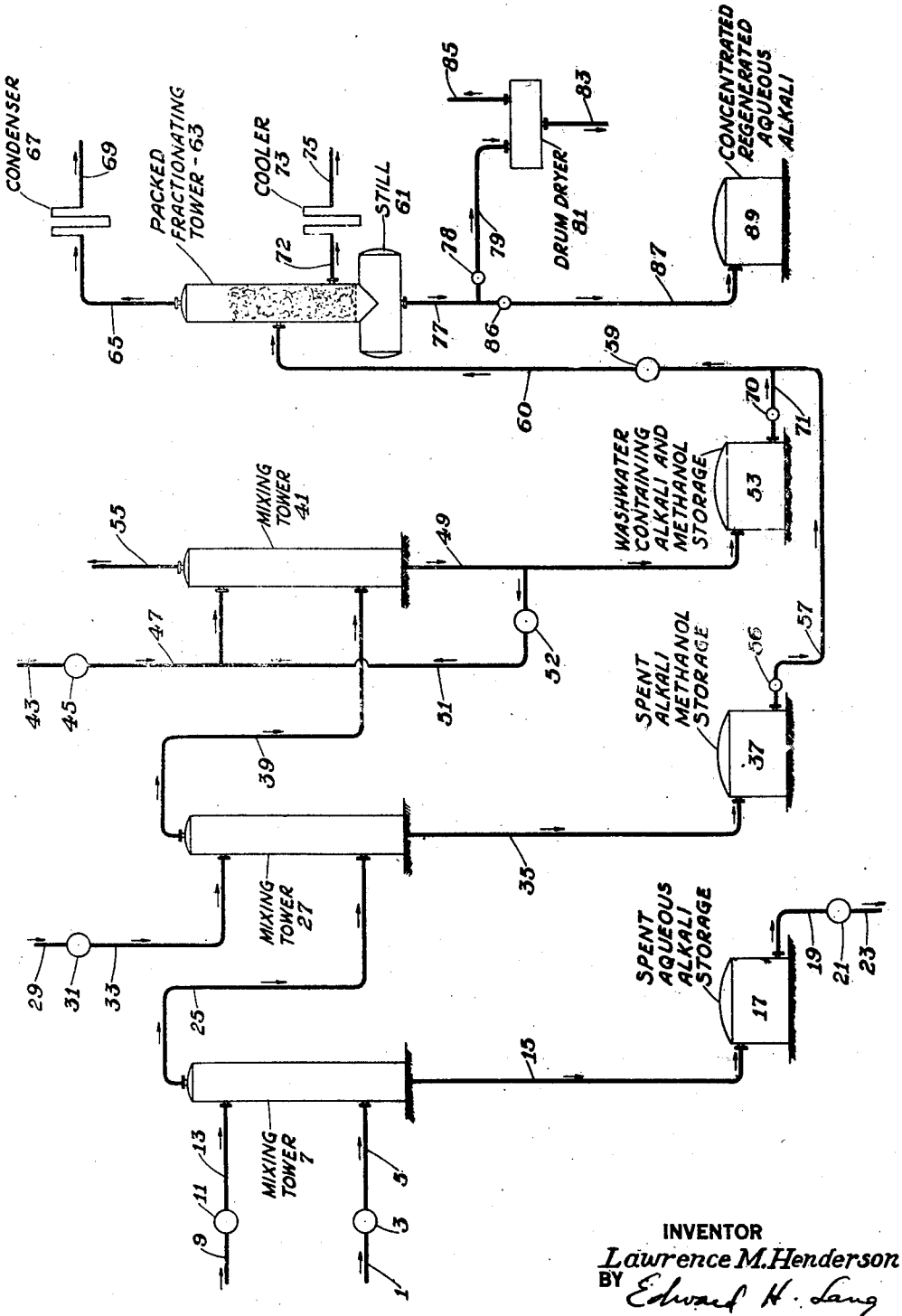
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ALKALI TREATMENT OF HYDROCARBON OILS

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ALKALI TREATMENT OF HYDROCARBON OILS

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This invention relates to an improved method of treating hydrocarbon oils and more particularly to a process of sweetening and desulphurizing petroleum distillates such as are obtained by the distillation and/or cracking of petroleum oils, and to the subsequent recovery of the treating reagent.

