

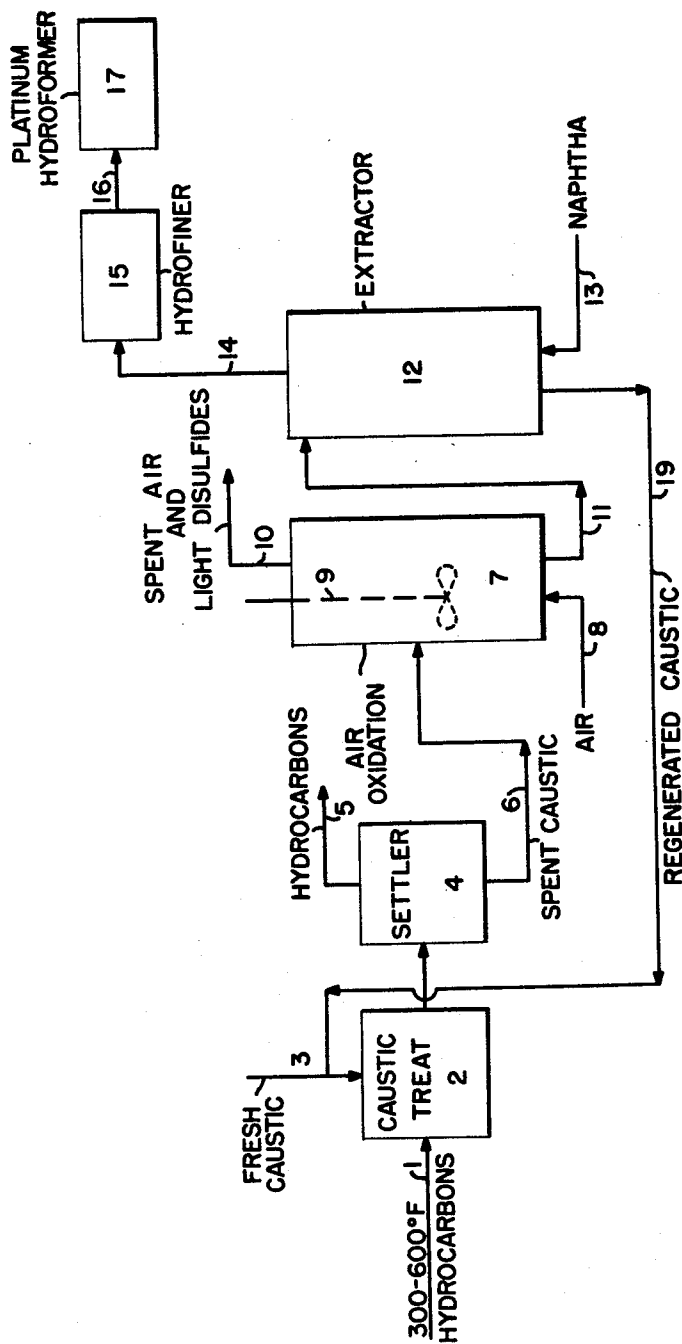
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SPENT CAUSTIC TREATING PROCESS

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SPENT CAUSTIC TREATING PROCESS

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The present invention relates to an improved process for the recovery of motor fuel aromatics from spent caustic used to wash heavy naphthas, kerosenes and heavier middle distillate fractions. More particularly, the present invention relates to caustic treating particularly a petroleum fraction boiling from about 300° F. to about 600° F., regenerating the caustic material for further use in the process, and recovering aromatics from the aryl sulfur compounds removed by the caustic. Most particularly, the present invention relates to the recovery of aromatics boiling to about 400° F. suitable for use in high octane gasolines by treating the spent caustic material by oxidation to convert thiophenolates to aryl disulfides, washing the treated caustic with platinum hydroformer naphtha feed to absorb the aryl disulfides and passing the combined naphtha and extracted disulfides to the conventional hydrofining treatment used ahead of platinum hydroforming where the disulfides are converted to aromatics.

