Jan. 4, 1949. J. A. BOLT 2,457,975

REMOVING MERCAPTANS

Filed March 9, 1944 2 Sheets-Sheet 1

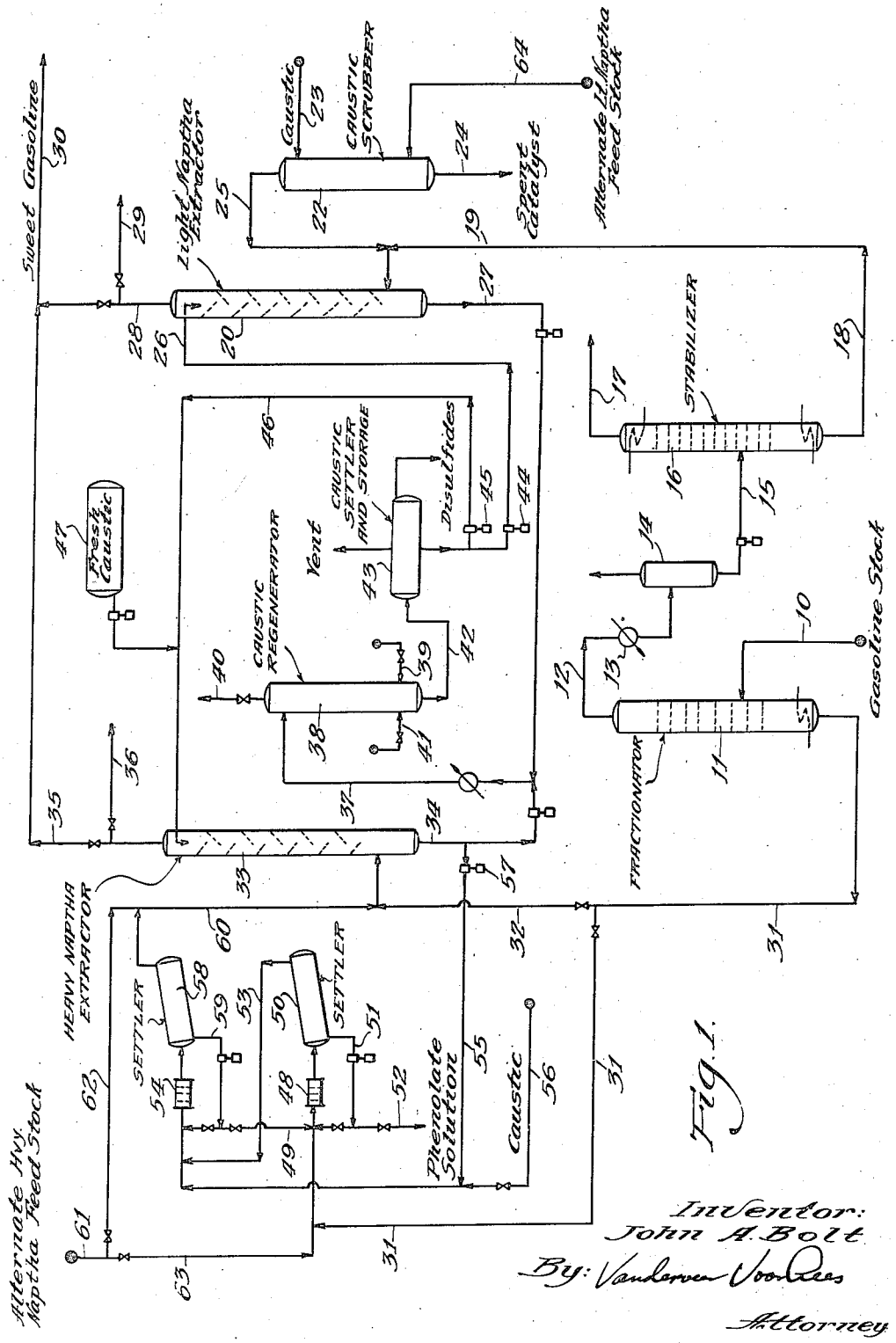


Fig. 1.