More specifically this invention relates to a novel method of sweetening and desulphurizing gasoline and naphthas containing undesirable malodorous sulfur compounds such as mercaptans and to the recovery of the treating reagent wherein an untreated distillate is first contacted with aqueous alkali solution to remove hydrogen sulfide and low boiling mercaptans, and then contacted with alkali methanol to remove higher boiling mercaptans as alkali mercaptides. The alkali methanol after separation from the distillate may be recovered by distillation. The higher boiling mercaptans may be recovered by heating the residual mercaptides in the presence of water whereby the mercaptides hydrolyze to mercaptans and distill off. The aqueous as well as the alcoholic alkali solution may be recovered and regenerated if desired. For reasons of economy, sodium hydroxide is the preferred alkali, although other alkalies may be used.

An object of the invention is to provide a method for sweetening and lowering the sulphur content of mineral oils, particularly petroleum distillates.

Another object of the invention is to provide a method for sweetening and lowering the sulfur content of hydrocarbon oils and distillates in such manner that valuable mercaptans may be recovered.

A further object of the invention is to provide a method of sweetening hydrocarbon oils and distillates with alkali methanol in such manner that the methanol and alkali can be readily and economically recovered for further use.

Still another object of the invention is to provide a method of sweetening hydrocarbon oils and distillates by means of alkali methanol in which loss of methanol is reduced to a minimum, thereby lowering the cost of the process.

Other objects of the invention will become apparent from the following detailed description and accompanying drawing of which the single figure is a diagrammatic elevational view of apparatus suitable for carrying out the invention.

The benefits obtained by treating petroleum distillates with either aqueous or alcoholic alkali are well known in the art, but the recovery of methanol and regeneration of the alkali by methods heretofore available, has been considered too expensive to permit commercial success of the operation.

Untreated petroleum distillates usually contain, among other compounds, a group of compounds known as mercaptans. These compounds cause the distillates to have a bad odor, which is a considerable detriment in marketing the products containing them.

A very sensitive test has been developed which will show the presence of extremely small amounts of these compounds. This is the well known doctor test (Federal Test Specification 520.31). Distillates which do not show a reaction in the doctor test are said to be negative to the test, or sweet.

There are a number of well known methods of eliminating mercaptans as such from petroleum distillates. In the case of the lighter distillates such as gasoline, kerosine and various special naphthas, mercaptans are frequently eliminated by conversion to less offensive smelling sulfur compounds commonly presumed to be disulfides. While these methods do not remove the mercaptan sulfur from the distillates, there is a considerable improvement in odor as a result of the treating process. Materials frequently used to achieve these results are sodium plumbite (doctor solution), and calcium or sodium hypochlorite. The use of sodium plumbite is objectionable in that in a commercial operation control of the addition of elementary sulfur necessary to complete the sweetening reaction is difficult, and excessive addition of sulfur results in a material degradation of the product being treated by causing the loss of octane number, lead susceptibility and frequently difficulty with meeting the usual corrosion tests. The use of hypochlorite is open to the objection that some distillates, especially cracked distillates, treated by this method seem to be much less color stable than the untreated distillates.

I have now discovered that by my method of treating petroleum distillates with alkali methanol, I am not only able to accomplish results that ordinarily are not possible with most treating reagents, but in addition, I am able to recover or regenerate the used methanol solution in a much more satisfactory and economical method than has heretofore been possible.

