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TREATMENT OF HYDROCARBON DISTILLATES

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This invention concerns a method for treating hydrocarbon distillates and more particularly, a method for sweetening such distillates and removing the elementary sulfur therefrom.

Usually the distillates treated according to the present process are of petroleum origin and of motor fuel boiling range. However, sour distillates of higher than gasoline boiling range, and from other hydrocarbon sources such as, for example, shale oils, coal tars, etc., may also be treated according to the invention.

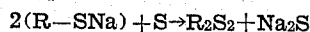
Practically all hydrocarbon distillates require some form of treatment in order to yield marketable products. Light hydrocarbon distillates such as gasoline in particular, generally require sweetening in order to improve the odor and likewise to eliminate possible corrosive properties. Among the sweetening methods which have been used for this purpose is the so-called sodium plumbite or doctor process wherein distillate is contacted with a solution of litharge in sodium hydroxide, followed by the addition of elementary sulfur to bring about decomposition of the lead mercaptides to alkyl di- and poly-sulfides and lead sulfide. In order to obtain a good break, i. e., separation of lead sulfide from the distillate, it is usually necessary to add an excess of elementary sulfur over that required theoretically to accomplish the actual sweetening reaction. Various methods have been proposed for reducing the amount of elementary sulfur necessary, but in the majority of cases doctor sweetened distillate contains so-called "free-sulfur" in solution. When sweetening gasoline it is known that considerable excess sulfur can be added at the time of doctor sweetening without producing a corrosive gasoline. This may sometimes amount to as much as 0.02% without showing a positive corrosion test. Nevertheless, the other desirable properties of both cracked and straight-run gasolines may suffer materially, for example, the color stability, octane number, and susceptibility to tetraethyl lead may be markedly reduced. In the case of cracked gasolines the copper dish gums may be increased, the storage stability as indicated by the oxygen bomb induction period may be shortened and susceptibility to stabilization by means of gum inhibitors may be markedly decreased.

Various methods have been practiced for removing the excess free sulfur from gasoline and other distillates thereby improving the quality of the sweetened product. In cases where the sweetened gasoline is actually corrosive, it has sometimes been the practice to mix it with the

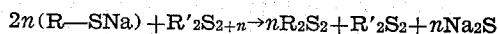
sour gasoline and return it to the sweetening operation and then use greater care in the addition of sulfur. This particular method, however, is of no great importance except in the case of corrosive gasolines, since it does not eliminate the necessity for adding excess sulfur during the process to obtain a good break or provide a means for removing the sulfur substantially completely. The use of alkali metal polysulfides and metallic mercury has been practiced for this purpose.

In one specific embodiment the present invention comprises sweetening hydrocarbon distillate by means of doctor solution and amounts of elementary sulfur in excess of that required to decompose the lead mercaptides, separating the sweetened distillate, contacting it with a solution of an alkali metal hydroxide containing a low-boiling mercaptan in amount equal to 1 to 10 mol per cent of the sodium hydroxide present, separating the distillate, and washing it with a solution of an alkali metal hydroxide.

The excess free sulfur is removed from the distillate by means of the solution of alkali metal mercaptide. Usually the solution contains sufficient low-boiling mercaptan, preferably ethyl, methyl, or propyl mercaptan, to react with from 1 to 10 per cent of the alkali metal hydroxide present in the solution, and ordinarily the amount of mercaptan is of the order of 2.5 and 5 mol per cent of the caustic present. When larger amounts of mercaptans or higher molecular weight mercaptans are used, there is a tendency for part of the mercaptan to pass into the distillate because of hydrolysis of the alkali metal mercaptide. It is preferred to use an alkali metal mercaptide solution of sufficient dilution that none of the mercaptan is extracted by the distillate and/or use a final wash with alkali hydroxide solution. Ordinarily sodium hydroxide is the alkali metal hydroxide used although potassium and lithium hydroxides are also useful. The reactions involved in elimination of the free sulfur are not entirely known but are possibly of the type



or



The latter equation represents a possible reaction when the sulfur is in the form of alkyl polysulfides containing $2+n$ sulfur atoms per molecule. R and R' represent organic groups such as alkyl or aryl groups.

The term free sulfur as used herein is not in-

tended as being altogether synonymous with elementary sulfur. It is doubtful that the sulfur remaining dissolved in the distillate after doctor treatment is in the form of elementary sulfur, but possibly as alkyl-poly-sulfides which have been found to be particularly detrimental to the properties of the distillates.

The process may be applied to distillates which contain free sulfur naturally but which are sweetened by other methods than the doctor process, such as, for example, the hypochlorite method, and the so-called copper sweetening method, neither of which employ elementary sulfur or effect its removal from distillates during sweetening. In these cases as in those mentioned, the sulfur is removed by treating the sweetened gasoline with a solution of alkali metal mercaptide in a solution of an alkali metal hydroxide.

The process is carried out at any temperature suitable for the sodium plumbite sweetening method. This is normally atmospheric temperature, although in certain cases temperatures up to 150° F. have been employed and in some instances, lowered temperatures have been used.

Although the alkaline solution of mercaptide is usually used in aqueous solution, under certain circumstances non-aqueous or mixed non-aqueous solvents, or mixtures of water and non-aqueous solvents may be used. Such solvents may be selected from the group consisting of a mono- or poly-hydroxy alcohol, a mixture of a mono- and a poly-hydroxy alcohol, a glycol, a mixture of a glycol and a mono-hydroxy alcohol, glycerine, a mixture of glycerine and a mono-hydroxy alcohol, and a mixture of a mono-hydroxy alcohol with glycerine and minor amounts of water.

The final treatment with an alkali metal hydroxide solution is not a special feature of the present invention and can be dispensed with in certain cases. The step is used as an added safeguard, since in certain instances if the mercaptide concentration of the sulfur removing solution were too high, the resulting gasoline might possibly be slightly sour and this is corrected by the caustic wash. Likewise small portions of the sodium mercaptide solution may be entrained

with the gasoline, and the caustic wash tends to remove the entrained mercaptide, thus preventing its getting into the finished gasoline tanks.

The following example is given by way of illustration of the process in order to show its usefulness and applicability and should not be construed as limiting it to the exact conditions given therein.

A Mid-Continent cracked gasoline containing 0.02% of free sulfur was washed with a 10% sodium hydroxide solution to which sufficient methyl mercaptan had been added to react with 2.5% of the sodium hydroxide in the solution, whereby the free sulfur was reduced to less than 0.001%. The color dropped on exposure to sunlight from 30+ to 28, while the sample before sulfur removal dropped from 30+ to 17 and became hazy.

In this example the gasoline was washed with a 10% solution of sodium hydroxide following the treatment with the sodium mercaptide solution.

I claim as my invention:

1. A process for sweetening hydrocarbon distillates containing mercaptans which comprises treating the distillate with sodium plumbite solution and a quantity of elementary sulfur in excess of that required to convert the mercaptans to lead mercaptides, then treating the distillate with a solution of an alkali metal hydroxide containing a relatively small amount of a low-boiling mercaptan, the last-named solution being in sufficient amount to remove the excess sulfur from the distillate, and thereafter recovering the distillate without further plumbite treatment.

2. The process as defined in claim 1 further characterized in that the distillate, following the second-mentioned treatment, is washed with alkali metal hydroxide solution.

3. The process as defined in claim 1 further characterized in that the amount of low-boiling mercaptan in the second-mentioned solution is from 1 to 10 mol per cent of the alkali metal hydroxide present in the solution.

4. The process as defined in claim 1 further characterized in that said low-boiling mercaptan comprises methyl mercaptan.

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