Hydroforming is defined as an operation in which a gasoline boiling range naphtha is treated at elevated temperatures and pressures in the presence of a solid catalytic material and added hydrogen to effect an increase in octane number of the naphtha treated. The process is characterized by no hydrogen consumption or a net production of hydrogen therein. An extremely effective catalyst but one extremely sensitive to sulfur in the feed is platinum on activated alumina.

It has now been found that a much improved caustic treating process over other caustic treating methods available to the art is obtained by the method of the present invention. Thus, prior art non-regenerative caustic treating involves treating the spent caustic from naphtha washing with sulfuric acid to convert the alkali metal salts to water insoluble oils and the caustic to sodium sulfate. The oils are separated from the aqueous layer and may be treated to obtain desirable products. However, the sodium sulfate cannot be regenerated and again used and additionally presents a considerable disposal problem. Thus, due to the possible pollution of water streams, strict restrictions are placed by governmental bodies on the discharge of alkaline solutions into said streams.

An improved process over the non-regenerative caustic treating processes is that involving oxidation rather than acid treating of the spent caustic. Here, the sodium mercaptides or thiophenolates formed by the caustic treating are oxidized to disulfides and sodium hydroxide is liberated. The light or alkyl disulfides formed are vaporized overhead, and are removed by supplying large quantities of oxygen stripping gases. However, the heavier aryl disulfides such as the phenyl disulfides remain dispersed in the caustic solution. It has been proposed according to the prior art to merely return these disulfides to the process with the regenerated caustic solution. However, although this type of caustic treating removes the objectionable mercaptan odor, it does not remove these liquid aryl disulfides which are reabsorbed by the naphtha or hydrocarbon being treated. As is

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well known, sulfur in any form in gasoline is detrimental to the octane number of the gasoline and is also objectionable for corrosion reasons. The other alternative possible is that of treating these aryl disulfides with petroleum distillate so as to obtain two separate phases—an aqueous caustic phase and an oily phase containing the disulfides. However, according to the prior art, distillation is then required to separate the disulfides from the petroleum distillate so that the latter can then again be used in the process. It should be noted that the distillation of the aryl disulfides-petroleum distillate phase required was a costly operation.

According to the present invention, it has now been found that by caustic treating, particularly a cut of hydrocarbon materials boiling in the range of from about 300 to about 600° F., and air oxidizing the spent caustic, that the aryl disulfides may be recovered from the oxidized caustic by (1) washing with a naphtha stream to be platinum hydroformed, (2) separating the naphtha and dissolved aryl disulfides from the aqueous caustic and (3) converting the disulfides to extremely high octane aromatics by the ordinary hydrofining treatment given the naphtha prior to said platinum hydroforming. It is, of course, of great importance that this ordinary hydrofining will completely convert the disulfides so that an appropriately low sulfur level is maintained in the hydrofined feed supplied to the hydroformer.

Another advantage of the present process over prior art non-regenerative processes is that caustic treating to much lower levels of aryl mercaptans may be obtained since the caustic recycled to the process has been regenerated. As is well known, caustic treating is equilibrium limited as to the mercaptan sulfur extracted. Thus, it has been found, for example, that in terms of methyl mercaptans present in the naphtha that in caustic treating at 100° F. with 15° Bé. caustic, equilibrium is reached at 500 parts of methyl mercaptan in the caustic to one part in the naphtha. Likewise, with ethyl mercaptan this ratio is 100:1 and with propyl mercaptan 20:1. Thus, applying these equilibrium values in non-regenerative caustic treating, the caustic is recycled to a level, for example, of 5000 mg. mercaptan S/100 cc. of caustic. Thus, with such a caustic assuming an equilibrium of 100:1 the level of mercaptan sulfur in the feed naphtha cannot be reduced below 50 mg. mercaptan S/100 cc. of naphtha. It has been found that such levels are deleterious in that gum forming reactions are promoted and in gasoline, intake manifold deposits are encountered. Thus, according to the present process the spent caustic is not recycled and thus contains less than about 200, preferably less than about 100 mg. S/100 cc. as mercaptan sulfur.