My discovery is based on the fact that petroleum distillates containing mercaptan sulfur compounds may be treated with aqueous alkali solutions to substantially completely remove

those mercaptans whose boiling points are approximately the same or lower than the boiling point of commercial anhydrous methanol and when these petroleum distillates which have been treated with the aqueous alkali solution for the removal of the lower boiling mercaptans are treated with alkali methanol, the higher boiling mercaptans may be substantially completely removed and due to the difference in boiling points, the resulting alkali mercaptides may be readily separated by distillation from the methanol. Distillates thus treated will be found to have the mercaptan sulfur substantially removed, will be sweet to the doctor test, color stable and not only will pass the usual corrosion tests, but in addition will pass much more severe corrosion tests such as are frequently used in the paint and varnish industry. An example of such a severe corrosion test is described in H. A. Gardner's book entitled "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," eighth edition, page 801, and is hereinafter referred to as the varnish thinner corrosion test.

An examination of the boiling points of mercaptans commonly found in gasolines, kerosine and various special naphthas indicates that normal propyl mercaptan and mercaptans containing fewer carbon atoms boil approximately at or below the boiling point of commercial anhydrous methanol, which is 148° F. This is clearly shown in Table I:

Table I

Mercaptan	Boiling point
	°F.
Methyl	42- 43
Ethyl	97- 99
n-Propyl	153-154
n-Butyl	207-208
n-Amyl	260
secondary-Propyl	136-140
secondary-Butyl	183-185
secondary-Amyl	235

Borgstrom, Dietz and Reid have shown in their article in Industrial and Engineering Chemistry, volume 22, page 245, that lower boiling mercaptans up to and including propyl and isopropyl mercaptans are substantially completely removed by an aqueous caustic soda solution of 8.72% by weight (2.18 normal) sodium hydroxide. I have confirmed the results of these authors by treating a grade of petroleum distillate known as textile spirits to which had been added 0.022% sulfur as normal propyl mercaptan, with 10% solutions of aqueous sodium hydroxide. In one such experiment when 350 cc. of such textile spirits were shaken in a separatory funnel under an atmosphere of nitrogen with 88 cc. of 10% aqueous caustic solution and the treated spirits analyzed for mercaptan sulfur content, the treated material contained only 0.002% mercaptan sulfur. It is well known that mercaptans of lower molecular weight and lower boiling points than propyl mercaptan, are correspondingly more acidic and are even more effectively removed by an aqueous alkali treatment. It is therefore apparent that propyl mercaptan and lower molecular weight mercaptans are quite readily removed from light petroleum distillates by means of aqueous alkali. Thus, all of the mercaptans whose boiling points are approximately equal to or lower than the boiling point of methanol, may be removed with aqueous alkali. It is unnecessary to carefully regulate the quantity of aqueous alkali used so long as sufficient is used to react with the lower boiling mercaptans. A large excess may be used without interfering with the efficacy of the process.

Mercaptans may be substantially completely removed from commercial gasoline and a doctor sweet product obtained by a combination aqueous alkali-alkali methanol treatment as is clearly shown by the data in Table II:

Table II

Treat No.	Percent S as RSH in gasoline before treat	Treat	Percent S as RSH after treat	Doctor
#1	0.011	[1] 6-stage, 25% by vol. aqueous caustic.	0.002	Positive.
#2	0.002	1-stage, 5% by vol. [1] caustic-abs. methanol subsequent to treat 1.	0.000	Negative.
#3	0.048	[1] 6-stage, 25% by vol. aqueous caustic.	0.012	Positive.
#4	0.012	[1] 1-stage, 15% by vol. caustic 80% methanol. Subsequent to treat 3.	0.001	Negative.

[1] 12% by weight NaOH.

The gasoline treated by aqueous alkali followed by alkali methanol and shown in Table II were not only doctor negative, but were of much improved odor, color stable, and satisfactorily passed the severe varnish thinner corrosion test previously described. While the alkali-methanol used may contain varying amounts of water and still be reasonably effective for the removal of mercaptans, it has been found that mercaptans may be more completely removed when the methanol is substantially anhydrous material. Substantially anhydrous methanol as herein used is defined as methanol containing not substantially more than approximately 1% water.

