e.g. ethyl mercaptan were added, excess of this mercaptan remaining in the product would cause high corrosion and it would be necessary to prolong the reaction until all the excess ethyl mercaptan had been adsorbed. Consequently the addition of a $C_4-$ mercaptan would require a greater reaction time and caustic utilisation.

The corrosion ratings referred to in this specification were determined by the method described by A.S.T.M. D. 130.

Consider now the case when the present invention is used to remove sulfur from a sulfur-containing feed. The analysis of the sulfur content of the feed will indicate the amount of mercaptan to be added to bring the ratio of free sulfur to mercaptan sulfur within the prescribed range. If the added mercaptan is below $C_5$ any mercaptan remaining after the sulfur removal reaction will be adsorbed by the solid bed. However for economic reasons, the addition of a useless excess of mercaptan is not desired due to the wastage of alkali.

When the added mercaptan is a $C_5+$ mercaptan, any excess mercaptan remaining after the sulfur reaction will be slowly adsorbed by the caustic bed and therefore the product may contain impurities of this mercaptan. Fortunately, the applicants have found that $C_5+$ mercaptans remaining in the product do not give increased copper strip corrosion figure. But of course excess mercaptan in the feed would cause the product to fail the doctor test. However, for the removal of free sulfur from light petroleum gases the addition of $C_5$ mercaptans and above is preferred.

During the process of our invention, the alcohol or water contained in the feed is absorbed on the surface of the caustic alkali. The acidic sulfur bodies retained on the surface of the caustic alkali are washed by this absorbed layer and a concentrated aqueous or alcoholic solution of alkali mercaptides drips from the bottom of the column. This aqueous or alcoholic solution is readily separated from the petroleum product. In order to maximise the effect of the $C_1$ to $C_4$ alcohol or water used in this process, it is preferable to utilise the apparatus and process illustrated in the drawing accompanying this application. The fixed beds of potassium hydroxide or sodium hydroxide are contained in the towers **1** and **2**. The mercaptan-containing feed flows continuously through the apparatus in the following sequence, viz., via pipes **3**, **4**, tower **1**, separator **5**, pipe **6**, tower **2**, separator **7**. The water or alcohol may be dispersed in the distillate in the form of a haze. The alcohol or water added via pipe **8** mixes with the distillate in pipe **6** and the mixture flows down through tower **2**. In separator **7** the distillate is separated from the aqueous or alcoholic solution containing the mercaptides and any unused caustic alkali. The pure product is removed by pipe **9**. The aqueous or alcoholic solution or suspension collected in separator **7** is recycled via pipe **10** to mix with the fresh feed, viz., mercaptan-containing distillate entering the apparatus via pipe **3**. The mixture is then contacted over the alkali in tower **1** and the aqueous or alcoholic solution or suspension of mercaptides issuing from column **1** is collected and separated in separator **5**. The aqueous or alcoholic solution collected in separator **5** is run to waste or to a recovery system by pipe **11**. Columns **1** and **2** have means by which make-up of sodium or potassium hydroxide may be added during the operation of the process.

## EXAMPLE 1

A light virgin naphtha having the following inspection:

Distillation:

| | | |
|---|---|---|
| IBP | ° F. | 90 |
| 50% | ° F. | 142 |
| FBP | ° F. | 214 |
| Specific gravity | | 0.664 |
| Mercaptan number | | 16 |

was mixed with 0.1 vol. percent of methanol and was passed down a column packed with solid potassium hydroxide. The length of the column was 3.5 m. and the linear velocity of the naphtha feed through the column was 34 cms. per minute. The mercaptan number of the naphtha product from the column was 0.06. A continuous operation of the process was carried out and the potassium hydroxide consumption was 76 g. per barrel of naphtha, that is, 2.6 g. of potassium hydroxide were utilised for each gram of mercaptan sulfur removed.

## EXAMPLE 2

An aqueous caustic washed propane containing free sulfur having a corrosion rating of 4 was mixed with a mercaptan and contacted as a liquid phase with a solid bed of potassium hydroxide. The process was carried out as follows: a cylindrical drum 71" high and 17" diameter was filled with 225 kg. of potassium hydroxide. The particles of the potassium hydroxide have an average diameter of 1". A liquid propane stream was processed. The propane stream gave a copper strip corrosion number greater than 4 and contained 1.55 mgs. of water per litre of gas. 0.15 g. of ethyl mercaptan was added to each barrel of propane before percolation through the bed of potassium hydroxide. The propane stream was obtained and thereby containing required amount of water and the required ratio of free sulfur to

mercaptan sulfur was percolated through the bed at a rate varying between 100 to 200 b./d. After percolation the product had a copper strip corrosion number less than 1. The bed of caustic alkali had a life of about 15 days and the potassium hydroxide consumption was 150 gr. KOH/bbl.

The water content of the product was 0.3 mg. per litre of gas. The drying of the product is another advantage of the process of this invention and the conventional alumina drying of the product is not required.

As shown in Table I the corrosion number was improved from 4 to less than 1 thereby demonstrating the removal of the sulfur.

