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REFINING MINERAL OILS

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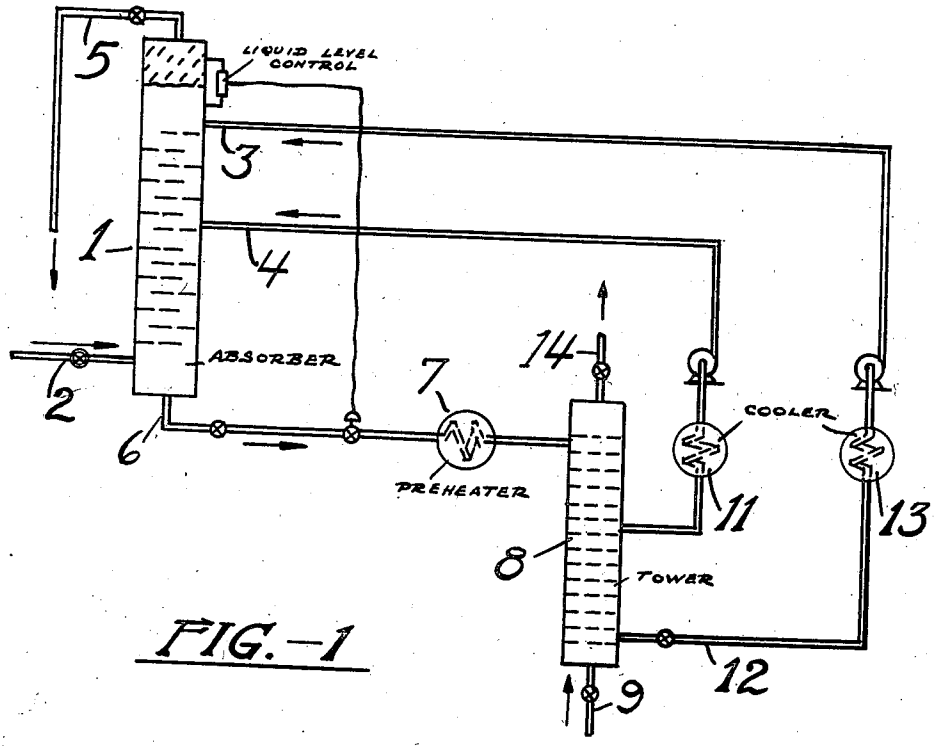


FIG.—1

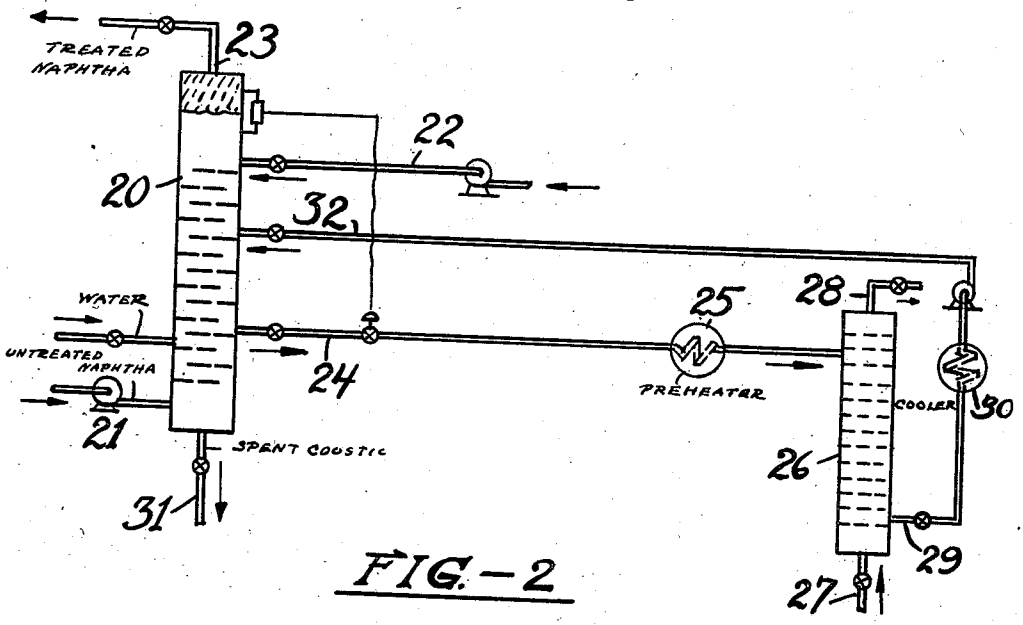


FIG.—2

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REFINING MINERAL OILS

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4 Claims. (Cl. 196—32)

