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PROCESS FOR THE REMOVAL OF MERCAPTANS FROM PETROLEUM DISTILLATES WITH AN AQUEOUS ALKALINE REAGENT CONTAINING LIGNIN AND THE REGENERATION OF THE SPENT ALKALINE REAGENT

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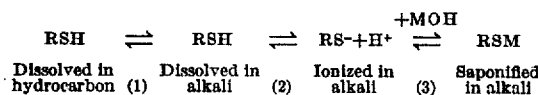
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This invention relates to the treatment of hydrocarbons to remove sulfur constituents normally present, and has specific reference to the removal of mercaptans from petroleum distillates.

The treatment of petroleum distillates, such as gasoline, to remove sulfur compounds stems from the objectionable character of such compounds, particularly from the standpoint of odor. It is desirable to "sweeten" the distillate by removal of sulfur constituents in the nature of free sulfur, hydrogen sulfide, mercaptans and thio compounds either by conversion to less objectionable sulfur-containing compounds, or by actual removal from the petroleum distillate.

It has long been known that sulfur compounds can be extracted from a hydrocarbon distillate to a great extent by washing with an aqueous solution of alkali, such as caustic soda. The more acidic compounds such as hydrogen sulfide go into solution readily, and their removal presents little problem.

Petroleum distillates commonly contain mercaptans in concentrations of from 0.001 to 0.1%, expressed as weight percent of mercaptan sulfur. The mercaptans are weakly acidic, and are often only partially removed by the alkali wash, so that the amount of mercaptans remaining present in the petroleum distillate is above the critical limit for a so-called "sweet" gasoline. This may be explained by the following equilibrium equation of mercaptans in a hydrocarbon distillate treated with an aqueous alkali solution:



It will be apparent that the concentration of mercaptans in the hydrocarbon phase can be kept at a desired low level if the equilibrium (1) is shifted by rendering the mercaptans more soluble in the alkali phase, or by maintaining a low concentration of mercaptans (either ionized or as mercaptides) in the alkali phase.

It has been proposed heretofore to facilitate mercaptan removal from hydrocarbon distillates by the addition of compounds to the alkali solution which renders the mercaptans more soluble therein, and then removing the dissolved mercaptans when the alkali solution is "spent" or

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has absorbed mercaptans to an extent that its mercaptan-removing action is lessened. The latter has been accomplished, for example, by stripping the mercaptans from the spent alkali solution with steam, by treating the alkali solution with a solution of elemental sulfur or polysulfides, by oxidizing the mercaptans with air, and by other known methods of mercaptan separation. The rate of oxidation of mercaptans in spent alkali solutions by treatment with air can be accelerated by adding suitable catalysts to the solution. Metallic oxidation catalysts and tannic acid have been proposed for this purpose.

In accordance with the present invention, it has been discovered that mercaptan reduction in hydrocarbons is effectively increased by using lignin in the aqueous alkali solution that is used to treat the hydrocarbon distillate, the alkali being treated with oxygen or an oxygen containing gas, such as air, at some stage during the process.

The process may be a single stage process, i. e., the hydrocarbons may be treated with the lignin-containing alkali in the presence of oxygen. The presence of the lignin assists in causing the solution of mercaptans in the caustic shifting equilibrium (1) to the right. The presence of the lignin also assists the oxygen in converting mercaptides to oxidation products, further shifting equilibrium (2) and (3) to the right. Generally the process is carried out in two steps in a commercial operation in which the lignin-containing caustic is contacted with the mercaptan-containing hydrocarbon, and the mercaptan-containing and lignin-containing caustic is treated with oxygen to convert the mercaptans to oxidation products. The two-step process is preferred and will be referred to hereinafter in describing the invention.

The hydrocarbon material treated may be any containing mercaptans. Generally they are from petroleum sources and the materials most commonly treated are distillates, such as naphthas, gasoline, kerosene, etc.

Lignin is readily available as by-products of processes involving the separation of cellulosic from non-cellulosic substances, such as the waste liquors from chemical wood pulping processes.

