The present invention relates, generically to a novel and improved method of desulphurization. More specifically, it deals with the removal of mercaptans from petroleum oils, liquefied petroleum gas, or the like.

A primary object of the invention is the elimination of mercaptans from mercaptan-bearing material by means of a solvent thereof, together with the subsequent regeneration of the solvent from the resultant mercaptide-saturated solution, whereby repeated use may be made of the same solvent.

A further object of the present invention is the provision of a continuous process for the removal of mercaptans from petroleum distillates or the like, including the step of oxidizing the mercaptides formed in the washing material, whereby the latter is freed therefrom and is adapted for re-use to remove additional mercaptans.

Other objects of the invention will become apparent from the detailed disclosure of the invention hereinafter set forth.

It is well known that sulphur compounds are present in practically all unrefined petroleum distillates and, also, that in many cases the sulphur content is so high that the petroleum product must be subjected to severe refining methods in order to reduce the sulphur content to specifications. Strong sulphuric acid is generally used for this purpose, but there are certain inherent objections to this method, particularly in the treatment of cracked distillates, which entails enormous losses of unsaturated hydrocarbons due to polymerization, and the consequent increase of the knocking tendency of the petroleum oil. Other methods have been proposed but none is in general use at the present time.

It is known, also, that the sulphur compounds found in petroleum distillates consist of hydrocarbon sulphide, mercaptans, alkyl sulphides, alkyl disulphides, and cyclic sulphur compounds. Of those named hydrogen sulphide is removed by an alkaline wash during the refining of the oil. Mercaptans are usually converted by some oxidation method to the corresponding disulphides, but the sulphur content of the oil is not lowered thereby. The other sulphur compounds are not changed or removed during the usual method of treating distillates.

The present invention provides a simple and efficient process for bodily removing the mercaptans from petroleum oil, gas, or liquefied petroleum gas, whereby the total sulphur content of the petroleum product is lowered by an equivalent amount. The mercaptans in the distillates from certain crudes constitute a relatively large fraction of the total sulphur content of the distillate and in these cases the reduction in the sulphur content is considerable. There are many other cases where it is desired to lower the sulphur content only .01 or .02% and this can also be readily accomplished by our process.

Mercaptans can be partially removed from petroleum naphtha, for example, by simple treatment with sodium hydroxide solution, but the solution soon reaches a more or less steady state of saturation and fails to remove additional quantities of mercaptans. This equilibrium, of course, depends on the distribution coefficients of the mercaptans between the sodium hydroxide and naphtha. The mercaptanes show wide differences in this respect as their molecular weight increases.

In other words, when the sodium hydroxide solution is treated with consecutive portions of mercaptan-bearing oil, it becomes “saturated” with butyl mercaptan long before it is “saturated” with ethyl mercaptan even though the two mercaptans are present in equivalent quantities. Therefore, when a naphtha containing mercaptans is passed through fresh sodium hydroxide, it is noticed that a large fraction of the mercaptans is removed from the first naphtha going through, but that the fraction removed with each successive portion of naphtha decreases rapidly and the sodium hydroxide becomes saturated when only a small fraction of the chemical equivalent of mercaptan has been taken up.

The term “saturated” is used to imply a state of ineffectiveness, i. e., the sodium hydroxide is said to be “saturated” when it will no longer remove a considerable part of the mercaptans present. The sodium hydroxide, however, cannot be thrown away at this point, as the cost thereof is too great.

According to the present invention, a method is provided for regenerating the mercaptide-saturated sodium hydroxide, thus making it possible to use it over and over again. The sodium hydroxide may be used in either a batch or a continuous method, the latter being preferred. It may be commingled with the oil, preferably in counter current relation to the petroleum oil or gas, and the “spent sodium hydroxide” removed to a separate tank for treatment. Free chlorine or a hypochlorite solution may then be added to the spent sodium hydroxide in the amount necessary to oxidize the mercaptides to the corresponding disulphides. This reaction is completed almost instantaneously. The disulphides which are
formed are not soluble in the sodium hydroxide and will separate as a layer to the top of the sodium hydroxide, from which they may be removed by decanting.

In order to get a complete and rapid removal of the disulphides from the sodium hydroxide, the latter is then given a wash with gas oil or the like, the disulphides being very miscible in such hydrocarbon material. The sodium hydroxide is then ready for re-use. The amount of chlorine which is added to the spent caustic depends naturally on the mercaptide content of the sodium hydroxide. Slightly less than the chemical equivalent of chlorine can be added but an excess should be avoided.

The concentration of the sodium hydroxide used in the process may vary over wide limits, although 2 to 5 normal (8 to 20 per cent) is preferred, since the hydroxide is concentrated (and hence mercaptan removal) is greatest in this range.