The present invention relates to the refining of mineral oils. The invention more particularly relates to a process by which sulfur compounds such as hydrogen sulfide and mercaptan compounds may be efficiently and economically removed from oils, particularly from petroleum oils. This invention is especially concerned with a process in which undesirable hydrogen sulfide and mercaptan compounds are removed from feed oils containing the same by means of a selective solvent or reagent wherein the undesirable constituents are removed from the oil in an initial stage and in which the reagent is regenerated efficiently in a secondary stage. In accordance with the present process, the mercaptan containing oil is contacted in a manner which is regulated with respect to the concentration and character of the particular mercaptan compounds present. The oil being treated just prior to removal of the same from the system is contacted with a relatively small amount of relatively mercaptan free solvent, while the feed oil introduced into the system is contacted with a relatively large quantity of partially mercaptan free solvent. The treated oil, substantially completely free of undesirable hydrogen sulfide and mercaptans, is withdrawn from one end of the system, while the solvent containing the removed undesirable constituents is removed from the other end of the system and passed to a regeneration zone. The solvent is regenerated in a manner to remove from an intermediate point in the regeneration zone a partially regenerated solvent which is returned to the treating unit as described and to remove as an end product in the regeneration zone a solvent relatively free of undesirable constituents which is utilized for contacting the feed oil prior to withdrawal of the feed oil from the solvent treating system.

It is well known in the art to utilize various solvents for the removal of sulfur compounds such as mercaptans from petroleum oils and to regenerate the spent solvent by various processes. Solvents usually employed for the removal of mercaptan compounds from petroleum oils are various aqueous alkalis, as for example sodium hydroxide and potassium hydroxide solutions. In these processes the mercaptan containing oil is treated with a sufficient quantity of alkali to convert the mercaptan compounds to the corresponding mercaptides. The quantity of aqueous alkali utilized depends upon the particular alkali being used, as well as upon the type of petroleum oil being treated, and the character of the mercaptan compounds present. When employing caustic soda, it is a conventional practice to employ aqueous solutions having a sodium hydroxide concentration in the range from about 10% to about 15%. The process for the removal of mercaptan compounds from feed oils is usually carried out in one or more mixing and settling zones or stages, or in countercurrent tower treating operations. In this latter type of operation, the practice is to contact the oil and solvent throughout the phase contacting paths. After contacting the oil, the spent alkali solution containing the sulfur compounds as mercaptides is regenerated by various processes. For example, the mercaptides may be oxidized to form the corresponding disulfides by treating the same with an oxygen containing gas. These disulfide compounds are then removed from the oil by a subsequent step such as a decantation operation. The mercaptides may also be hydrolyzed to form the corresponding mercaptans which may be removed by volatilization.

In general, the solvent is regenerated or stripped of undesirable constituents by countercurrent action of an immiscible or partially miscible fluid, usually by treating the solvent with inert gas or steam. The regenerated solvent is usually recycled to the extraction operation. These processes, however, have not been entirely satisfactory, due to the fact that the relatively higher molecular weight mercaptides are not readily oxidizable to disulfides. Furthermore, the relatively lower molecular weight mercaptides are not readily hydrolyzable to the corresponding mercaptans.