It will be seen, therefore, that by first removing those mercaptans which boil near or below the boiling point of methanol, by means of aqueous alkali, the higher boiling mercaptans can then be removed with alkali-methanol and since these mercaptans and their corresponding mercaptides boil above the boiling point of methanol, the methanol can readily be separated by distillation and reused for sweetening further quantities of sour distillates.

Substantially anhydrous alkali methanol (12% NaOH) is slightly soluble in the distillates treated, the solubility increasing as the methanol becomes more anhydrous. This is shown in Table III:

Table III

Percent by vol. methanol	Percent by vol. methanol soluble in gasoline
50	0.22
60	0.23
70	0.29
80	0.41
90	0.54
99.5	0.65

The data in Table III show that while the methanol is slightly soluble in the gasoline treated, the amount remaining in the gasoline is small enough to be satisfactorily removed and economically recovered by water washing the treated

gasoline. This is clearly demonstrated by the data in Table IV:

Table IV

Per cent by volume of methanol in water used to wash naphtha	Per cent by volume of methanol in naphtha retained in naphtha after treating
50.0	0.1
30.0	0.05
10.0	0.03

Methanol remaining in gasoline after treating with alkali methanol can be substantially completely recovered by washing seven volumes of the gasoline with one volume of water. The same water may be used many times, that is, until the concentration of methanol in the water is approximately 50% by volume, and still effect a substantially complete removal of methanol from the gasoline. The methanol in the aqueous solution of methanol which may or may not contain small quantities of alkali may be recovered by distillation.

When alkali methanol has been used to remove only the higher boiling mercaptans from petroleum distillates, the methanol may be readily separated by distillation from the alkali mercaptides dissolved in the spent treating reagent, as is shown by the following example. Anhydrous caustic methanol which had been used to treat distillates previously subjected to a preliminary aqueous caustic wash, was distilled and analyzed for mercaptan sulfur content. The methanol thus recovered was found to contain only 0.7% of the total amount of mercaptan sulfur which it had removed from the distillate treated. The balance of the mercaptan sulfur was left in the residue as sodium mercaptide together with the sodium hydroxide.

It will be apparent from the foregoing data that I have discovered a method of effectively removing mercaptan sulfur compounds from light petroleum distillates whereby the treated distillate is not only doctor sweet and of improved odor, but in addition suffers no loss of octane number, is of lower sulfur content, and passes very severe corrosion tests. At the same time, the preliminary aqueous alkali treatment which removes the low boiling mercaptans makes possible the subsequent separation of high boiling mercaptides from methanol in the spent alkali methanol solution by means of simple distillation, thus affording an economical and convenient means of recovering the treating materials for further use.

In the drawing, the numeral 1 represents, generally, a pipe for conveying petroleum distillate such as gasoline or naphtha from a source of supply to pump 3 which discharges through pipe 5 into the lower portion of mixing tower 7. In this tower the untreated distillate is thoroughly mixed with fresh aqueous alkali solution, conveyed from a suitable source of supply through pipe 9, pump 11 and pipe 13 into the upper portion of tower 7. Spent aqueous alkali solution separates from the commingled products and may be drawn off from the bottom of tower 7 through pipe 15 into a suitable storage tank 17. This solution may be transferred from storage tank 17 by means of pipe 19, pump 21 and pipe 23, to be reused or regenerated or discarded, whichever may be desired. Treated naphtha from which the hydrogen sulfide and lower boiling mercaptans have been removed by the aqueous alkali treatment, is withdrawn from the top of tower 7 through pipe 25 which is connected to the lower portion of tower 27. Substantially anhydrous alkali methanol is conveyed from a suitable storage through pipe 29, pump 31 and pipe 33 into the upper portion of mixing tower 27 and is therein commingled with the naphtha from tower 7 which enters through pipe 25. Alkali methanol containing therein high boiling alkali mercaptides may be withdrawn from the bottom of tower 27 through pipe 35 into a suitable storage tank 37. Naphtha from which the mercaptans have been substantially completely removed is withdrawn from the top of tower 27 by means of pipe 39 and discharged into the lower portion of tower 41 where methanol which has dissolved in the naphtha, is removed by means of washing with a small quantity of water. Water is conducted from a suitable source of supply through pipe 43, pump 45 and pipe 47 into the upper portion of tower 41 wherein it is commingled with the naphtha containing dissolved therein a small quantity of methanol. The wash water, which now contains methanol, may be withdrawn from the bottom of tower 41 by means of pipe 49 and recirculated through pipe 51 by means of pump 52 back into tower 41 for washing further quantities of naphtha; or when the methanol content of the wash water has reached the allowable maximum, it is withdrawn through pipe 49 and passed directly to a suitable storage tank 53 for accumulation prior to recovery of the methanol by distillation. Finished neutral naphtha is withdrawn from the top of tower 41 by means of pipe 55 and passes to suitable storage not shown.