With respect to the oxidative regeneration prior art process above described or previously mentioned, there the liquid aryl disulfides are not removed and are recycled so that these aryl disulfides are introduced into the naphtha treated. These disulfides are also very deleterious in terms of gum formation and engine deposits previously mentioned.

According to the present invention heavy naphthas, kerosenes, heavier middle distillate fractions or any petroleum stream boiling in the range of about 300° to about 600° F. may be treated. Material boiling in this range contains the thiophenols which can be particularly advantageously removed by the present process. Thus, it should be noted that thiophenols boil at a much higher temperature than the aromatics to which they can be converted. The first thiophenol, for instance, boils at 337° F. while the corresponding aromatic, benzene, boils at 176° F. Therefore, assuming that motor fuel aromatics are preferably limited to C₁₀ or C₁₁ and lighter material, the boiling point of the feed to the present

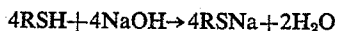
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process and thus of the thiophenols therein is preferably limited to below about 550°-600° F. Thus, the material especially advantageously treated by the present invention boils in the range of from 337° to 600° F.

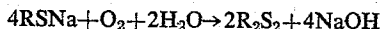
Referring now to the drawing, the hydrocarbons to be treated are supplied through line 1 to caustic treating zone 2. Fresh or regenerated caustic is also supplied to zone 2 through line 3.

The caustics utilized are by definition the hydroxides of alkali or alkaline earth metals or ammonia, sodium hydroxide being preferred. The actual treatment with aqueous caustic is carried out in the conventional manner and is not the essence of this invention, but for completeness the details are supplied herewith.

The hydrocarbons are treated in the liquid phase in zone 2 although a vapor phase treatment can be employed. The conditions are, e.g., a temperature of 70° to 130° F. and caustic concentration of 3° to 50° Bé., 3° to 25° Bé., being preferred and usual. The reaction with the thiophenols is as follows:



The conditions can be adjusted, depending on the type of acids present, the degree of extraction required and the type of operation such as once-thru or recycle mixer-settler operation or countercurrent treating. From zone 2, the combined hydrocarbon caustic stream is passed to settler 4. Here, hydrocarbons are separated overhead through line 5 and spent caustic solution containing the thiophenolates is sent to air oxidation in reactor 7 through line 6. The term "spent caustic solution" as used herein connotes the aqueous caustic solution after treatment of the hydrocarbon. In reactor 7, the spent aqueous caustic solution is oxidized with air to convert the contained thiophenolates to water-insoluble oils. This is done preferably by merely bubbling large amounts of air supplied through line 8 through the caustic solution which violently is agitated by stirrer. Another preferred method of contacting the spent caustic with air is by the use of an eductor. In this type of a reactor, the air is educted into the nozzle by the flow of the high pressure liquid caustic and is violently mixed within the nozzle before it is discharged into the vessel proper. Thus, extremely good contacting is obtained. In either event, the thiophenolates are converted to oily disulfides which are insoluble in the caustic solution and the light alkyl disulfides go overhead with the spent air through line 10. Conditions in the air oxidation step are temperatures of 50°-250° F. preferably 80°-130° F., pressures of 1-10 atmospheres, preferably 1-2 atmospheres, and oxygen utilization of 1-50%, preferably 10-50%. The reaction involved is as follows:



The air oxidized spent caustic is transferred from reactor 7 through line 11 to extractor 12. Naphtha to be used in platinum hydroforming is supplied to extractor 12 through line 13 wherein the aryl disulfides are extracted by the naphtha and the combined stream is passed from the extractor through line 14 to hydrofiner 15. The regenerated caustic stripped of disulfides is recycled to the process through line 19. In hydrofiner 15, the naphtha and extracted aryl disulfides are vaporized and are treated with hydrogen to convert these disulfides and the sulfur entering with the naphtha to H₂S. This H₂S is then removed overhead after suitable cooling in a condenser not shown and the liquid hydrocarbons are sent on to the platinum hydroformer 17 through line 16. Suitable catalysts for use in hydrofining are cobalt molybdate on activated alumina or platinum on activated alumina. Hydrofining conditions are 500° to 800° F., 100 to 1000 p.s.i.g. pressure and a treat gas rate of 100 to 1500 SCF of hydrogen per barrel of feed supplied. From hydrofiner 15, the desulfurized stream is passed through line 16 to platinum hydroformer 17 as is conventional in the art.

