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REFINING OF HYDROCARBON OILS

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This invention relates to improvements in the refining of hydrocarbon oils, and contemplates more specifically the desulphurization or removal of objectionable sulphur compounds from petroleum oils. The presence of sulphur compounds even in relatively minor amounts, is objectionable. Extensive research and development work has been carried out recently, directed to the solving of this problem.

This application is a continuation in part of our application Serial No. 432,550, filed March 1, 1930, which latter case is a continuation of application of Serial No. 99,366, filed Apr. 2, 1926.

The present invention is directed to a refining step which will meet this problem and will result in the production of a commercial saleable oil of high character. The particular embodiment of the present invention contemplates the treatment of cracked distillates, although it is to be understood that the invention broadly contemplates the treatment of petroleum oils of any gravity and including crude oil which has not been previously treated.

The invention will be more particularly explained as directed toward the refining of the cracked distillate having a relatively large per cent of olefin and aromatic hydrocarbons.

These cracked distillates in addition to the olefin and aromatic hydrocarbons, contain paraffines and napthenes. It is known at the present time that objectionable sulphur compounds can be substantially removed from these cracked distillates by subjecting the distillates to a very drastic treatment with sulphuric acid. However, in this drastic treatment of cracked distillates, the olefins and aromatics react with the sulphuric acid, particularly the olefins, and are destroyed so far as motor fuel value is concerned. Hence, while accomplishing one desirable object, a very undesirable loss is sustained. Further the destruction of the olefin hydrocarbons is simultaneously accompanied by the destruction of a certain proportion of the sulphuric acid because of the reaction which takes place between these substances, thus necessitating the use of increased and excessive amounts of sulphuric acid.

The present invention is directed to the removal of substantially all of these sulphur compounds without using this drastic treatment. We propose to subject the distillate to the action of liquid sulphur dioxide which dissolves the olefin and aromatic hydrocarbons. It is understood, of course, that the mixture of distillate and liquid sulphur dioxide is agitated for the length of time necessary to thoroughly mix the constituents with each other. After being allowed to settle, it will be found that the liquid sulphur dioxide and dissolved olefin and aromatic hydrocarbons will fall to the bottom, and the mixture will separate into two layers, the paraffines and napthenes comprising the top layer. Care must be taken, of course, not to use an excessive amount of liquid sulphur dioxide, as this may result in dissolving some of the napthenes.

The bottom liquid sulphur dioxide layer is then separated from the layer containing paraffines and napthenes. For the sake of convenience, we will refer to the paraffine and napthene layer as the residue, although it is to be understood that it is in no sense a residue. This residue may then be subjected to a violent or drastic treatment with sulphuric acid followed by an alkali treatment, if desired. It may be pointed out here that the residue is capable of being subjected to a drastic sulphuric acid treatment without suffering losses which would result if the original pressure distillate containing the olefin and aromatic hydrocarbons had been subjected to this drastic treatment. This results in the removal of a substantial quantity of the objectionable sulphur compounds from this residue.

Now referring to the other layer which was removed, the liquid sulphur dioxide may be removed by evaporation and recovered. The aromatic and olefin hydrocarbon constituents are then subjected to a gentle refining action such as small proportions of sulphuric acid followed by an alkali, if desired, and an earthy adsorbent, or any of the usual refining treatments. This latter treatment will sub-

stantially remove the objectionable sulphur compounds from the aromatic and olefin hydrocarbons. The two treated bodies may then combine together again to produce a commercial pressure distillate suitable for use as a motor fuel upon subsequent redistillation and from which has been removed the objectionable sulphur compounds. It is understood, of course, that where we have referred to an alkali, a plumbite solution may be used in addition to the alkali.

It may be found in some cases that the proportions of olefins and aromatics is so high that no separation will take place upon treatment with liquid sulphur dioxide. In such cases, it is proposed to add to said oil light distillate or other oil to decrease the relative proportions of olefins and aromatics so that proper separation will occur.