Spent alkali methanol may be withdrawn from storage tank 37 by means of valve 56, pipe 57 and pump 59, together with a suitable amount of alkali methanol wash water from tank 53, conveyed through valve 70, pipe 71 to pump 59, and transferred to still 61 by means of pipe 60 and fractionating tower 63. In still 61 the mixture of wash water containing methanol and spent alkali methanol is heated to the minimum temperature required for distillation of methanol, which may be fractionated in tower 63, removed through pipe 65, condensed in condenser 67 and conveyed to suitable storage through pipe 69. This methanol is then available for making up additional alkali methanol for use in the process.

The temperature at the top of tower 63 while sufficiently high to permit the distillation of methanol is not high enough to permit water and mercaptans or mercaptides to pass overhead. Water and mercaptans may be taken off as a side stream at a lower point in fractionating tower 63 such as through pipe 72, cooler 73, pipe 75 and conveyed to a suitable accumulator tank not shown where the mercaptans and water readily separate. The mercaptans may be recovered as such by simple decantation.

The still bottoms or residue which consist of highly concentrated aqueous alkali and containing not more than a very small quantity of mercaptides, may be withdrawn from still 61 through pipe 77, valve 78 and pipe 79 into drum drier 81 and recovered as solid substantially anhydrous regenerated alkali suitably withdrawn at 83. Water vapor may be removed through pipe 85. As an alternative method the concentrated aqueous alkali may be withdrawn from still 61 through pipe 77, valve 86 and pipe 87 to storage

tank 89 for subsequent use in making up aqueous alkali solution for possible use in the preliminary wash in the process or for other suitable uses.

Thus it will be seen that I have devised a method for not only sweetening hydrocarbon oils but for desulfurizing such oils. Mercaptans are removed in such a manner that the methanol can be continuously recovered and reused in a continuous cycle. The higher boiling mercaptans can likewise be recovered with ease and sold as a valuable product of commerce.

No expensive, highly specialized equipment is required for carrying out the process and while the process as herein described is well adapted for carrying out the objects of the present invention, various modifications and changes may be made without departing from the substance of the invention. My invention includes all modifications falling within the scope of the appended claims.

I claim:

1. A process of treating untreated hydrocarbon oil containing mercaptans boiling above and below the boiling point of methanol which comprises contacting said oil in a primary treating zone with sufficient aqueous alkali solution whereby the removal of substantially all mercaptans the boiling points of which are not substantially above the boiling point of methanol is effected, separating said oil and said alkali solution, then contacting the oil in a second treating zone with substantially anhydrous alkali methanol effecting removal of mercaptans, the boiling points of which are higher than the boiling point of methanol, as mercaptides in the alkali methanol solution, separating said oil from said alkali methanol, recovering the methanol from the spent alkali methanol by fractional distillation thereof and recycling the methanol to the process.