In practicing the present invention, waste liquors containing lignin may be added to the

aqueous alkali solution directly, or the lignin content may be isolated from the waste liquors by acid precipitation and then added to the caustic solution. Lignin derivatives, such as the disodium salt or other alkali metal salts, may be employed satisfactorily. Standardized grades of lignin are presently available commercially and it may be desirable to employ lignin of a uniform reproducible grade in carrying out the present invention.

The alkali solution to be used may be any of those normally employed for such purposes, such as caustic soda, caustic potash, alkali metal carbonates, and other equivalent alkali compounds. The concentration of the caustic may be any concentration which will remove mercaptans to the desired extent, the preferred concentration being between 5° Bé. to 25° Bé. (about 3 to 20%), the optimum strength being 10 to 15% in aqueous solution.

The lignin constituent may be employed in an amount sufficient to facilitate mercaptan removal, concentrations of 0.5 to 10% being suitable, and amounts of 2 to 4% by weight of the caustic solution being optimum.

In carrying out the method of the present invention, it is preferred to prewash the hydrocarbon distillate with caustic to remove the more readily removable sulfur constituents, such as free sulfur and hydrogen sulfide, thus avoiding undue sulfur contamination of the caustic containing lignin, employed in the separation of the mercaptans. The mercaptan extraction is effected at temperatures at which the mercaptans pass readily to the caustic phase, temperatures between 50° F. and 200° F. being preferred and best results being obtained with a temperature approximating 100° F.

The mercaptan extraction with aqueous alkali solution, in a two-step operation, may be accomplished in any known way. In practice, it has been found desirable to employ sufficient caustic to extract the mercaptans to the desired extent, for example, 10 to 1000 volumes of caustic with 100 volumes of hydrocarbon distillate, carrying the liquids through a single stage or a counter current multi-stage extraction process, as desired, to effect removal of the mercaptans from the hydrocarbon distillate.

Suitable additives to aid in solution of the mercaptans in the caustic, other than the lignin, may be employed. It has been found that advantageous results are obtained by allowing natural cresol and xylol, components normally present in the hydrocarbon, to build up in concentration in the caustic.

Oxidation of the mercaptans in the spent caustic containing the lignin may be accomplished in any known manner, such as by passing oxygen or an oxygen-containing gas through the caustic solution. Advantageous results may be obtained by use of superatmospheric pressures, although the advantages of the invention are not limited to employment of this expedient. Pressures from atmospheric to 250 lbs. sq. in. have been employed satisfactorily.

The temperature at which the mercaptan oxidation step may be carried out should be such as to accomplish removal of the mercaptans and a temperature of between 50° F. and 200° F. is satisfactory, desirable results being obtained with a temperature of 125° F.

The following experimental data substantiates the effectiveness of lignin to facilitate the removal of mercaptans from the caustic. In carrying out

the experiments, "Indulin A" is a commercially available lignin product obtained by acidifying the waste liquor from a sulfate and soda paper pulp process, whereas "Indulin C" is the disodium derivative of "Indulin A."

[All values in grams]

Lignin Additive in 15% NaOH	Mercaptan Sulfur per Liter of Caustic		
	Initial Mercaptan Conc.	Mercaptan Conc. After 18 Min. Treatment with Air	Oxidation Rate Per Min.
None	8.3	4.2	.27
4% "Indulin A"	8.3	1.3	.45
4% "Indulin C"	8.3	0.0	.55
None	1.1	.7	.027
4% "Indulin C"	1.1	.18	.062

From the above results it will be seen that the caustic which contains lignin may be regenerated by the removal of mercaptans or mercaptides therefrom much more readily than can the caustic which does not contain lignin.

The following experimental data show the effectiveness of lignin in an alkali solution for facilitating the removal of mercaptans from gasoline, using 100 volumes of gasoline which was shaken with 25 volumes of 15% sodium hydroxide solution in an inert atmosphere. The results are shown in the following table:

Lignin Additive in 15% NaOH	Mercaptan Sulfur in Hydrocarbon Distillates	
	Initial Mercaptan Conc.	Mercaptan Conc. After Caustic Extraction
None	Per cent 0.10	Per cent 0.075
5% "Indulin C"	0.10	0.041

The above data show the effectiveness of lignin in facilitating the action of the caustic in removing mercaptans from a hydrocarbon distillate such as gasoline.

