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PROCESS OF REFINING MINERAL OILS

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This invention concerns the treatment of mineral oils, such as petroleum distillates and has for its purpose to free them of undesirable constituents and compounds, while at the same time improving their quality as motor fuels by raising their lead susceptibility. Lead susceptibility is that property of gasolines which determines the amount of increase in anti-knock value for a given quantity of tetraethyl lead added. Since more and more emphasis has been placed of late on the anti-knock requirements of motor fuels, and since the process of artificial raising of anti-knock ratings of gasolines through the addition of special compounds, such as tetraethyl lead, is rather expensive, it is of the utmost importance to develop a type of gasolines which either possess high natural anti-knock properties, or have a high lead susceptibility, that is, can be brought up to certain anti-knock rating specifications by the addition of relatively small quantities of said anti-knock compounds. However, gasolines which, like those from sour West Texas crudes have a high initial anti-knock value in comparison with gasolines made from sweet crudes, such as Mid-Continental or Pennsylvanian, also have a lesser lead susceptibility and so require a larger amount of lead than the latter to bring them up still higher in the scale of anti-knock ratings.

It is the purpose of this invention to transform gasolines of comparatively low lead-susceptibility into gasolines of higher susceptibility without appreciably decreasing the initial anti-knock rating of the gasolines so treated. Thus, the use of this method provides a means of manufacturing high-octane gasolines with a reduced consumption of tetraethyl lead. Another advantage of the process is that, while improving the fuel quality of petroleum distillates, it simultaneously provides an efficient and economical way of freeing them of undesirable components, which is especially important in case of gasolines obtained from sour crudes and containing relatively large amounts of sulfur and sulfur compounds, which gasolines, as mentioned have a comparatively low lead-susceptibility.

Many methods were developed in the prior art to desulfurize, deodorize, decolorize and purify petroleum products both in the liquid and in the vapor phase. Some of these methods involve distilling the petroleum oils and passing their vapors in contact with metallic oxides, sometimes mixed with quicklime, so as to remove a considerable portion of the sulfur in the oil. Different temperatures at which this process may be carried out were specified to make the removal of sulfur compounds by the metallic oxides more complete, and in some cases the suggestion was made to follow this desulfurizing process by sulfuric acid and caustic alkali treatments. The sulfuric acid treatment, however, has the drawback of very seriously impairing the lead susceptibility of the distillates, presumably by causing the formation of certain compounds which tend to neutralize or minimize the effect of tetraethyl lead when it is first added to gasoline, and thus causing an effect known as the lead susceptibility lag. Our work was therefore directed to coordinating these two treatments by combining an oxide treatment under certain operating conditions with a sulfuric acid treatment at those particular concentrations at which the sulfuric acid should be used to avoid this disadvantage when supplementing the refining action of the metallic oxides.

The improvement introduced by our invention consists in combining the process of treating oil vapors with iron oxide under suitable temperature conditions and removing undesirable products of reaction by passing the treated vapors through an alkali solution, with the process of treating the condensed oil with sulfuric acid of definite critical concentrations, so as to obtain a final product not only substantially free of sulfur compounds, and possessing markedly improved fuel characteristics, but also in the case of lighter distillates, having a greater lead susceptibility.

Our process can be equally well applied to cracked and to straight run distillates, containing a relatively high percentage of sulfur. While our process can be accomplished by various means and methods, a preferred way of successfully carrying it out will be briefly described here.

The oil vapors to be refined are passed through a refining tower containing finely divided ferric oxide, preferably in the form of iron oxide ore, and maintained at a temperature of about 550° F. or above, and under a superatmospheric pressure, if desired. The vapors may be passed through the tower either in a vertical direction or a lateral direction; it is preferable, however, in

case of vapors tending to form polymers, to pass the vapors downward through the tower. During this contact the hydrogen sulfide and the sulfur compounds in the oil vapors are catalytically acted upon and partly combined with the iron oxide of the packing with the formation of iron sulfides. The time of contact is so regulated as to produce a substantially sweet product, i. e. substantially free of mercaptans, but containing some H_2S which may be readily removed either by fractional condensation of the treated vapors, preferably in the presence of steam, or by passing the vapors through another tower filled with iron oxide, or by washing it out with an alkali solution, such as caustic soda, soda ash solution or milk of lime. The vapors, or their condensate, may then be subjected to a further rectification or fractionation, if desired, and the distillate selected for further treatment is then contacted with sulfuric acid of a concentration preferably not less than about 95% and not more than about 100%. The most efficient concentration for removing the remaining sulfur compounds from the distillates treated in the above described manner appears to be about 98%; lower concentrations usually fail to desulfurize treated distillates, while higher concentrations have a harmful effect on the gasoline, such as the lag in the action of tetraethyl lead mentioned above. From 2.5 to 5 lbs. of sulfuric acid of a concentration of about 98% per barrel of gasoline distillate usually suffice to give the best results, since the use of larger amounts of concentrated acid has undesirable effects similar to those caused by the use of an acid of too high a concentration. It should be noted that a much smaller quantity of acid is required for treating a gasoline that has already passed in contact with iron oxide than for a gasoline not so treated. This is ascribed, at least in part, to certain chemical changes within treated distillates caused by the catalytic action of sulfides of iron, formed in the refining tower as reaction products of oxides of iron and sulfur-bearing compounds of the oil, and tending to transform mercaptans and disulfides into sulfides with evolution of hydrogen sulfide. Since sulfides are much more soluble in sulfuric acid than mercaptans, this catalytic action of the iron sulfides is very important in preparing the oil vapors for the final step of the process. Since natural ferric sulfide, or a ferric sulfide prepared by igneous processes is ineffectual as a catalyst for sweetening of oil, it may be surmised that ferric sulfide and/or other sulfides of iron, are formed in the contact mass in a particularly active state,—an assumption which is further substantiated by the ease with which this sulfide is regenerated to the initial ferric oxide.