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The amount of aryl mercaptans in the hydrocarbon feed stream to be caustic treated may be equivalent to .001 to 1% by weight sulfur. After caustic treating the level of these aryl mercaptans in the hydrocarbon stream will be reduced at least 50%, preferably at least 90% to a level of less than .001 wt. percent sulfur. With reference to other sulfur in the feed (i.e. non mercaptan sulfur) this, of course, not removed in caustic treating. These aryl mercaptans are particularly deleterious in that they form gum and catalyze gum formations reactions in gasolines. In the air oxidation step the amount of thiophenyl sulfur in the feed may amount to 10-1000 mgs. of sulfur per 100 cc. caustic (i.e., copper number). After air oxidation, at least 30%, preferably at least 70% of this thiophenol sulfur will have been converted to aryl disulfides. In the extraction step the amount of platinum hydroformer feed supplied to the extractor would be in the range of 1 to 100 naphtha per vol. caustic. In the extraction step at least 90% of the aryl disulfides will be removed from the caustic before it is recycled to the process. In the hydrofining step at least about 90% of the aryl disulfides will be converted to aromatics, or stated another way, at least about 90% of the aryl disulfide sulfur will be removed.

An indication of the effect of the oxidative regeneration process described on the spent caustic can be seen from the following experimental results obtained at atmospheric pressure and ambient temperatures in a 250 cc. laboratory shaking bomb open to the atmosphere and containing 50 cc. caustic.

(1) Spent caustic containing 4.4 wt. percent of thiophenol sulfur which had been used to treat light catalytic naphtha was found to be reduced 38.6% in thiophenol sulfur after 17.8 hours in the bomb. After 46 hours the reduction in thiophenol sulfur was found to be 93.2%.

(2) Spent caustic containing 2.1 wt. percent of thiophenol sulfur which had been used to treat a heavy catalytic naphtha was found to be reduced 54.4% in thiophenol sulfur after 12.3 hours in the bomb. After 41 hours the reduction in thiophenol sulfur was found to be 91.4%.

(3) Spent caustic containing 0.8 wt. percent of thiophenol sulfur which had been used to treat a light heating oil from catalytic cracking was found to be reduced 50% in thiophenol sulfur after 9.5 hours in the bomb. After 25 hours the reduction in thiophenol sulfur was found to be 75%.

From this data it can be calculated, e.g.

$$\frac{38.6\% (4.4) \text{ wt. percent reduction in sulfur}}{17.8 \text{ hours}}$$

that regardless of the level of the sulfur present, approximately .1 wt. percent sulfur reduction per hour is obtained. Of course, more efficient contacting would be obtained in commercial equipment such as the eductor or the turbomixer described than that obtained in this laboratory shaking bomb and thus considerably less processing time would be required.

It can thus be seen that the efficiency of the present process oxidation step is high.

The present process may be carried out as described in the following example.

Example I

A hydrocarbon stream boiling in the range of 300°-600° F. containing 0.3 wt. percent of sulfur of which 0.03 wt. percent sulfur is in the form of aryl mercaptans is supplied to caustic treater 2. The stream is treated in the ratio of 1 vol. of caustic to 10 vol. of naphtha with 15° Bé. sodium hydroxide at ambient temperature and the treated naphtha is found to contain less than 0.001 wt. percent sulfur in the form of aryl mercaptans and 0.27 wt. percent total sulfur. The spent caustic containing 0.3 wt. percent sulfur thiophenolates is air oxidized at 100° F. in a vessel violently agitated by a stirrer using an amount of air such that 10 wt. percent oxygen utiliza-