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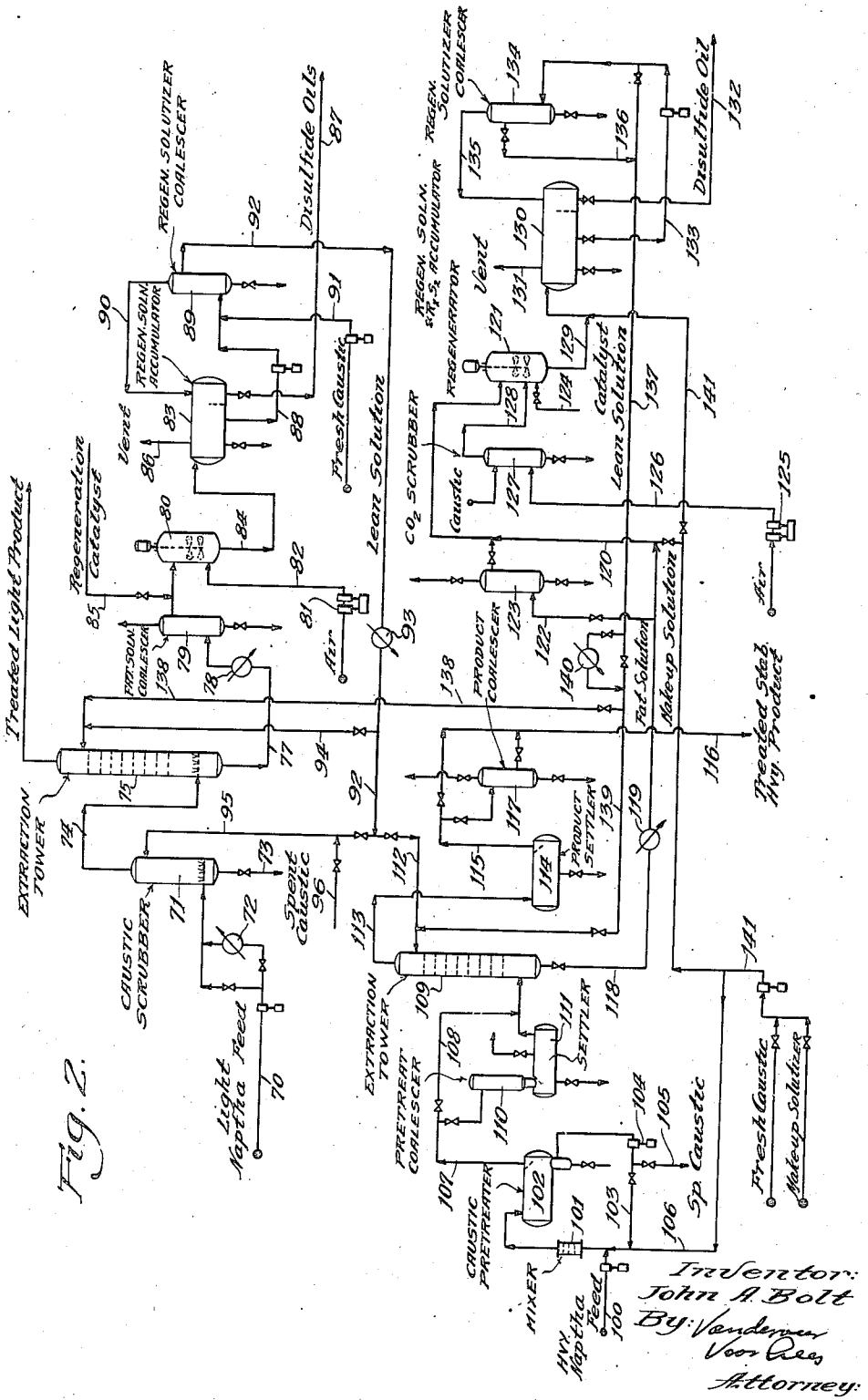


Fig. 2.

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REMOVING MERCAPTANS

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7 Claims. (Cl. 196—32)

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This invention relates to the process of removing mercaptans from sour petroleum distillates such as gasoline and naphthas. In particular, the invention relates to the treatment of petroleum distillates containing, besides mercaptans, certain phenolic constituents having a beneficial effect on maintaining the oxidation stability of the distillate and supplying "solutizer" needed for extraction of mercaptans by caustic solutions.