The entire process can be carried out at ordinary room or plant temperatures since all the reactions proceed rapidly.

Other alkalis such as potassium hydroxide, calcium hydroxide, sodium zincate, etc., may be substituted for the sodium hydroxide.

This process is applicable to any petroleum oil, liquid petroleum gas, or gas containing mercaptans.

The alkyl disulphides can be recovered from the absorbent gas oil by either ordinary distillation or flash evaporation. Large quantities of the disulphides can thus be obtained.

What is claimed and desired to be secured by Letters Patent is:

1. A process for desulphurizing mercaptan-containing petroleum oil, wherein the petroleum oil is subjected to the action of an alkaline wash whereby mercaptans are removed from the oil and mercaptides are formed in the wash, the steps of separating the spent alkaline wash from the petroleum oil, treating the spent wash with a chlorine-yielding oxidizing agent whereby mercaptides contained in the wash are converted into insoluble disulphides, separating the disulphides from the alkaline wash whereby the wash is regenerated, and returning the regenerated wash to the system for re-use.

2. A continuous process for desulphurizing mercaptan-containing petroleum oil, comprising intimate contacting the oil to be desulphurized with a mercaptan-removing aqueous sodium hydroxide wash whereby mercaptans are extracted from the oil and are converted to sodium mercaptides soluble in the wash, separating the mercaptide-containing wash from the oil, oxidizing the mercaptides in the wash to the corresponding disulphides by the addition of a chlorine-yielding oxidizing agent in an amount substantially equivalent to the mercaptide concentration in the wash, separating the disulphides from the wash whereby the wash is regenerated, and returning the regenerated sodium hydroxide wash to the system for re-use in further desulphurizing the petroleum oil.

3. A continuous process for desulphurizing mercaptan-containing petroleum oil and the like, comprising contacting the oil with an aqueous alkaline wash whereby mercaptans are extracted from the oil and are converted to mercaptides which are soluble in the wash, separating the mercaptide-containing wash from the oil, oxidizing the mercaptides in the wash to the corresponding disulphides by the addition of a chlorine-yielding oxidizing agent in an amount substantially equivalent to the mercaptide concentration in the wash, separating the disulphides from the wash whereby the wash is regenerated, and returning the regenerated alkaline wash to the system for re-use in the extraction of additional mercaptans from the oil.

4. The method of desulphurizing mercaptan-bearing petroleum oil, comprising contacting the oil with an aqueous caustic wash whereby a portion of the mercaptans are removed from the oil by conversion to mercaptides soluble in the wash, separating the mercaptide-containing wash from the oil, regenerating the wash by adding thereto a chlorine-yielding oxidizing agent in an amount substantially equivalent to the mercaptide concentration in the wash, separating the resultant disulphides from the regenerated caustic wash, and returning the regenerated wash for use in removing additional mercaptans from the oil.

5. The process of desulphurizing mercaptan-bearing petroleum oil, comprising washing the petroleum oil with an aqueous solution of about 8 to 20 per cent sodium hydroxide whereby a portion of the mercaptans are removed from the oil by conversion to mercaptides soluble in the sodium hydroxide solution, separating the mercaptide-containing solution from the oil, reacting the mercaptide-containing solution by adding thereto a chlorine-yielding oxidizing agent while out of contact with the oil, separating the disulphides from the resultant reactivated sodium hydroxide solution, returning the reactivated solution to the system, and repeating the process until the mercaptans are substantially eliminated from the petroleum oil.

6. A continuous process for desulphurizing mercaptan-containing petroleum oil, comprising intimately contacting the oil to be desulphurized with a mercaptan-removing aqueous sodium hydroxide wash whereby mercaptans are extracted from the oil and are converted to sodium mercaptides soluble in the wash, separating the mercaptide-containing wash from the oil, oxidizing the mercaptides in the wash to the corresponding disulphides by the addition of a chlorine-yielding oxidizing agent in an amount substantially equivalent to the mercaptide concentration in the wash, separating the disulphides from the wash whereby the wash is regenerated, and returning the regenerated sodium hydroxide wash to the system for re-use in further desulphurizing the petroleum oil.

7. A continuous process for desulphurizing mercaptan-containing petroleum oil and the like, comprising contacting the oil with an aqueous alkaline wash whereby mercaptans are extracted from the oil and are converted to mercaptides which are soluble in the wash, separating the mercaptide-containing wash from the oil, oxidizing the mercaptides in the wash to the corresponding disulphides by the addition of an alkaline hypochlorite solution in an amount substantially equivalent to the mercaptide concentration in the wash, separating the disulphides from the wash whereby the wash is regenerated, and returning the regenerated alkaline wash to the system for re-use in the extraction of additional mercaptans from the oil.

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