

UNITED STATES PATENT OFFICE

2,314,576

METHOD FOR TREATING OILS

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No Drawing. Application October 15, 1940,
Serial No. 361,257

9 Claims. (Cl. 196—30)

This invention relates to a method for treating oil, and relates more particularly to metallic manganites or permanganites having selective adsorptive properties for sulphur compounds and to a method relating to the use of such compounds in the desulphurization of oils.

The presence of sulphur compounds is frequently regarded as detrimental to the quality of various oils. For example, gasoline produced from sulphur-containing petroleum may contain sulphur compounds which are injurious from the standpoint of obnoxious odor and also from the standpoint of corrosion, particularly as due to the formation of corrosive acids during the process of combustion. Also, the presence of sulphur compounds may tend to reduce the efficacy of anti-knock compounds added to the gasoline. Sulphur compounds also constitute an objectionable constituent in many other types of petroleum products, for instance, kerosene, fuel oils, lubricating oils, and the like.

No completely satisfactory method is available for the selective removal of the sulphur-containing impurities. Many methods, such as the well known sweetening or doctor treatment, make no attempt to remove the sulphur compounds but simply to convert them into less odorous form. When the attempt is made to remove sulphur compounds by treatment with conventional refining agents, such as sulphuric acid, the necessary rigorous treatment is such as to simultaneously result in the degradation of many valuable constituents of the oil. This is particularly true in the case of cracked gasoline which is subject to substantial loss in olefins and other valuable fuel constituents when rigorously treated for sulphur reduction.

It is an object of the present invention to provide a composition adapted to selectively adsorb sulphur-containing compounds and to provide a method for its efficacious use in the desulphurization of oil.

The present invention rests in part on my discovery that manganites and permanganites of metals forming highly insoluble sulphides possess the property of selectively adsorbing sulphur compounds from oils into which such manganites may be brought into contact.

By the term "manganite" I have reference to salts of manganous acid, HMnO_2 , of which the anhydride, Mn_2O_3 , is well known. By the term "permanganite" I have reference to salts of permanganous acid, H_2MnO_3 , corresponding to the anhydride, Mn_2O_4 . It will be noted that in the manganite the manganese is trivalent and that

in permanganite the manganese is tetravalent.

The manganite and permanganite salts may be either simple or complex, depending on the molal ratios of the metal and manganese. For example, I may employ silver manganite, AgMnO_2 , or I may employ poly-manganites having the generic formula $\text{Ag}_2\text{O} \cdot (\text{Mn}_2\text{O}_3)_n$, in which n is a simple integer that can be as high as 10 or more. Similarly, I may employ silver permanganite in the normal form, Ag_2MnO_3 , or in the acid form, AgHMnO_3 , or in the complex poly-permanganite form, $\text{Ag}_2\text{O} \cdot (\text{MnO}_2)_n$, n again being an integer. The terms "manganite" and "permanganite" are deemed generic to the various species, such as the normal, acid and poly salts.

Various methods known to the art may be employed for the direct manufacture of the metallic manganites and permanganites, but I find that the best results are obtained by first synthesizing an alkali metal manganite or permanganite and then converting the alkali metal salt into the desired metallic salt by a process of base exchange such as will presently be described.

The alkali metal manganites and permanganites may be variously produced. For example, it is known that when $\text{Mn}(\text{OH})_2$ is oxidized in the presence of an alkali the brown substance produced contains more or less alkali combined with the MnO_2 in the form of alkali permanganite. Lime permanganites, such as $\text{CaO} \cdot \text{MnO}_2$ and $\text{CaO} \cdot 2\text{MnO}_2$ are produced in the Weldon manganese recovery process for the manufacture of chlorine, and such alkaline earth permanganites may also be used as intermediates in a manner similar to the alkali permanganites. Alkali permanganites are also produced in certain instances during alkaline oxidation with manganate and permanganate.

The known methods for production of alkali manganites are somewhat similar, and may depend upon alkaline hydrolysis of a manganic salt or controlled oxidation or reduction of lower and higher valenced manganese compounds, preferably in alkaline media. A particularly advantageous way to obtain the alkali metal manganite is to fuse a mixture of manganese dioxide and caustic alkali as described in greater length in my copending application entitled "Catalysts and preparation," Serial No. 361,258, filed October 15, 1940.

The alkali metal manganite or permanganite, preferably in powdered form, may be placed in an aqueous solution of a water soluble salt of the metal which it is desired to associate with the manganite or permanganite. Base exchange

rapidly takes place between the solid and liquid phases with the result that the desired metal is fixed by the manganite or permanganite with simultaneous formation of an alkali metal salt in the solution.

Thus, for example, a finely powdered potassium manganite may be stirred into an aqueous solution containing silver nitrate in quantity approximately equivalent to the alkali associated with the manganite. A short period of contact suffices to complete the base exchange and the silver manganite, after washing with water and drying, is in suitable form for its use in desulphurization.

According to the method of preparation, a manganite, permanganite, or mixed manganite and permanganite salt may be obtained. Also, there may frequently be more or less uncombined manganese sesquioxide or dioxide in anhydrous or hydrated form. I may employ all of such mixtures as adsorbents, although in general the most active adsorbents are those which contain a substantial content of the desulphurizing metal, typically silver.

While it may reasonably be assumed that the active silver (or other metallics) constituent associated with the manganese, sesquioxide or dioxide in an insoluble form is actually present as a true manganite or permanganite and properly termed as such, I do not wish to be bound by any theory as to the precise molecular structures involved, and where reference is made to manganite or permanganite salts, I wish only to imply that the metallic oxides and the manganese dioxide or sesquioxide are in some associated form, which form is characterized by its insolubility in water and its properties of selectively adsorbing sulphur compounds as herein described.