One of the objects of the invention is to effect sweetening or removal of mercaptans by extraction with caustic alkali solutions while retaining in the treated distillate the desirable phenols. Another object of the invention is to provide a combination process for simultaneously removing mercaptans from two stocks, one of which is substantially free of phenols and incapable of supplying the phenolic solutizer desired in the process. Other objects of the invention will be apparent from the following description:

According to my invention, a stock rich in phenols is extracted with caustic alkali simultaneously with the extraction of a stock poor in phenols and the phenols are transferred from the phenols-rich stock to the phenols-poor stock by dissolving them in the caustic solution which is recycled in both sweetening operations. I have also provided a method for sweetening gasoline containing hydrogen sulfide in which the gasoline is separated into a heavy fraction and a light fraction from which the hydrogen sulfide is removed by stabilization, after which each fraction is processed separately for removal of mercaptans and finally recombined to reconstitute the desired sweet gasoline.

My invention is illustrated by drawings in which Figure 1 shows diagrammatically a simplified apparatus for carrying out the process and Figure 2 shows a modified flow diagram of a plant for treating two stocks. Referring to Figure 1, sour gasoline which may be a cracked gasoline, a straight-run gasoline or a mixture thereof, usually containing hydrogen sulfide, is charged by line 10 to fractionating column 11 wherein the light naphtha fraction is separated by vapor line 12 condensed in condenser 13 leading to receiver 14, whence the light naphtha is withdrawn by line 15 and forced into stabilizing tower 16 wherein fixed gases including propane and hydrogen sulfide are removed by line 17. The stabilized light naphtha is then conducted by lines 18 and 19 to mercaptan extractor 20.

In mercaptan extractor 20, the naphtha flows upward countercurrent to a stream of caustic solution containing dissolved phenols which increase the solubility of mercaptans in the caustic. For this purpose a solution containing about 10 to 30 per cent of caustic soda or caustic potash may be employed having a phenols concentration of about 5 to 30 per cent, preferably about 15 to 20 per cent. The phenols extracted by the caustic from the distillates are mainly cresols and xylenols. The caustic solution is introduced into extractor 20 by line 26 and withdrawn by line 27, while the extracted naphtha is discharged by line 28, whence it may be withdrawn from the process by line 29, or blended with heavy naphtha in line 30 as hereinafter described.

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The heavy naphtha fraction from fractionating tower 11 is conducted by lines 31 and 32 to mercaptan extractor 33 wherein it is intimately contacted countercurrently with a caustic solution containing phenols similar to the caustic solution employed in extractor 20 hereinabove described. Extractors 20 and 23 may be provided with suitable baffles or packing to give effective contact between the liquid phases therein. Obviously, a series of countercurrent stages may be used in lieu of tower extractors. Mercaptans are dissolved by the caustic-phenols solution which is withdrawn at the bottom of the extractor by line 34, while the sweetened naphtha is withdrawn by line 35 and may be discharged from the system by line 36 or blended with the treated light naphtha fraction in line 30 hereinabove described.

The alkali solution withdrawn from extraction towers 20 and 33 is conducted through lines 27, 34, and 37 to caustic regenerator 38, wherein mercaptans are removed and the caustic solution is restored to a condition suitable for the extraction of further quantities of mercaptans from the naphtha streams in extractors 20 and 33. Regenerator 38 may be a baffled or packed tower, an agitated vessel, or a series of vessels arranged for countercurrent treatment of the caustic solution. Various methods of regeneration may be employed. One method is to distil off the mercaptans in a current of steam introduced by line 39, the mercaptans escaping by line 40. Another method is to oxidize the mercaptans at a lower temperature by introducing air or oxygen through line 41. On oxidation the mercaptans are converted to disulfides which are insoluble in the caustic and separate therefrom as an oil. When using this method of regeneration, it is preferred to separate the disulfides from the caustic solution and prevent them from being returned to the naphtha streams in which they are soluble. In this case it is desirable to warm the solution, e. g., to 80–150° F. and to employ an oxidation catalyst

to accelerate the oxidation reaction. For this purpose polyphenols may be used, such as hydroquinone, pyrogallol, catechol, tannic acid, etc., the amount of catalyst being of the order of 0.1 to 2 per cent. Oxides of certain metals may also be used as promoters such as the oxides of lead, copper, nickel, cobalt and vanadium, these oxides being suspended or dissolved in the caustic solution.