In operations of this character, the oil being treated contains various mercaptans which boil over a relatively wide range. For example, when treating petroleum oils boiling in the motor fuel boiling range, some of the mercaptans present comprise methyl mercaptan, ethyl mercaptan, the various propyl mercaptans, and the butyl mercaptans. The procedure thus employed is to contact the feed oil containing these various mercaptans with the particular solvent being used in sufficient quantity to substantially completely remove the least soluble mercaptan, which quantity is considerably in excess of that required for removal of the more soluble mercaptans. This procedure is not particularly desirable, in view of the wide variance in the solubility characteristics of the respective mercaptans in any particular solvent. It is of an especial disadvantage if it is desired to regenerate the solvent and to recycle the same to the solvent treating system. This is due to the fact that an excessive amount of stripping medium is required in order to remove the more soluble mercaptans from the relatively large amount of solvent which is employed for the removal of the less soluble mercaptans from the feed oil.

We have now discovered a process by which it is possible efficiently and economically to remove hydrogen sulfide and particularly undesirable mercaptan compounds from feed oils containing the same and to handle the spent solvent in a

manner by which the dissolved constituents are readily removed and the solvent regenerated whereby it may be recycled to the system. The process of our invention may be readily understood by reference to the attached drawing illustrating modifications of the same. Referring specifically to Figure 1, for purposes of illustration it is assumed that the feed oil comprises a petroleum oil boiling in the motor fuel boiling range and contains mercaptan compounds boiling in the range of methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl mercaptan, and higher boiling mercaptans. The feed oil is introduced into contacting zone 1 by means of feed line 2. For purposes of illustration it is assumed that contacting zone 1 comprises a countercurrent treating tower containing suitable distributing and contacting means. The feed oil flows upwardly through countercurrent treating tower 1 and contacts downflowing solvent which is introduced by means of lines 3 and 4. For purposes of illustration it is assumed that the solvent comprises an aqueous solution of sodium hydroxide. The feed oil flowing upwardly through tower 1 initially contacts in the lower section partially regenerated solvent which is introduced into the system by means of line 4 and partially spent solvent from the upper section. The feed oil contacts relatively completely regenerated solvent in the upper section of tower 1, which solvent is introduced by means of line 3. Conditions are adjusted with respect to solvent to oil ratios, as well as operating conditions such as temperature, so as to free the feed oil substantially completely of the various mercaptan compounds which are soluble in the sodium hydroxide solution. The treated feed oil, free of undesirable mercaptan compounds, is withdrawn from tower 1 by means of line 5 and handled in any manner desirable. The spent solvent solution containing dissolved therein the undesirable mercaptan constituents as mercaptides, is withdrawn from tower 1 by means of line 6, preferably heated in preheater 7, and introduced into the upper section of a solvent recovery zone 8. The spent solvent flows downwardly through solvent recovery zone 8 and contacts an upflowing stripping medium which is introduced by means of line 9. For purposes of description, it is assumed that the stripping medium comprises open steam or an equivalent gas, or vapors generated by a reboiler. At an intermediate point in the solvent recovery zone a partially regenerated solvent stream is withdrawn by means of line 10, cooled in cooler 11, and recycled to the intermediate point in tower 1 by means of line 4. A relatively small amount of the solvent flows through the lower section of regenerating zone 8 and contacts the stripping steam under conditions of higher steam to solvent ratio and consequently more severe stripping. The relatively small quantity of solvent which is substantially completely regenerated is withdrawn from solvent recovery zone 8 by means of line 12, cooled in cooler 13 and recycled to the upper section of tower 1 by means of line 3. The stripping steam and mercaptans removed from the solvent in solvent regeneration unit 8 are removed overhead by means of line 14 and handled in any manner desirable, usually by condensing the steam and heavy mercaptans and passing the non-condensed vapors to a burning line. When stripping steam is supplied by means of a closed coil reboiler, a partial reflux of the condensed vapors is employed.

Referring specifically to Figure 2, feed oil, which for the purpose of description is taken to be a volatile petroleum naphtha such as that obtained by high pressure gas absorption and therefore containing considerable quantities of hydrogen sulfide, is introduced into treating zone 20 by means of line 21. For purposes of description it is assumed that treating zone 20 comprises a countercurrent treating tower containing suitable distributing and mixing means. The feed oil flows upwardly through treating zone 20 and initially contacts in lower treating sections a partially regenerated solvent which for the purpose of illustration is assumed to be an aqueous solution of sodium hydroxide introduced by means of line 32 and partially spent solvent from the upper treating section. The treated oil finally contacts fresh solvent in the upper section of treating zone 20 which is introduced by means of line 22.

