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TREATMENT OF CRUDE PETROLEUM

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This invention relates to the treatment of crude petroleum and particularly to an effective procedure for fixing certain sulfur compounds which are present in crude petroleum to prevent formation of deleterious sulfur compounds in the products of distillation thereof.

It is well known that most crude petroleums contain sulfur, some of which may be present as hydrogen sulfide, the remainder being in the form of complex compounds, the exact natures of which are not known. When such crudes are distilled, reactions occur which result in the formation of mercaptans and disulfides. These latter compounds are not generally found in crude petroleums.

Hydrogen sulfide when present is best removed by well known methods such as the use of an alkaline wash. The present invention is not directed to the elimination of hydrogen sulfide which, if present in any substantial amount, should be eliminated prior to application of the method as hereinafter described.

It is the object of the invention to provide a simple and commercially practical procedure for the treatment of crude petroleum to stabilize or otherwise modify sulfur compounds other than hydrogen sulfide which may be present so that upon distillation of the crude the sulfur compounds do not decompose or react to produce mercaptans, disulfides or other deleterious sulfur compounds in the distillates.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification, in which the prefered procedure is set forth.

I have discovered that crude petroleums containing sulfur compounds other than hydrogen sulfide can be successfully treated to avoid the formation of deleterious sulfur compounds such as mercaptans and disulfides in the distillates by adding to the crude petroleum relatively small amounts of oil soluble cupric compounds such as cupric naphthenate, resinate, oleate, stearate, tallate and abietate and the like or mixtures thereof as treating agents. As hereinbefore indicated, hydrogen sulfide, if present, should be removed by an alkaline wash or otherwise before adding the treating agent. After such addition of the treating agent, the crude petroleum containing sulfur in forms other than hydrogen sulfide can be subjected to distillation in the usual manner, and the distillates will be found to be substantially free from hydrogen sulfide, mercaptans, disulfides and other deleterious sulfur compounds which otherwise would be present.

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The treating agents may be added directly to the crude petroleum treated. However, control is effected more readily by first dissolving the treating agent in a solvent such as naphtha, gasoline, kerosene, gas oil, white oil or the like. The solution of the treating agent can then conveniently be added continuously to a stream of crude petroleum in the desired proportions by means of a proportioning pump or other equivalent apparatus.

The treating agent may be added to the crude petroleum at atmospheric temperature. Subsequent heating is limited to the temperature required to effect the desired distillation of the petroleum. Excessive temperatures are not advantageous, and distillation temperatures below 300° C. are preferably employed. The invention does not contemplate the conversion of sulfur compounds to copper sulfide. The high temperature required to effect this reaction should not be employed.

An important and totally unexpected advantage of the procedure as described is that in many cases a very low molecular percentage of copper will fix the sulfur compounds in a crude petroleum. It has long been known that to eliminate mercaptans, etc., from distillates it is necessary to use about one atom of copper for each atom of sulfur. Also, when sulfur compounds are reacted at high temperature with copper compounds to form copper sulfide, it is necessary to have one atom of copper for reaction with each atom of sulfur. Since the atomic weight of sulfur is about one-half that of copper, it has been necessary in the treatment of distillates to use an amount of copper equal to approximately twice the weight of the sulfur present. In the treatment of crude petroleum in accordance with the present invention, I have found it to be possible in many cases to prevent the occurrence of mercaptans and disulfides in the distillates by the use of an amount of copper equal to only about 3.6% by weight of the sulfur present in the crude. It is to be understood, however, that all crudes are not amenable to such treatment with the small proportion of copper mentioned. The variation in the amount of copper required is doubtless dependent upon the type of sulfur compound as well as the amount thereof. In each case, the minimum amount of copper compound may be determined by small scale tests. In general, the amount required is considerably less than the atomic equivalent of the sulfur present in the crude petroleum.

The following samples will serve to illustrate the preferred procedure:

Example I

504 grams of crude petroleum containing 0.3% by weight total sulfur were placed in a suitable distilling flask with a solution of cupric naphthenate in Nujol containing the equivalent of 0.053 gram of copper. This weight of copper was 3.5% of the sulfur in the crude petroleum. The mixture was heated and distilled in the usual manner. The distillate was collected in two fractions having end point temperatures comparable to those of gasoline and kerosene. Each fraction was tested qualitatively for the presence of hydrogen sulfide, mercaptans and disulfides. The first fraction, boiling point 38–190° C., and the second fraction, boiling point 190–240° C., were both free from hydrogen sulfide, mercaptans and disulfides.

Example II

500 grams of another crude petroleum containing 2.28% by weight total sulfur and a solution of cupric naphthenate in Nujol containing the eqivalent of 2.85 grams of copper were distilled similarly. The weight of copper used here was 25% of the weight of sulfur present in the crude petroleum. The first fraction, boiling point 42–190° C., contained no hydrogen sulfide, mercaptans or disulfides. The second fraction, boiling point 190–220° C., contained no mercaptans or disulfides, but traces of hydrogen sulfide were present.

Both of the crude oils mentioned were also distilled without the addition of any treating agent. Distillates at the temperatures mentioned in the preceding example contained hydrogen sulfide, mercaptans and disulfides. It is evident, therefore, that the treatment of the crude petroleum in the manner specified stabilized or otherwise modified the sulfur present therein so that upon distillation it was not carried over into the distillates in the forms in which sulfur usually appears therein. It is also evident from the examples that less than atomic ratios of copper are required in the treatment of crude petroleum in order to eliminate the undesirable sulfur compounds in the distillates.

Various changes may be made in the details of procedure and in the proportions of the treating agents employed without departing from the invention or sacrificing the advantages thereof.