After regeneration, the caustic solution is conducted by line 42 to storage 43, whence it is withdrawn as needed by pump 44, discharged through line 26 to the top of extractor 20, and by pump 45 discharged through line 46 to extractor 33. Fresh caustic solution may be added as make-up to the system from supply tank 47.

Where a gasoline stock charged at 10 contains an excessive amount of phenols, as in the case of certain cracked gasolines and heavy naphtha from special crudes, it is sometimes found that the phenols accumulate in the caustic solution to an excessive amount, interfering with liquid separation and requiring that some of the solution be discarded from the system from time to time. In order to avoid this, it is desirable in these cases to pretreat the heavy naphtha fraction rich in phenols to remove part of the phenols therefrom before charging it to the mercaptan extractor 33. The pretreatment is conveniently accomplished by conducting the heavy naphtha through valved line 31 to mixer 48, wherein it is contacted with an alkaline solution introduced by line 49. The alkali is settled in settler 50 and recycled by line 51 back to mixer 48. From time to time excess accumulation of alkali solution is withdrawn from the system by line 52. This solution may be substantially neutral, the alkaline constituents having been largely neutralized by phenols and/or organic acids such as naphthenic acids contained in the heavy naphtha stream charged by line 31. The naphtha is withdrawn from settler 50 by line 53 leading to mixer 54, werein it is contacted with an alkaline stream introduced by line 55. For this purpose fresh caustic soda introduced by line 56 may be employed or, if desired, a portion of the caustic solution may be withdrawn from the mercaptan extraction system by pump 57. The mixture of caustic solution and naphtha from mixer 54 is settled in settler 58, the caustic being recycled to the mixer by line 59, while the naphtha is conducted to the mercaptan extractor by line 60.

If desired, other phenols-containing stocks may be treated in mercaptan extractor 33 simultaneously with the heavy naphtha fraction from fractionator 11 or in lieu thereof. Cracked heavy naphtha from either the thermal or catalytic cracking process may be supplied for this purpose by line 61 and this stock may be charged directly to the extractor 33 by line 62 or it may be given a preliminary alkali treatment to reduce the concentration of phenols and acids while charging it to mixer 48 by line 63. Likewise naphtha stocks poor in phenols may be charged to mercaptan extractor 20 from an independent source, indicated by line 64. Light virgin naphtha, casinghead gasoline, stabilized cracked naphtha, etc., may be treated in this way. Liquid hydrocarbons absorbed from refinery gases or natural gas, commonly known as absorption naphtha, comprised principally of C_4 and C_5 hydrocarbons, may be thus treated. They contain substantially no phenols and, after treatment with the phenol-caustic solution in my process, they absorb sufficient phenols from the solution to exert a beneficial antioxidant effect, thereby protecting the hydrocarbon distillate against gum formation resulting from atmospheric oxidation in storage and handling. Before charging to extractor 20, it is usually desirable to wash with alkali to remove H_2S and some mercaptans as shown in washer 22, caustic being supplied by line 23 and discarded by line 24, the stock being transferred by line 25 to tower 20.

Referring now to Figure 2, a light naphtha stock substantially free of phenols is charged by line 70 to wash tower or caustic scrubber 71, the temperature being regulated by by-passing a portion of the stream through heat exchanger 72. In scrubber 71 any hydrogen sulfide present is absorbed by a suitable alkali solution and discarded by line 73, while the naphtha flows by line 74 to extraction tower 75. Here it is contacted countercurrently with a caustic solution containing a mercaptan solvent or solutizer as hereinabove described. The naphtha substantially free of mercaptans is discharged from the system by line 76 while the fat solution is withdrawn by line 77, forced through heater 78 and coalescer 79, thence into regenerator 80. Coalescer 79 is simply a chamber with suitable contacting surface, e. g., metal wool or other packing, to provide for more complete separation of naphtha and caustic.

A supply of air is injected into regenerator 80 from compressor 81 and line 82, the temperature in the regenator suitably being about 80 to 150° F. as hereinbefore described in connection with Figure 1. A regeneration temperature of 120 to 130° F. is usually satisfactory. The regeneration reaction may be accelerated by operating under pressure, for example, 1 to 10 atmospheres gauge. Mechanical agitation is provided in the regenerator to obtain rapid and intimate contact between air and caustic solution. The regeneration reaction is substantially as hereinbefore described, mercaptans being largely oxidized to disulfides which separate from the caustic solution and which are subsequently removed in regenerated solution accumulator 83, the caustic being transferred thereto by line 84. Regeneration catalyst, for example, tannin, is introduced by line 85 as needed. Unused air is discarded by vent 86 while disulfides are withdrawn as an oil from settler 83 by line 87.