The oil substantially free of undesirable mercaptan compounds is withdrawn from the unit by means of line 23 and handled in any manner desirable. A major proportion of the spent sodium hydroxide solution is withdrawn from zone 20 by means of line 24, passed through preheater 25 and introduced into the upper section of regeneration zone 26. The spent sodium hydroxide solution flows downwardly through regeneration zone 26 and contacts an upflowing stripping medium which is introduced by means of line 27, and which for purposes of description is assumed to be steam. The steam and volatilized mercaptans are removed from zone 26 by means of line 28 and handled in any manner desirable, usually by condensation of the steam and heavy mercaptans and passing the noncondensed vapors through a burning line. The regenerated sodium hydroxide is withdrawn by means of line 29, passed to cooler 30, and introduced into zone 20 by means of line 32. A portion of the spent caustic solution which is not withdrawn from treating zone 20 by means of line 24 passes into the lower section where it may be diluted with water and contacts the incoming liquid under conditions to remove hydrogen sulfide substantially completely from the same. This portion of spent caustic is withdrawn from the system by means of line 31 and handled in any manner desirable, usually by disposal as a waste by-product.

The process of the present invention may be widely varied. The process essentially comprises contacting a feed oil with a particular solvent in a manner that the ratio of solvent to oil is adjusted to remove the particular undesirable constituents depending upon their relative solubility in the solvent. Although the process may be adapted for the treatment of various mixtures by means of any desirable selective solvent, it is particularly applicable in the treatment of petroleum oils for the removal of mercaptan compounds when utilizing alkali metal hydroxide solutions.

The untreated feed oil is initially contacted with a relatively large volume of solvent, sufficient in quantity to absorb and remove substantially all of the higher boiling or less soluble mercaptans such as the propyl and butyl mercaptans, and considerably in excess of the quantity required for removal of the less soluble mercaptans. The spent caustic from this operation enters the upper section of a regeneration tower, where it is stripped in a countercurrent manner with a limited amount of steam, just sufficient to

nearly completely hydrolyze and vaporize the high boiling, less soluble mercaptans such as the propyl and butyl mercaptans. This quantity of steam is insufficient to remove all of the more soluble mercaptans such as the methyl and ethyl mercaptans, and as a result these lighter mercaptans are only partially stripped from the solvent in the upper regeneration section. At the approximate center of the regeneration tower, or bottom of the upper regeneration section, a major portion of the downflowing solvent is withdrawn from the tower, cooled and returned to the approximate center of the treating tower, or top of the lower treating section, where it contacts additional feed oil for substantially complete removal of the heavy, less soluble mercaptans.

If the action described in the above paragraph were carried out alone, without the auxiliary action, to be described below, of the upper treating and lower regenerating section, it is evident that the incomplete stripping of light, more soluble mercaptans in the upper regenerating section would impair the absorption efficiency of the recycled solvent, so that on incomplete absorption of light, more soluble mercaptans would take place on its subsequent reuse in the treating tower. During an intial starting period of such a process, the solvent would build up an increasing concentration of light mercaptans until the quantity of light mercaptans removed by the partial stripping with a limited quantity of steam in the regeneration section became just equal to the quantity of light mercaptans absorbed by the partially regenerated solvent in the treating section. Under these conditions, the mercaptan absorption and solvent regeneration process described would effect a nearly complete removal from the feed oil of heavy, less soluble mercaptans, but only a partial or fractional removal of light, more soluble mercaptans.

In order to make possible a nearly complete removal of the more soluble mercaptans without an increase in quantity of stripping medium, the action of the lower regenerating and upper stripping sections is necessary. In the lower regenerating section, the small fraction of partially regenerated solvent not withdrawn from the tower is allowed to continue to flow down countercurrent to the same quantity of stripping medium used in the upper regenerating section. By this means, a considerably higher ratio of stripping medium to downflowing solvent is effected in the lower regenerating section, using the same amount of stripping medium in both sections. The small volume of nearly completely regenerated solvent is removed from the bottom of the regenerating tower, cooled and recycled to the top of the treating tower, where it is effective in nearly completely removing the considerable quantity of light mercaptans remaining in the feed oil after its initial countercurrent contact with the large volume of partially regenerated solvent.