It has been found further that in some cases it is unnecessary to subject the portions of distillate which remain undissolved by the liquid sulphur dioxide to further treatment, and that the only treatment required following the separation with liquid sulphur dioxide is on the dissolved portion of the oil.

As examples of experimental results obtained the following is cited:

A California cracked distillate was treated with liquid sulphur dioxide, separating the oil into an upper layer, comprising 80% of the distillate treated, and a lower layer, containing 20% of the original oil dissolved in liquid sulphur dioxide. The lower layer was separated from the upper layer and the liquid sulphur dioxide removed by permitting it to vaporize under atmospheric conditions. The remaining sulphur dioxide was removed by treatment with caustic soda. The dissolved portion of the oil was then treated with concentrated sulphuric acid, using an amount equivalent to two pounds per barrel on the original distillate. The sulphur content of the oil thus treated was 0.35. When the original oil was treated with two pounds of sulphuric acid per barrel of distillate, the sulphur content was 0.42%. Treatment according to the process of the present invention thus caused a reduction in sulphur of approximately 20%, which is greater than that by ordinary acid treatment based on the sulphur content of the treated oil. The solution and polymerization losses when the oil was treated by the process of the present invention as described was less than 1%, whereas by ordinary sulphuric acid treatment the losses were greater than 1%.

In another treatment, an upper or undissolved layer corresponding to 75% of the original oil was obtained, and a lower layer corresponding to approximately 25% of the original oil was obtained. The lower layer, or the portion of the oil dissolved in liquid sulphur dioxide, was treated with sulphuric acid in an amount equivalent to approximately six pounds per barrel based on the original oil. Sulphuric acid treatment was applied to the lower layer after freeing it from sulphur dioxide. The percentage of sulphur in the treated oil after blending back the dissolved and undissolved portions was 0.25%. The loss based on the original oil was 2.4%, including polymerization and solution losses. When the original pressure distillate was treated with approximately six pounds of acid per barrel without a preliminary separation with sulphur dioxide, the sulphur content was 0.3% and the percentage loss was 3.2%. A reduction in sulphur content according to the present invention was approximately 20% based on the sulphur content of the original oil when compared with ordinary sulphuric acid treatment, and a total saving of approximately 25% in losses were effected based on the total losses when treating according to the present invention.

Similar improvements may be obtained when treating both layers.

We claim as our invention:

1. A method of refining hydrocarbon distillates containing sulphur and saturated and unsaturated hydrocarbons for the removal of sulphur therefrom which comprises treating the distillate with a quantity of liquid sulphur dioxide sufficient to dissolve said unsaturated hydrocarbons but insufficient to substantially affect said saturated hydrocarbons, separating the resultant solution of unsaturated hydrocarbons in sulphur dioxide from said saturated hydrocarbons, treating the separated saturated hydrocarbons with sulphuric acid to remove objectionable sulphur compounds therefrom, separating the dissolved unsaturated hydrocarbons from the sulphur dioxide solution, and combining the separated unsaturated hydrocarbons with the treated saturated hydrocarbons.

2. A method of refining hydrocarbon distillates containing sulphur and saturated and unsaturated hydrocarbons for the removal of sulphur therefrom which comprises treating the distillate with a quantity of liquid sulphur dioxide sufficient to dissolve said unsaturated hydrocarbons but insufficient to substantially affect said saturated hydrocarbons, separating the resultant solution of unsaturated hydrocarbons in sulphur dioxide from said saturated hydrocarbons, treating the separated saturated hydrocarbons with sulphuric acid to remove objectionable sulphur compounds therefrom, separating the dissolved unsaturated hydrocarbons from the sulphur dioxide solution, separately treating the separated unsaturated hydrocarbons to remove objectionable compounds therefrom, and combining the treated unsaturated hydrocarbons with the treated saturated hydrocarbons.

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