Regenerated caustic solution passes by line 88 to coalescer 89 where entrained disulfides are removed by line 90 and returned to the accumulator 83. Fresh caustic may be added as make-up to the system by line 91. The regenerated lean caustic solution now passes by line 92 through cooler 93 and line 94 back to the extraction tower 75 for the treatment of further quantities of naphtha. If it is desired to discard a portion of the caustic solution from the system for any reason, it may be passed by line 95 to scrubber 71 where the unused alkali content may be exhausted before discarding through line 73. Otherwise fresh caustic solution supplied by line 96 may be used for the operation of scrubber 71.

Simultaneously with the operation just described, the heavy naphtha feed stock containing phenols, particularly cresols and xylenols, is charged by line 100 through mixer 101 and thence to settler 102. In mixer 101 it is intimately contacted with a caustic alkali solution, e. g., caustic soda supplied by line 103 and recycled from the bottom of settler 102 by pump 104. The purpose of the pretreatment is, as hereinabove indicated, to remove from the heavy naphtha excess amounts of phenolic substances which would oth-

erwise accumulate in the subsequent extraction stage. It is satisfactory to operate the caustic pretreater 102 in a semi-continuous fashion, withdrawing a part of the caustic solution at intervals through line 105 when the free alkali content becomes quite low and recharging make-up to the pretreater by line 106. Washed naphtha then passes by lines 107 and 108 to extraction tower 109 or, if necessary, entrained caustic solution from the pretreater may be more effectively separated by diverting through pretreat coalescer 110 and settler 111.

In extraction tower 109 the heavy naphtha stream flows upwardly countercurrent to a stream of regenerated caustic-phenols solution supplied by lines 92 and 112. The extracted naphtha flows from the top of tower 109 by line 113 leading to settler 114 and thence by line 115 to product line 116. If necessary to remove entrained caustic solution or solutizer solution, the stream may be diverted through coalescer 117 as indicated in the drawing.

The spent caustic solution from the extractor 109 or so-called "fat solution" is withdrawn by line 118 through heater 119 where it is heated to a suitable regeneration temperature and thence by line 120 to regenerator 121. If desired, the caustic solution may be diverted by line 122 through coalescer 123 to remove entrained naphtha. The operation of regenerator 121 is substantially the same as that of regenerator 80, a suitable regeneration catalyst being introduced as needed by line 124. Air is supplied to regenerator 121 from compressor 125 and line 126 leading to CO_2 scrubber 127 where carbon dioxide is removed by a suitable alkali and thence by line 128 to the regenerator. The regenerated caustic solution is conducted by line 129 to solution accumulator and disulfide separator 130, unused air being vented by line 131 and disulfide oil being withdrawn by line 132. Regenerated caustic solution is conducted by line 133 to coalescer 134 where any entrained disulfides are separated and returned by line 135 to separator 130. The lean caustic solution passes by line 136, 137, 138 and 139 to extraction towers 75 and 109 for the treatment of further amounts of light naphtha and heavy naphtha stocks. If desired, the lean solution may be by-passed through cooler 140 to assist in maintaining the temperature of the extractors at about room temperature or below, e. g., from 30 to 80° F., the extraction efficiency being greater at the lower temperature. Fresh caustic and make-up solutizer, if needed, can be supplied to the system by line 141 from which they are introduced to the regenerator 121 or to the caustic accumulator 130.

In the operation of this system regenerated caustic solution from accumulator 130 may be continuously or intermittently charged to extraction tower 75 while the regenerated caustic solution from accumulator 83 may be similarly transferred to extraction tower 109. It is preferred to operate the system by recycling the caustic solution between accumulator 83 and extractor 75 simultaneously while recycling caustic solution from accumulator 130 and extractor 109, and then to periodically transfer caustic solution between the light naphtha and the heavy naphtha systems. In this way each system may be accurately controlled with respect to the rate of feeding and amount of regeneration required. In extractor 75 the light naphtha stock containing substantially no phenols absorbs a part of the phenols from the caustic solution charged by line 138,

providing a treated light product containing sufficient phenols to exert a beneficial oxidation stabilizing effect thereon. In extractor 109 exactly the reverse action occurs, the phenols contained in the stock charged accumulating in the caustic solution in an amount sufficient to make up for those phenols lost by absorption in extractor 75. The amount of prewashing in caustic pretreater 102 is regulated either continuously or intermittently to maintain in the system the desired concentration of phenols for effective mercaptan extraction, e. g., about 5% to 30% by volume of the caustic solution employed.