It is not intended that the process of the present invention be limited to certain conditions of temperature and pressure hereinbefore described, for the many variations possible in carrying out the invention will be apparent to those skilled in the art.

We claim:

1. In a method of improving hydrocarbons the step of contacting a mercaptan-containing hydrocarbon distillate in the liquid phase with an aqueous alkaline reagent having lignin dissolved therein.

2. In a method of improving hydrocarbons the step of contacting a mercaptan-containing hydrocarbon distillate in the liquid phase with an aqueous alkaline reagent having lignin dissolved therein in the presence of oxygen.

3. In a method of improving mercaptan-containing hydrocarbon distillate in liquid phase by treating the same with an aqueous alkaline reagent, the step of contacting a mercaptan-containing aqueous alkaline reagent with oxygen in the presence of lignin dissolved therein, whereby the aqueous alkaline reagent may be recycled for reuse in further treating said hydrocarbon.

4. In a method of improving hydrocarbons the steps of contacting a mercaptan-containing hydrocarbon distillate in the liquid phase with an

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aqueous alkaline reagent having lignin dissolved therein to remove mercaptans from the hydrocarbon, and treating the mercaptan-containing and lignin-containing alkaline reagent with oxygen to remove mercaptans from the reagent, whereby the aqueous alkaline treating reagent may be recycled to the hydrocarbon treating step.

5. In a method of improving hydrocarbons the steps of contacting a mercaptan-containing hydrocarbon distillate in the liquid phase with an aqueous alkaline reagent having lignin dissolved therein, separating the hydrocarbon from the alkaline reagent containing the mercaptan, to remove mercaptans from the hydrocarbon, and treating the mercaptan-containing and lignin-containing alkaline reagent with oxygen to remove mercaptans from the reagent, said lignin having been obtained from a sulfate and soda pulp process, whereby the aqueous alkaline treating reagent may be recycled to the hydrocarbon treating step.

6. In a method of improving hydrocarbons the steps of contacting a mercaptan-containing hydrocarbon with an aqueous caustic solution having lignin dissolved therein, separating the hydrocarbon from the caustic solution containing the mercaptan, to remove mercaptans from the hydrocarbon, and treating the mercaptan-containing and lignin-containing caustic solution with oxygen to remove mercaptans from the reagent, said lignin having been obtained from a sulfate and soda pulp process, whereby the aqueous alkaline treating reagent may be recycled to the hydrocarbon treating step.

7. In a method of improving hydrocarbons containing sulfur compounds, comprising contacting a hydrocarbon distillate in the liquid phase with a first alkaline solution to remove free sulfur and hydrogen sulfide constituents normally present, and contacting the distillate with a second aqueous alkaline solution having lignin dissolved therein, said lignin having been obtained from a sulfate and soda pulp process.

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8. In a method of improving hydrocarbons the step of contacting a mercaptan-containing hydrocarbon distillate in the liquid phase with an aqueous alkaline reagent having lignin dissolved therein, said lignin having been obtained from a sulfate and soda paper pulp process.

9. In a method of improving hydrocarbons the step of contacting a mercaptan-containing hydrocarbon distillate in the liquid phase with an aqueous alkaline reagent having lignin dissolved therein, in the presence of oxygen, said lignin having been obtained from a sulfate and soda paper pulp process.

10. In a method of improving mercaptan-containing hydrocarbon distillate in liquid phase by treating the same with an aqueous alkaline reagent, the step of contacting a mercaptan-containing aqueous alkaline reagent with oxygen in the presence of lignin dissolved therein, said lignin having been obtained from a sulfate and soda paper pulp process, whereby the aqueous alkaline reagent may be recycled for reuse in further treating said hydrocarbon.

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