I claim:

1. A method of treating sulfur-containing crude petroleum to prevent formation of deleterious sulfur compounds in distillates subsequently obtained therefrom, which comprises adding to the sulfur-containing crude petroleum an oil-soluble cupric compound in amount such that the copper content thereof is less than the atomic equivalent of the sulfur present in the crude petroleum to which the cupric compound has been added, and heating the crude petroleum containing the cupric compound to temperatures necessary to effect distillation of volatile fractions, but below that temperature at which substantial conversion of the sulfur compounds to copper sulfide will take place.

2. The method of treating sulfur-containing crude petroleum to prevent formation of deleterious sulfur compounds in distillates subsequently obtained therefrom, which comprises adding to the sulfur-containing crude petroleum an oil-soluble cupric compound in amount such that the copper content thereof is between about 3.5% and 25% of the weight of the sulfur present in the crude petroleum to which the cupric compound has been added and heating the crude petroleum containing the cupric compound to temperatures necessary to effect distillation of volatile fractions but below that temperature at which any substantial amounts of copper sulfide will be formed.

3. The method of treating sulfur-containing crude petroleum to prevent formation of deleterious sulfur compounds in distillates subsequently obtained therefrom, which comprises adding to the sulfur-containing crude petroleum an oil-soluble cupric compound in amount such that the copper content thereof is between about 3.5% and 25% of the weight of the sulfur present in the crude petroleum to which the cupric compound has been added and heating the crude petroleum containing the cupric compound to temperatures below about 300° C. to effect distillation of volatile fractions whereby any substantial formation of copper sulfide is avoided.

4. The method of treating crude petroleum containing sulfur compounds other than hydrogen sulfide to prevent formation of deleterious sulfur compounds in distillates subsequently obtained therefrom, which comprises adding to the sulfur-containing crude petroleum an oil-soluble cupric compound in amount such that the copper content thereof is less than the atomic equivalent of the sulfur present in the crude petroleum to which the cupric compound has been added and heating the crude petroleum containing the cupric compound to temperatures below about 300° C. to effect distillation of volatile fractions, whereby any substantial formation of copper sulfide is avoided.

5. The method of treating crude petroleum containing sulfur compounds to prevent the formation of deleterious sulfur compounds in distillates subsequently obtained therefrom, which comprises eliminating hydrogen sulfide from the crude petroleum, adding to the sulfur-containing crude petroleum an oil-soluble cupric compound in amount such that the copper content thereof is less than the atomic equivalent of the sulfur present in the crude petroleum to which the cupric compound has been added and heating the crude petroleum containing the cupric compound to temperatures below about 300° C. and below that temperature at which an appreciable amount of copper sulfide will be formed, to effect distillation of volatile fractions.

6. In a method of treating sulfur-containing crude petroleum substantially free of hydrogen sulfide to prevent the formation of deleterious sulfur compounds in distillates subsequently obtained therefrom, which comprises adding to the sulfur-containing crude petroleum cupric naphthenate in amount such that the copper content thereof is less than the atomic equivalent of the sulfur present in the crude petroleum to which the cupric naphthenate has been added and heating the crude petroleum containing the cupric naphthenate to temperatures necessary to effect distillation of volatile fractions, but below that temperature at which an appreciable amount of copper sulfide will be formed.

7. The method of treating sulfur-containing crude petroleum substantially free of hydrogen sulfide to prevent the formation of deleterious sulfur compounds in the distillates subsequently obtained therefrom as set forth in claim 6 in which the cupric compound added to the crude oil is cupric resinate.

8. The method of treating sulfur-containing

crude petroleum substantially free of hydrogen sulfide to prevent the formation of deleterious sulfur compounds in the distillates subsequently obtained therefrom as set forth in claim 6 in which the cupric compound to be added to the crude oil is cupric oleate.

9. In the treatment of sulfur-containing crude petroleum in which an oil-soluble cupric compound is added to the crude petroleum and the crude petroleum with the added cupric compound is distilled to obtain volatile fractions; the improvement in which the amount of the cupric compound in the crude petroleum during the distillation is less than the atomic equivalent of the sulfur present and the temperature of the distillate is maintained below that at which substantial conversion of sulfur to copper sulfide will take place.

10. In the treatment of sulfur-containing crude petroleum in which an oil-soluble cupric compound is added to the crude petroleum and the crude petroleum with the added cupric compound is distilled to obtain volatile fractions; the improvement in which the amount of the cupric compound in the crude petroleum during the distillation is less than the atomic equivalent of the sulfur present and the temperature of the distillate is maintained below about 300° C., whereby substantial conversion of sulfur to copper sulfide is avoided.

11. In the treatment of sulfur-containing crude petroleum in which an oil-soluble cupric compound is added to the crude petroleum and the crude petroleum with the added cupric compound is distilled to obtain volatile fractions; the improvement in which the amount of the cupric compound in the crude petroleum during the distillation is between about 3.5% and 25% of the atomic equivalent of the sulfur present and the temperature of the distillate is maintained below about 300° C., whereby substantial conversion of sulfur to copper sulfide is avoided.

12. In the treatment of sulfur-containing crude petroleum substantially free of hydrogen sulfide in which an oil-soluble cupric compound is added to the crude petroleum and the crude petroleum with the added cupric compound is distilled to obtain volatile fractions; the improvement in which the amount of the cupric compound in the crude petroleum during the distillation is between about 3.5% and 25% of the atomic equivalent of the sulfur present and the temperature of the distillate is maintained below about 300° C., whereby substantial conversion of sulfur to copper sulfide is avoided.

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