The concentration of phenols employed in the caustic solution in extractor 75 may be the same as that employed in extractor 109 but because the mercaptans contained in the light naphtha are more readily extractable than those contained in the heavy naphtha, I may operate extractor 75 with a lower phenols concentration than extractor 109. For example, extractor 75 may suitably be operated with a caustic solution having a phenols concentration of about 5 to 12 per cent by volume whereas extractor 109 may suitably operate at a phenols concentration of 8 to 25 per cent by volume, the concentration being regulated by the amount of phenols removed in pretreater 102. The addition of solutizer by line 141 is usually practiced only in starting up the system or in case of accidental loss of phenols from the system.

In addition to the transfer of phenols from the heavy stock to the caustic solution to enhance its effectiveness for extracting mercaptans from the light stock, there is also the advantage of accumulating light mercaptans, especially methyl and ethyl mercaptans from the light stock. These light mercaptans are more soluble in the caustic solution than the heavy mercaptans in the stock supplied to extractor 109 and are also less readily oxidized. Consequently, when the caustic solution is regenerated by oxidation, they remain in the caustic solution while the heavier mercaptans are converted to disulfides and eliminated. The light mercaptans remaining in the solution serve to protect the oxidation catalyst from over-oxidation.

The terms "light naptha" and "heavy naptha" used in the claims are employed in the sense usual in the petroleum refining industry to mean low boiling naptha and high boiling naptha, both napthas boiling largely within the gasoline boiling range.

Having thus described my invention what I claim is:

1. The process of removing mercaptans from a soure light naphtha substantially free of phenols which comprises continuously contacting said light naphtha with a caustic alkali solution containing phenols as a solutizer sufficient to substantially increase the solubility of mercaptans therein, thereby extracting mercaptans from said naphtha and simultaneously decreasing the concentration of phenols in said caustic solution owing to the distribution of phenols between said caustic solution and said naphtha, separating said caustic solution from said naphtha, removing mercaptans from said caustic solution thereby regenerating it for further use, recycling said regenerated caustic solution to the naphtha extraction step and controlling the phenols concentration of said caustic solution by contacting a regulated portion of it with a stream of heavy naphtha containing a substantially higher concentration of phenols than said light naphtha

first mentioned, and returning the said portion to the light naphtha contacting cycle.

2. The process of claim 1 wherein mercaptans are removed from said caustic solution by distillation.

3. The process of claim 1 wherein mercaptans are removed from said caustic solution by oxidation to disulfides by the action of molecular oxygen in the presence of an oxidation catalyst thereby converting mercaptans to insoluble disulfides, and said disulfides are separated from said caustic solution before recycling to said extraction step.

4. The process of claim 1 wherein the concentration of phenols in said caustic solution is maintained in the range of about 5 to 12% by volume.

5. The process of removing mercaptans from sour heavy naphtha containing a substantial amount of phenols comprising contacting said heavy naphtha with a caustic solution containing phenols as a solutizer for mercaptans whereby mercaptans and phenols are extracted by said caustic solution, separating said caustic solution from said heavy naphtha, removing mercaptans from said caustic solution thereby regenerating it for further use, recycling the regenerated caustic solution to the extraction step of the process and preventing excessive accumulation of phenols in said caustic solution by contacting a controlled portion thereof with a stream of sour light naphtha substantially free of phenols whereby excess phenols are transferred to said light naphtha as a result of the distribution of phenols between said naphtha and said caustic solution, then returning said portion to the heavy naphtha contacting cycle.

6. The process of claim 5 wherein the said heavy naphtha is subjected to a preliminary alkali extraction treatment to remove part of the phenols and assist in controlling the phenols concentration of said caustic solution.

7. The process of claim 5 wherein the concentration of phenols in said caustic solution is maintained in the range of about 8 to 25% by volume.

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