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tion is obtained. After air oxidation, the stream contains less than 10 mg. of thiophenol sulfur per 100 cc. caustic. The oxidized spent caustic is extracted with 10 volumes of 100° to 300° F. boiling range naphtha to 1 volume of caustic. This naphtha contains 0.03 wt. percent sulfur. After extraction of the regenerated caustic contains 0.001 wt. percent of aryl disulfide sulfur. The naphtha feed to the hydrofiner contains 0.03 wt. percent sulfur as aryl disulfides. After hydrofining the total sulfur is 0.001 wt. percent. Hydrofining conditions are 650° F., 400 p.s.i.g., 1 v./hr./v., 1500 s.c.f./bbl. of H₂. The catalyst is cobalt molybdate on activated alumina.

The foregoing description contains a limited number of embodiments of the present invention. It will be understood that this invention is not limited thereto since numerous variations are possible without departing from the scope of the following claims.

What is claimed is:

1. The process which comprises caustic treating an aryl mercaptan-containing petroleum stream boiling in the range of about 300° to about 600° F., separating the spent caustic containing extracted mercaptans as thiophenolates from the treated petroleum stream, air oxidizing the spent caustic at 50-250° F., 1-10 atmospheres' pressure, and with 1-50% oxygen utilization, washing the oxidized caustic with 1-100 vols. of naphtha per volume of caustic to extract aryl disulfides, recycling the washed caustic back to the caustic treating step, hydrofining the naphtha containing extracted aryl disulfides, and platinum hydroforming the hydrofined naphtha.

2. The process of claim 1 in which caustic treating is conducted so as to reduce the level of aryl mercaptans in the treated hydrocarbons to below .001 wt. percent sulfur.

3. The process of claim 1 in which caustic treating is conducted so as to remove at least 50% of the aryl mercaptans present in the feed stream.

4. The process of claim 1 in which air oxidation of the spent caustic is conducted so as to obtain at least a 30% conversion of thiophenol sulfur to aryl disulfides.

5. The process of claim 1 in which the oxidized caustic is washed with 1 to 100 volumes of naphtha per volume of caustic.

6. The process of claim 1 in which hydrofining is conducted at such severity as to obtain removal of at least about 90% of the aryl disulfide sulfur.

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7. The process which comprises caustic treating an aryl mercaptan containing petroleum stream boiling in the range of about 300° to about 600° F., separating the spent caustic containing extracted mercaptans as thiophenolates from the treated petroleum stream, air oxidizing the spent caustic at 50-250° F., 1-10 atmospheres pressure, and with 1-50% oxygen utilization, washing the oxidized caustic with 1-100 vols. of naphtha per volume of caustic to extract aryl disulfides, recycling the washed caustic back to the caustic treating step and hydrofining the naphtha containing extracted aryl disulfides.

8. The process which comprises caustic treating an aryl mercaptan-containing petroleum stream boiling in the range of about 300° to about 600° F., separating the spent caustic containing extracted mercaptans as thiophenolates from the treated petroleum stream, air oxidizing the spent caustic at 80-130° F., 1-2 atmosphere pressure, and with 10-50% oxygen utilization, washing the oxidized caustic with 1-100 vols. of naphtha per volume of caustic to extract aryl disulfides, recycling the washed caustic back to the caustic treating step, hydrofining the naphtha containing extracted aryl disulfides, and platinum hydroforming the hydrofined naphtha.

9. The process of claim 8 in which caustic treating is conducted so as to remove at least 90% of the aryl mercaptans present in the feed stream.

10. The process of claim 8 in which air oxidation of the spent caustic is conducted so as to obtain at least a 90% conversion of thiophenolates to aryl disulfides.

11. The process of claim 8 in which hydrofining is conducted at 500° to 800° F., 100 to 1000 p.s.i.g., and a treat gas rate of 100 to 150 s.c.f. of hydrogen per barrel of feed so as to obtain at least about 90% conversion of aryl disulfide sulfur.

12. The process of claim 8 in which the caustic recycle contains less than about 100 milligrams sulfur/100 cc. of caustic as mercaptain sulfur.

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