In an operation such as described with respect to Figure 2, the untreated feed oil containing a considerable quantity of hydrogen sulfide as well as a mixture of mecaptans of wide variance in solubility characteristics is first contacted with just sufficient quantity of caustic to neutralize and remove the comparatively acidic hydrogen sulfide. This caustic is obtained as spent caustic from the upper mercaptan removal sections, and may therefore be diluted with water to "spring" the mercaptans from solution before neutralization of hydrogen sulfide. Since caustic spent with hydrogen sulfide is extremely difficult to regenerate, it is in the usual case withdrawn from the treating unit and disposed of as a waste product. This lower section, then, serves for the initial removal of hydrogen sulfide in a manner economical both from a standpoint of equipment cost and as will be seen below from the standpoint of operating efficiency.

The upflowing feed oil, after its initial wash for removal of hydrogen sulfide, next contacts caustic for removal in order of heavy mercaptans and light mercaptans, as described in the process illustrated by Figure 1. An essential difference in this process from that of Figure 1, however, is that the small volume of caustic fed to the top of the treating tower for nearly complete removal of light mercaptans is supplied as fresh caustic to make up that disposed of as waste following neutralization of hydrogen sulfide, whereas in the process illustrated in Figure 1 this stream of caustic is one nearly completely regenerated on the lower stripping tower section.

The solvent may be introduced into the treating zone at any desired number of points, which will depend in general upon the character of the feed oil and the type of constituents it is desired to remove. The solvent which is introduced into the treating zone at a plurality of points is introduced in a manner that the volume of flow of the solvent decreases in the direction of flow of the feed liquid.

When treating petroleum oil boiling in the motor fuel boiling range, and when introducing the solvent at two points, it is preferred that the substantially completely regenerated solvent be introduced at the top of the tower, and that the greater quantity of incompletely regenerated solvent be introduced at a point where the upflowing liquid is substantially free of propyl and butyl mercaptans and higher boiling mercaptans. This is generally in the center section of the tower.

The regenerated solvent may be segregated into any number of streams depending upon the number of streams of solvent introduced into the treating system. For example, when treating a petroleum oil containing mercaptans boiling in the range from methyl to butyl and higher boiling mercaptans, and employing two points of introduction of the solvent, it is preferred that a solvent stream be withdrawn from the regeneration tower at a point where the down flowing solvent stream is free of propyl and butyl mercaptans.

Any desirable temperature or pressure may be employed. It is preferred to employ temperatures in the range from about 75° F. to 100° F. in the treating system and a pressure of about the vapor pressure of stocks treated. The temperatures employed in the regeneration zone should be sufficient so that the solvent is regenerated to the desired degree. For example, when regenerating an alkali metal hydroxide solution which has become spent in the removal of mercaptans from petroleum oils boiling in the motor fuel boiling range, it is preferred to employ temperatures in the range from about 220° F. to about 230° F. and pressures of about one atmosphere.

In order to illustrate the invention further, the following examples are given which should not be construed as limiting the same in any manner whatsoever:

Example 1

Operations were conducted for the removal of various mercaptan compounds from petroleum oils boiling in the motor fuel boiling range, using as a reagent a 12° Baumé sodium hydroxide solution. The minimum amount of caustic necessary to accomplish substantially complete removal of the individual mercaptan is as follows:

Compound	Minimum volume of 12° Baumé caustic per 100 volumes naphtha for complete removal of mercaptan
Methyl mercaptan	0.1
Ethyl mercaptan	0.5
Propyl mercaptan	2.0
Butyl mercaptan	13.0

From the above it is readily apparent that the amount of sodium hydroxide solution used when operating to remove all mercaptans is excessive with respect to methyl, ethyl, and propyl mercaptans. This situation is aggravated when it is considered that in a commercial operation with ordinary treating towers it is necessary to use from 1.2 to 2.0 times the minimum values given here to insure nearly complete absorption.