This regeneration may be effected in our process by passing steam at a suitable temperature, such as about 550° F. through the contact mass after its activity begins to decrease. The regeneration process is exothermal, and the temperature of the catalytic mass is usually raised by 150° to 200° F. during this operation. Large amounts of hydrogen sulfide are evolved, and also some free sulfur. When the evolution of hydrogen sulfide has stopped, air is blown through the tower, still maintained at a temperature preferably above 500° F., in order to oxidize the ferrous oxide back to the original ferric oxide. It is advantageous to finish the operation by passing steam through for a short time to remove traces of organic acids that may have formed during the process.

The following table shows the results obtained by our process as compared with methods used previously.

Desulfurization, sweetening and lead susceptibility of Hendrick's straight run gasoline

Gasoline	Lead susceptibility tetraethyl, ccs. of lead* required per gallon of gasoline	Sulfur	
		Mercaptans	Total
1. Untreated	4.0	.135	.173
2. Treated with iron oxide only	4.1	.020	.077
3. No. 1 acid treated (5 lbs. of 98% acid/bbl.)	4.6	.090	.122
4. No. 2 acid treated (2½ lbs. of 98% acid/bbl.)	2.4	.005	.011
5. No. 2 acid treated (5 lbs. of 90% acid/bbl.)	4.0	.020	.068
6. Same using 5 lbs. of 80% acid/bbl.	4.0	.020	.077
7. Same using 5 lbs. of 70% acid/bbl.	4.0	.020	.077

* To raise the octane number from 60 to 78 by the C. F. R. research method.

This table shows the desulfurizing and sweetening action of our process, and especially its value with regard to raising the lead susceptibility of fuels. Thus, straight run gasolines treated by our process show a considerable increase in lead susceptibility and require only about half the tetraethyl lead needed by gasolines treated, for example, with sulfuric acid alone, which show the lead-susceptibility lag effect described above. It is also seen that in case of using sulfuric acid of other concentrations than the critical ones, disclosed in this specification, no such favorable results can be obtained.

We claim as our invention:

1. In the process of refining a vaporized straight run gasoline having a relatively low lead susceptibility, the steps of passing the vaporized gasoline through and in contact with finely divided ferric oxide mass maintained at a temperature of the order of 550° F., thereby partly removing sulfur-bearing substances from the gasoline and partly transforming them into compounds more soluble in concentrated sulfuric acid than said substances, condensing the treated vapors, and then treating the condensate with a concentrated sulfuric acid of 95 to 100% concentration, thereby substantially removing the sulfur-bearing compounds and raising the lead susceptibility of the gasoline.

2. In the process of refining a vaporized straight run gasoline having a relatively low lead susceptibility, the steps of passing the vaporized gasoline through and in contact with finely divided ferric oxide mass maintained at a temperature of the order of 550° F., thereby partly removing sulfur-bearing susbtances from the gasoline and partly transforming them into compounds more soluble in concentrated sulfuric acid than said substances, thereafter neutralizing the treated gasoline with an alkali, and then treating the gasoline with a concentrated sulfuric acid of 95 to 100% concentration, thereby substantially removing the sulfur-bearing compounds and raising the lead susceptibility of the gasoline.

3. In the process of refining a straight run gasoline containing sulfur compounds and having a relatively low lead susceptibility, the steps of passing the gasoline in the vaporous state through and in contact with a finely divided ferric oxide mass, maintained at a temperature of the order of 550° F., to remove a portion of the

sulfur bearing compounds from the gasoline and to convert a portion of the ferric oxide to highly active ferric sulfide of greater activity than ferric sulfide formed outside of this process, said highly active sulfide being capable of transforming at the said temperature mercaptans and disulfides to sulfides, condensing the vapors and then treating the condensate with concentrated sulfuric acid of 95 to 100% concentration, thereby substantially removing the sulfur bearing compounds and raising the lead susceptibility of the gasoline.

4. In the process of refining a vaporized straight run gasoline having a relatively low lead susceptibility, the steps of passing the vaporized gasoline through and in contact with finely divided ferric oxide mass maintained at a temperature of the order of 550° F., thereby partly removing sulfur-bearing substances from the gasoline and partly transforming them into compounds more soluble in concentrated sulfuric acid than said substances, condensing the treated vapors, and then treating the condensate with a sulfuric acid of 98% concentration, thereby substantially removing the sulfur-bearing compounds and raising the lead susceptibility of the gasoline.

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