*Table I*

| Product | Vol. Litre | Injected mercaptan | | Corrosion before test | KOH, Kgr. | Contact time, min. | Corrosion after test |
|---|---|---|---|---|---|---|---|
| | | Ethyl, mgr. S/100 cc. | Amyl, mgr. S/100 cc. | | | | |
| C3 LPG--- | 1.0 | -------- | 1.0 | J-9 | 3.0 | 5 | less than 1. |
| C3 LPG--- | 1.0 | 1.0 | -------- | J-9 | 3.0 | 5 | Do. |

## EXAMPLE 3

Table II demonstrates the interaction of free sulfur and amyl-mercaptan in a heptane solution by shaking the solution with solid potassium hydroxide. It will be observed that the product obtained gave a satisfactory corrosion rating.

*Table II*

| Fuel | Fuel Volume, cc. | Added free sulfur, mgr. S/100 cc. | Added amyl mercaptan, mgr. S/100 cc. | KOH pellets, gr. | Mixing time, min. | Corr. test |
|---|---|---|---|---|---|---|
| n-$C_7$-------- | 100 | 4 | 2 | 20 | 5 | less than 1. |
| n-$C_7$-------- | 100 | 5 | 2 | 20 | 5 | Do. |
| n-$C_7$-------- | 100 | 6 | 2 | 20 | 2 | Do. |
| n-$C_7$-------- | 100 | 8 | 2 | 20 | 2 | Do. |
| n-$C_7$-------- | 100 | 9 | 2 | 20 | 2 | Do. |

Heptane solutions containing 1 mg. of free sulfur per 100 cc. gave corrosion ratings of 4. (Use of pressure with light petroleum gas sweetening.) In this example the reactants were shaken together. Without shaking the surface of the solid alkali became coated and reaction ceased. The applicants' invention is based on the discovery that by the inclusion of water or a $C_1$ to $C_4$ alcohol in the feed, the reaction will take place by percolating the feed over the alkali.

Since it has already been stated that the removal of mercaptans $C_5$ and below may be effected by percolation over solid potassium hydroxide by the process of the present invention, it will therefore be realised that the present invention may be advantageously applied to a feed that has previously been extracted in either aqueous alkali or by percolation over solid alkali. By this means, the lower mercaptans will be removed from the feed by adsorption upon the solid caustic and then the unabsorbed higher mercaptans will react with added sulfur by the process described. It is preferred that the first stage of this preferred embodiment be carried out to give a product with a corrosion number of less than 2 before treatment by the second stage.

## EXAMPLE 4

This example demonstrates an application of the process to sweetening of a light virgin naphtha having a mercaptan number of 6.5. Free sulfur as indicated by Table III was added and the naphtha-containing sulfur shaken with solid potassium hydroxide. The results obtained are recorded in Table III.

*Table III*

| Product | Volume, cc. | Mercaptan number | KOH, gr. | Treating agent | Free S, mgr. | Contact time,[1] min. | Doctor test | Corrosion number |
|---|---|---|---|---|---|---|---|---|
| LVN------ | 100 | 6.5 | 20 | KOH | 20 | 2 | DP | Greater than 4. |
| LVN------ | 100 | 6.5 | 20 | KOH | 20 | 1 | DNP | |
| LVN------ | 100 | 6.5 | 20 | KOH | 19 | 2½ | DP | 2. |
| LVN------ | 100 | 6.5 | 20 | KOH | 18 | 3 | DP | |
| LVN------ | 100 | 6.5 | 20 | KOH | 18 | 2 | BP | 2. |
| LVN------ | 100 | 6.5 | 20 | KOH | 17 | 6 | DP | |
| LVN------ | 100 | 6.5 | 20 | KOH | 17 | 5 | BP | less than 1. |
| LVN------ | 100 | 6.5 | 20 | KOH | 17 | 4 | DNP | |
| LVN------ | 100 | 6.5 | 20 | KOH | 16 | 16 | P | |
| LVN------ | 100 | 6.5 | 20 | KOH | 16 | 14 | DNP | |
| LVN------ | 100 | 6.5 | 20 | KOH | 15 | 35 | DNP | Do. |

[1] The LVN is thoroughly mixed with the treating agent by way of a shaking machine.

The method of reporting the doctor test as given in Table III is by the method desrcibed in "Standard Methods for Testing petroleum and Its Products," Institute of Petroleum, 30/56.

The light virgin naphtha used in this example was produced by topping an Aramco crude to give a sour naphtha of the following inspection data:

Distillation:

| | |
|---|---|
| IBP | ° F-- 90 |
| 50% | ° F-- 142 |
| FBP | ° F-- 214 |
| Specific gravity | 0.664 |
| Mercaptan number, average | 16.18 |

The sour naphtha was caustic washed to give a mercaptan number of 6.5 and then used in the experiment of this example.

In this example the reactants were shaken together. Without shaking the surface of the solid became coated and reaction ceased. The applicants' invention is based on the discovery that by the inclusion of water or a $C_1$ to $C_4$ alcohol in the feed the reaction will take place by percolating the feed over the alkali.