For the purpose of adsorbing sulphur the acidic manganese is preferably associated with a metal whose sulphide is highly insoluble, preferably, silver or copper. I find silver to be the best metal to employ, since the silver manganite and permanganite possess such high desulphurizing power as to more than offset any increased cost of reagents.

The process of desulphurization may be illustrated with respect to the specific treatment of gasoline. By contacting a gasoline containing sulphur compounds with an adsorptive agent of the kind described, typically silver manganite or permanganite, I may effect selective adsorption proceeding to the degree of practically complete sulphur removal provided that sufficient of the adsorptive material is employed. For most practical purposes it is sufficient to reduce the sulphur content to within a tolerated or specified limit, and for such purposes a relatively small portion of the adsorptive agent generally suffices.

The adsorption is relatively rapid and in practice may be realized under various conditions. For example, the adsorbent in powdered form may be added to a batch of gasoline and maintained in suspension by agitation until the desired adsorption is complete and then removed suitably by filtration.

Alternatively, the gasoline may be caused to flow as a continuous stream through a bed comprising sulphur adsorptive agents of the type described. For this purpose the adsorptive agent may be best manufactured in forms which permit their aggregation as a relatively porous bed, as by compression into pellets or admixture into granular or porous supporting material.

Frequently it is advantageous to combine the sulphur adsorbent with conventional adsorbents such as clay, fuller's earth, and the like, which are effective primarily on colored compounds and highly unsaturated hydrocarbons. Suitable mixtures may be formed simply by admixture of powdered sulphur adsorbent and granular clay in the dry state. Preferably, the powdered sulphur adsorbent is mixed into wet plastic clay and the resulting mixture is then dried and ground to a suitable size for percolation, contact filtration or the like.

The sulphur adsorbents of the type described may also be employed for vapor phase treatment of the gasoline or other oil. The gasoline may be vaporized and caused to flow through an adsorptive bed comprising the sulphur adsorbent, suitably at a temperature in the neighborhood of the dew point of the vaporous mixture. This aspect of my invention forms a particularly advantageous adjunct to the vapor phase clay treatment of cracked gasoline, in which connection there may be very conveniently employed fuller's earth or similar clay in which the sulphur adsorbent has been previously incorporated, for example, by the wet method described above.

Mercaptans are very readily removed from gasoline by liquid or vapor phase treatments of the kind just described, to give sweet gasoline of undiminished or increased lead susceptibility. In addition by employing more prolonged contact or a greater proportion of the sulphur adsorbent the sulphur content may be reduced to, or below any value normally specified for commercial quality gasoline.

A very important feature of my invention is the regeneration of the spent sulphur adsorbent which in its spent condition comprises a layer of adsorbed sulphur compounds overlying the surface of the adsorbent in such a manner as to mask its further activity. If desired this adsorbed sulphur-containing material may be removed by solvent extraction with a relatively powerful solvent such as aromatic hydrocarbons, alcohols, and the like, but I find a more convenient and economic method of regeneration consists merely in exposing the spent adsorbent to the action of air or other oxygen-containing gases at temperatures sufficient to initiate and maintain the combustion of the sulphur-containing material. The temperatures necessary for this regeneration are insufficient to harm the manganese adsorbent which accordingly may be used over and over again in a cycle involving regeneration of the kind described. Various means normally employed for the roasting and regeneration of spent clays may be used to accomplish regeneration of the sulphur adsorbent as herein described.

It will be understood that the details of the above description are exemplary rather than limiting and it will be obvious to one skilled in the art that various modifications of the described composition and process may be employed without departing from the essence of my invention as defined by the scope of the appended claims.

I claim:

1. In the process for desulphurizing oils the step comprising contacting a sulphur-containing oil with an adsorptive agent containing a compound of an acidic oxide of manganese in which the valence of the manganese is not more than four with a metal whose sulfide is highly insoluble in said oil.

2. In the process of desulphurizing oils the step comprising contacting a sulfur-containing oil with a compound of an acidic oxide of manganese in which the valence of the manganese is not more than four with a metal whose sulfide is highly insoluble in said oil.

3. In the process for desulphurizing oils the step comprising contacting a sulfur-containing oil with a compound of an acidic oxide of manganese in which the valence of the manganese is not more than four with a metal selected from the group consisting of silver and copper.

4. In the process for desulphurizing oils the step comprising contacting a sulfur-containing oil with a compound of an acidic oxide of manganese in which the valence of the manganese is not more than four with silver.

5. In the process for desulphurizing oils the step comprising contacting a sulfur-containing oil with a compound of an acidic oxide of manganese in which the valence of the manganese is not more than four with copper.

6. The method of desulfurizing oils comprising contacting said oil with an adsorptive agent

including a compound of an acidic oxide of manganese in which the valence of the manganese is not more than four with a metal selected from the group consisting of silver and copper, recovering the adsorptive agent charged with sulfur compounds, and regenerating said agent by removing the sulfur.

7. The method of desulfurizing oils comprising contacting said oil with an adsorptive agent including a compound of an acidic oxide of manganese in which the valence of the manganese is not more than four with a metal selected from the group consisting of silver and copper, recovering the adsorptive agent charged with sulfur compounds, regenerating said agent by heating in the presence of an oxygen-containing gas, and employing the regenerated agent to similarly desulfurize further quantities of oil.

8. The process of claim 7 in which the adsorptive agent is silver manganite.

9. The process of claim 7 in which the adsorptive agent is silver permanganite.

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