Example 2

Operations were conducted determining the minimum pounds of steam necessary per gallon of 12° Baumé sodium hydroxide solution necessary substantially completely to remove the various mercaptans from the solution. The data secured are as follows:

Compound	Minimum pounds steam per gallon 12° Baumé caustic for complete stripping of individual mercaptan
Methyl mercaptan	11.0
Ethyl mercaptan	4.0
Propyl mercaptan	1.0
Butyl mercaptan	.02

From this data it is readily apparent that to a large degree the stripping steam employed for the complete regeneration of a solvent containing a mixture of mercaptans is utilized in the removal of the relatively low boiling mercaptans.

On the basis of 100 gallons of naphtha treated with 15% caustic to absorb all mercaptans from methyl through butyl, the following approximate amounts of steam are required for nearly complete stripping of various mercaptans from the entire volume of caustic:

Compound	Pounds steam per 100 gallons naphtha to strip 15% caustic treat of nearly all of the mercaptan (1.5×minimum quantity)
Methyl mercaptan	250
Ethyl mercaptan	92
Propyl mercaptan	22
Butyl mercaptan	4.5

It is evident from the above data that the steam required for removal of the low boiling mercaptans is relatively high. It is also evident that if these mercaptans are not removed their concentration in the caustic will build up until the absorption effiiency of the caustic for low boiling mercaptans is prohibitively low.

Example 3

In another operation a feed oil boiling in the motor fuel boiling range and containing mercaptans was treated with 15 gallons of caustic per 100 gallons of feed oil. The spent caustic was then treated with 22 pounds of steam per 15 gallons of spent caustic, which was sufficient to strip the propyl and butyl mercaptans. 14 gallons per 100 gallons of feed were removed and recycled to an intermediate point in the absorber as described. The remaining one gallon of caustic per 100 gallons of oil feed was stripped with the same amount of steam used on the total 15 gallons, at a higher ratio of steam to caustic, by which it was possible to effect nearly complete removal of methyl and ethyl mercaptans. The one gallon of solvent per 100 gallons of feed, free of all mercaptans, was recycled to the upper section of the countercurrent treater, as described.

From the above data, it is apparent that the amount of steam required is 22 pounds as compared to 200 pounds when employing the conventional process described in Example 2.

What we claim as new and wish to protect by Letters Patent is:

1. Process for the removal of mercaptan compounds from petroleum oils, utilizing an alkaline solution, which comprises introducing the feed oil into one end of an absorption zone, introducing a substantially sulfur-free solvent into the other end of said absorption zone, introducing a partially regenerated solvent into an intermediate point of said absorption zone, countercurrently contacting the feed oil with said solvent, removing a treated oil from the treating zone, removing a spent solvent from the other end of said treating zone, and regenerating the same in a regeneration zone in a manner to remove a portion of the regenerated steam from an intermediate part of said regeneration zone, which stream is recycled to said intermediate point of said absorption zone, and removing from said regeneration zone a substantially sulfur-free solvent which is recycled to said absorption zone as defined.

2. Process as defined by claim 1 in which the ratio of solvent to oil throughout said absorption zone is only slightly greater than the minimum requirement for the complete removal of the individual mercaptans.

3. Process for the removal of mercaptans from petroleum oils, which comprises countercurrently treating said petroleum oils with an alkaline solution in an absorption zone under conditions in which the ratio of solvent to oil decreases in the direction of flow of the oil, separating the spent alkaline solution and regenerating the same in a regeneration zone, employing a stripping fluid under conditions in which the ratio of stripping fluid to alkaline solution increases in the direction of flow of said alkaline solution.

4. Process as defined by claim 3 in which an intermediate stream is withdrawn from said regeneration zone and recycled to an intermediate point in said absorption zone, and in which a substantially completely regenerated alkaline solution stream is withdrawn from the lower section of said regeneration zone and recycled to the upper section of said absorption zone.

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