The applicants have observed that after the process has been in operation without the use of water or alcohol the surface of the alkali becomes dirty, and the efficiency of the process decreases. It has been found that the process of the present invention is dependent on the inclusion of a $C_1$ to $C_4$ alcohol and/or water in the feed.

mixture. The water may be introduced into the feed mixture in the form of a haze, for example by passing steam into the feed. It is preferred that the concentration of alcohol or water added is sufficient to remove the impurities on the surface of the alkali but without causing the bed of alkali to disintegrate or fuse into a solid mass. We have found that concentrations from 0.05% volume to 1% volume and preferably from 0.07% to 0.15% of alcohol to be suitable. The desired amount of alcohol or water may be added batchwise or continuously to the feed. Methanol is the particularly preferred alcohol which may be injected continuously.

We have found that it is particularly advantageous to include the solid alkali in the water or the alcohol which is added to the feed. The alcohol or water is preferably saturated with potassium hydroxide or sodium hydroxide. We have discovered that by the addition of further alkali to the bed by this means prolongs the life of the fixed caustic bed.

The water or alcohol included in the feed causes a solution containing alkali and adsorbed sulfur impurities to separate out as droplets from the bottom of the column. A similar solution separates when the added water or alcohol contains sodium or potassium hydroxide. This insoluble liquid should be collected at the bottom of the column and run to waste. Alternatively mercaptans may be recovered from this liquid and used in further processes. The alkali may also be recovered.

The product obtained from the foregoing process may be further purified by percolating the feed over a bed of a mixture of active charcoal with the sodium or potassium hydroxide. It is preferred that from 1 to 50 wt. percent active charcoal be mixed with the solid alkali. The particle size of the active carbon may be above 0.05 but preferably is from 0.8 to 2.0 mm.

## EXAMPLE 5

By shaking a LVN sample with a mixture of KOH pellets and active carbon, a doctor pass product with good corrosion is obtained. Table V shows how the quantity of active carbon, the presence of water and/or sulfur affects the rate of sweetening reaction and the life of the feed. The contact time indicated is the minimum time required to obtain a DP product.

*Table IV*

| Product | Volume, cc. | Mercaptan number | Water Content, cc. | Free S, mgr./100 cc. | KOH, gr. | Act. Carb., gr. | Contact time, min. | Doctor test |
|---|---|---|---|---|---|---|---|---|
| LVN | 300 | 20 | ---------- | 3 | 20 | 10 | 3 | DP |
| LVN | 300 | 20 | ---------- | 3 | 20 | 1 | 12 | DP |
| LVN | 300 | 20 | 2 | 3 | 20 | 1 | 7 | DP |
| LVN | 300 | 20 | 2 | ---------- | 20 | 1 | 9 | DP |

What is claimed is:

1. A process for removing sulfur impurities from a petroleum distillate which comprises adjusting the composition of said distillate whereby said distillate contains in the range of about 0.01 to 5.0 wt. percent of a compound selected from the group consisting of water and $C_1$ to $C_4$ alcohols, passing said distillate over a fixed bed of a solid alkali metal hydroxide selected from the group consisting of potassium hydroxide, sodium hydroxide and mixtures thereof, and recovering a petroleum distillate reduced in sulfur impurities.

2. The process of claim 1 wherein said sulfur impurities are free sulfur and soluble mercaptans are added to said distillate prior to passing said distillate over said fixed bed.

3. The process of claim 2 wherein said soluble mercaptans are $C_4$–$C_{12}$ mercaptans.

4. The process of claim 2 wherein the ratio of free sulfur to mercaptan is within the range of about 2.5:1 to 4.5:1.

5. The process of claim 1 wherein said sulfur impurities are mercaptans and free sulfur is added to said distillate whereby the ratio of free sulfur to mercaptan is greater than 2:1 prior to passing said distillate over said fixed bed.

6. The process of claim 5 wherein the ratio of free sulfur to mercaptan is within the range of about 2.5:1 to 4.5:1.

7. The process of claim 1 wherein said water content is adjusted by passing steam into the distillate.

8. The process of claim 1 wherein said alcohol is methanol.

9. The process of claim 1 wherein said fixed bed contains from 1 to 50 wt. percent of activated charcoal.

10. The process of claim 1 wherein said sulfur impurities are free sulfur and mercaptans and wherein the ratio of free sulfur to mercaptans is greater than 2:1.

11. A process for removing sulfur impurities from a petroleum distillate which comprises adding to said distillate a liquid compound selected from the group consisting of water and $C_1$ to $C_4$ alcohols whereby said distillate contains in the range of about 0.01 to 5 wt. percent of said compound, passing said distillate over a fixed bed of a solid alkali metal hydroxide selected from the group consisting of potassium hydroxide, sodium hydroxide and mixtures thereof, and recovering a petroleum distillate reduced in sulfur impurities.

12. The process of claim 11 wherein said liquid compound contains solid alkali metal hydroxide selected from the group consisting of potassium hydroxide and sodium hydroxide.

13. The process of claim 11 wherein said sulfur impurities are free sulfur and mercaptans and wherein the ratio of free sulfur to mercaptans is greater than 2:1.

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