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# UNITED STATES PATENT OFFICE

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## PURIFYING PETROLEUM OILS

No Drawing.

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This invention relates to purifying petroleum products; and it comprises a method of "acid treating" petroleum oils and petroleum products wherein certain acid alkyl sulfates are used in lieu of, or in addition to, sulfuric acid, said acid alkyl sulfates being advantageously materials made by absorbing ethylene and other gaseous olefins from still gases with sulfuric acid; all as more fully 10 hereinafter set forth and as claimed.

All petroleum oils and products, such as paraffin, are "treated" at one stage of manufacture or another with sulfuric acid. Sometimes fuming acid is used and sometimes weaker acid. The sulfuric acid treatment is followed by a washing treatment with alkali. The exact nature of the actions exerted by the sulfuric acid in this treatment are still a controversial matter and are probably different with different oils. The acid however decolorizes the oil, removes sulfur and withdraws some components of the oil; these being the most reactive portions and hence the portions most subject to change.

15 The result is that the oil is stabilized against the action of air, light, etc. To some extent, the action of the acid causes polymerization. Some acid products in the nature of sulfonic acids go into the oil, whence they are withdrawn by the subsequent alkali treatment. All in all, the action of the acid is beneficial but it is accompanied with some loss of oil; and the greater the amount of acid used for a given degree of decolorization, the greater the cost of treatment.

Sometimes, as in the case of cracked products containing considerable proportions of unsaturated compounds, the action of the sulfuric acid causes too great a loss of oil to permit thorough "treatment."

We have found that certain alkyl sulfuric acids, carrying methyl, ethyl or propyl groups, exercise a specific and advantageous action in decolorizing oils; and we have further found that this action can be usefully employed in connection with the ordinary sulfuric acid treatment. Alkyl sulfates suitable for our purposes may be obtained by causing ordinary still gases containing gaseous olefins to react with sulfuric acid; either

with the ordinary concentrated acid or with fuming acid. Still gases coming from stills in which cracking is going forward contain ethylene and propylene as well as smaller quantities of higher olefins, such as propylene and butylene. Sulfuric acid of 1.84 specific gravity reacts readily with propylene (and butylene) but not with ethylene; and if there is any object in so doing, there may be a two-stage acid treatment of the still 55 gas with acid; first with 1.84 acid which will form propyl sulfuric acid and then with fuming acid which will form ethyl sulfuric acid. But we ordinarily use a single treatment with fuming acid forming a mixture of ethyl sulfuric and propyl sulfuric acids as the mixture is adapted to our purposes. Butyl sulfuric acid while not as desirable for our purposes as the other two, may still be used. However the amount of butylene in still gases 60 going through condensers in contact with cool oily distillate is commonly quite small and its presence and the formation of butyl sulfuric acid may be disregarded. Still higher olefins, such as the amylanes, are substantially completely removed by the scrubbing action occurring in the condensers. In gases specially made by exposing oil to a gas making temperature, say, 700° C., the proportion of ethylene and propylene together may rise 65 as high as 50 per cent in an oil-scrubbed gas. If the gas is not scrubbed, it may carry considerable proportions of the higher olefins.

In producing alkyl sulfuric acids from still gases, the gas and acid may be brought 75 into reaction in any ordinary type of scrubbing apparatus. In general it is not worth while seeking any high degree of conversion of the acid into alkyl compounds since we ordinarily use an excess of sulfuric acid in 80 our treating process.

Ethyl sulfuric acid can also be made by the reaction of ordinary ethyl alcohol with sulfuric acid. Methyl sulfuric acid can be made by the reaction of methyl alcohol 85 (methanol) with sulfuric acid.

In using still gases and sulfuric acid to form alkyl sulfates with an incomplete conversion of the sulfuric acid, as is done in the most advantageous embodiment of our in- 100

vention, the preliminary steps of our process, looked at in one way, may be regarded as covering a preliminary subjection of acid to be used in "treating" oil to the action of still gases or oil gas.