2. A process of rendering untreated hydrocarbon oil containing sulfur compounds boiling above and below the boiling point of methanol sweet and non-corrosive whereby said oil is commingled with sufficient aqueous alkali in a primary treating zone whereby removal of substantially all weakly acidic sulfur compounds the boiling points of which are not substantially above the boiling point of methanol is effected, separating said oil and said aqueous alkali solution, commingling said oil with sufficient substantially anhydrous alkali methanol in a second treating zone to remove as mercaptides in the alkali methanol solution sulfur compounds the boiling points of which are higher than that of methanol, separating said oil from said alkali methanol, recovering methanol substantially free of sulfur compounds from said separated alkali methanol by distillation thereof and recycling the recovering methanol.

3. Process in accordance with claim 2 where the alkali is sodium hydroxide.

4. Process in accordance with claim 2 where the anhydrous alkali methanol contains not substantially over 1% of water.

5. The process of removing sulfur compounds from petroleum distillate containing mercaptans boiling above and below the boiling point of methanol which comprises treating said distillate with sufficient aqueous alkali whereby substantially all hydrogen sulfide and mercaptans boiling below the boiling point of methanol are removed, separating the aqueous caustic alkali from the distillate, then treating the distillate with anhydrous caustic alkali methanol in quantities sufficient to remove substantially the remaining mercaptans present in the distillate as mercaptides in the alkali methanol solution, separating the alkali methanol from the distillate, recovering methanol substantially free of mercaptans from said separated alkali methanol by fractional distillation thereof and recycling the recovered methanol.

6. In a process of treating a substantially methanol-immiscible hydrocarbon oil containing sulfur compounds boiling above the boiling point of methanol that is substantially free of hydrogen sulfide and from which substantially all mercaptans having boiling points not substantially higher than the boiling point of methyl alcohol have been removed, the steps of commingling said hydrocarbon oil with substantially anhydrous alkali methanol to remove as mercaptides in the alkali methanol solution sulfur compounds the boiling points of which are higher than that of methanol, said alkali methanol being present in a quantity in excess of that required for reaction with said sulfur compounds, separating said hydrocarbon oil from said alkali methanol, recovering methanol substantially free of mercaptans from said separated alkali methanol by fractional distillation thereof and recycling the recovered methanol.

7. A continuous process of treating untreated hydrocarbon oil containing mercaptans boiling above and below the boiling point of methanol which comprises contacting said oil with sufficient aqueous alkali solution whereby removal of substantially all n-propyl mercaptan and mercaptans having lower boiling points than said n-propyl mercaptan is effected, separating said oil and said alkali solution, contacting the oil with sufficient substantially anhydrous alkali methanol to effect removal as mercaptides in the alkali methanol solution of mercaptans the boiling points of which are higher than the boiling point of n-propyl mercaptan, separating said oil from said alkali methanol, recovering the methanol substantially free of mercaptans from the spent alkali methanol by fractional distillation thereof and recycling the recovered methanol.

8. Process in accordance with claim 7 in which the oil is repeatedly washed with water following separation of the alcoholic alkali solution until the alcohol content of the water is approximately 50% and the alcohol is then separated from the water by distillation and recycled.

9. In a process for removing mercaptans from low boiling hydrocarbon oil containing mercaptans boiling above and below the boiling point of methanol and which has been preliminarily treated with aqueous alkali solution to remove hydrogen sulfide and lower boiling mercaptans contained in the oil, the steps which comprise contacting the oil with caustic alkali methanol solution to remove substantially all the remaining mercaptans in said oil as mercaptides in the alkali methanol solution, then contacting the oil with water to wash residual methanol from the oil, separating the water and the alkali-methanol solution from the oil and subjecting the mixed water and alkali-methanol solutions to fractional distillation to recover therefrom substantially mercaptan-free methanol and substantially mercaptan-free alkali solution and recycling the methanol for treatment of further quantities of mercaptan-containing hydrocarbon oil.

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