We contemplate the use of either the dialkyl sulfates or the mono-alkyl sulfates. Both have been found efficient for our purposes. Dialkyl sulfates containing two alkyls, such as methyl ethyl sulfate, may be used. But where we use the alkyl sulfate in conjunction with sulfuric acid, as we ordinarily do, the use of the di-alkyl sulfates is equivalent to the use of the mono-alkyl sulfates.

On adding a small proportion of any alkyl sulfate to petroleum oil and agitating, two layers are formed. The lower layer consists of the reagent carrying with it most of the color-bearing constituents of the oil, while the upper layer is oil. This oil may carry a little of the alkyl sulfuric acid in solution; the amount being the greater the higher the alkyl. This is one of the reasons for preferring methyl, ethyl and propyl sulfuric acids to their higher homologs. Methyl sulfate and ethyl sulfate do not dissolve to any substantial extent. In the event that any substantial amount of alkyl sulfuric acid remains with the oil, the oil may be steamed to cause hydrolysis. The upper layer of oil can finally be washed with soda as usual.

Di-methyl sulfate and di-ethyl sulfate are but little soluble in petroleum oils and the solubilities of the mono-methyl sulfate and mono-ethyl sulfates are still less. On the other hand, the di-butyl and di-propyl sulfates are considerably more soluble.

In a typical embodiment of our invention, a sample of colored oil was treated with a mixture of 90 per cent di-ethyl sulfate and 10 per cent of concentrated sulfuric acid, 10 per cent of the volume of the oil being used. The oil was better decolorized than by the action of an equivalent amount of sulfuric acid. The color given was approximately No. 2 on the N. P. A. scale. Still better results were obtained with a mixture consisting of 80 per cent sulfuric acid and 20 per cent of ethyl hydrogen sulfate (ethyl sulfuric acid).

Alkyl sulfuric acids, alone or in admixture with sulfuric acid, will produce lighter colored oils than will the same amount of sulfuric acid alone. Good results are also obtained by treating the oil first with alkyl sulfuric acid, alone or in admixture with sulfuric acid, and then following with a treatment with a sulfuric acid alone. The oil obtained by this double treatment is unusually light in color and the loss of oil is not great.

A Venezuela lubricating distillate "treated" with 10 pounds of sulfuric acid per barrel gave a darker product than the same oil treated with 8 pounds of a mixture consisting

of 80 per cent sulfuric acid and 20 per cent ethyl hydrogen sulfate followed by treatment with two pounds of sulfuric acid. The product produced by this double treatment was much lighter than that given by sulfuric acid alone and its stability was as good.

What we claim is:—

1. In the treatment of petroleum oils for decolorization and purification, the process which comprises subjecting such an oil to the action of alkyl hydrogen sulfates; the said alkyl hydrogen sulfates being selected from the lower members of the alkyl series.

2. In the treatment of petroleum oil for decolorization and purification, the process which comprises subjecting such an oil to the action of alkyl hydrogen sulfates in admixture with sulfuric acid; the said alkyl hydrogen sulfates being selected from the lower members of the alkyl series.

3. In the treatment of petroleum oils for decolorization and purification, the process which comprises subjecting such an oil to the action of alkyl sulfates and subsequently treating with sulfuric acid; the said alkyl hydrogen sulfates being selected from the lower members of the alkyl series.

4. In the purification of petroleum oils, the process which comprises treating such an oil with concentrated sulfuric acid containing alkyl sulfuric acids corresponding to the gaseous olefins of still gas resulting from the cracking of hydrocarbon oils.

5. In the purification of petroleum oils, the process which comprises subjecting said oils produced during a cracking step to the action of mixed alkyl hydrogen sulfates resulting from the reaction of still gases and sulfuric acid, the said still gases being produced during said cracking step.

In testimony whereof, we have hereunto affixed our signatures at Pittsburgh, Pennsylvania, this 5th day of April, 1928.

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