

## UNITED STATES PATENT OFFICE

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PROCESS OF REMOVING SULPHUR FROM  
MINERAL OIL DISTILLATESEverett C. Hughes, Cleveland, Ohio, assignor to  
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corporation of OhioNo Drawing. Application July 19, 1937,  
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3 Claims. (Cl. 196—32)

This invention relates to the treatment of mineral oil distillates, and more particularly for removal of sulphur; and it is among the objects of the invention to provide a process which is easy of application, and capable of operation with reagent materials readily available and of low cost, and capable of yielding products of highly satisfactory character. Other objects and advantages will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

The mineral oil distillate to be treated, is, in accordance with the invention, subjected to the action of a nascent metal oxide or hydroxide and carbon dioxide. A carbonate decomposable in the treating temperature range is a convenient means of providing such metal compound and carbon dioxide, and the temperature ranges below such as would occasion undesired cracking of the distillate, ordinarily in practice not generally exceeding about 875° F., while the lower limit will be determined by the decomposition activity of the particular carbonate applied, and generally will not be lower than about 300° F. Such carbonates as magnesium carbonate, dolomite and the like are of particular advantage. Other carbonates which can be employed are for instance also manganese carbonate, chromium carbonate, cobalt carbonate, ferrous carbonate, nickel carbonate, zinc carbonate, cadmium carbonate, cuprous carbonate, lead carbonate, basic lead carbonate, sodium acid carbonate, etc. Natural ores or compounds, such as magnesite, siderite, cerusite, hydromagnesite, brucite, or other easily decomposed hydroxides, as  $Mn(OH)_2$ ,  $Pb(OH)_2$ ,  $Al(OH)_3$ ,  $Cu(OH)_2$ ,  $Zn(OH)_2$ , etc. may be employed, or artificially prepared compounds, the former having advantages of direct availability and low cost. In using carbonates it is also of advantage to add steam, this assisting to catalyze and decompose the carbonates. Where conditions permit, I may subject the distillate to be treated, to the action of a mass of the carbonate or bed thereof, the liquid distillate being maintained in contact for the desired time, or distillate vapors may be contacted with the mass. The treating agent may also be put into the distillate in finely divided condition or as a water slurry. As above-indicated, the mixture

is maintained at a temperature below cracking and yet sufficiently high to be within the decomposing temperature range of the carbonate. The time required depends upon the conditions and the efficiency of contact in any given instance, from a fraction of a minute to sixty minutes or more, up to two or three hours. In some cases I may subject the distillate to the action of a mass of the carbonate for a relatively short time, as for instance by flowing the distillate through the mass, the time being for instance 0.1 to 10 minutes, and then the distillate may be washed with a fairly strong caustic alkali solution, such procedure involving a very short total time consumption and facilitating continuous-type operation as well. Operating at the active decomposing temperature range of the carbonate, the latter decomposes and nascent oxide or hydroxide is presented in contact with the distillate, and at the same time carbon dioxide, or steam in the case of hydroxides, is produced, furthering the breaking-down of particles and increasing the intimacy of contact and agitation.

Sufficient pressure may be employed to keep the petroleum distillate in liquid phase during the treatment, as necessary, or the carbonate may be contacted with the vapors, preferably counter-currently. Agitation may be supplied in either case, as desired. The great activity of desulphurizing action in this manner, as contrasted with the action by a metal oxide, is well illustrated for instance in the case of  $MgO$ . Treating a cracking-coil distillate thus with  $MgO$  reduced the total sulphur and mercaptans by only 0.001 per cent. On the other hand, by treating with a nascent oxide and carbon dioxide in similar temperature range, by decomposing magnesite, viz at a temperature of 600° F., the total sulphur was reduced by 0.038. In similar manner, siderite at such temperature reduced the total sulphur by 0.024 per cent and rendered the distillate sweet.

As an example: A raw distillate having total sulphur 0.069 and mercaptan sulphur 0.015, was contacted with magnesite for sixty minutes at a temperature of 600° F. and pressure 300 pounds per square inch. The product contained 0.031 total sulphur and no mercaptan sulphur.

As another example: A distillate having total sulphur 0.069 was treated with siderite for sixty minutes at a temperature of 425° F., and 170 pounds pressure per square inch. The product was sweet, the sulphur being reduced to 0.045.

As another example: A raw distillate having 0.049 total sulphur and 0.013 mercaptan sulphur was passed through a bed of magnesite, the con-

tact time being about two minutes, the temperature being 600° F. and the pressure 80 pounds per square inch. The distillate was then subjected to a wash with a 15° Bé. NaOH solution at atmospheric temperature. The product contained 0.028 total sulphur and no mercaptan sulphur.

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10 Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:

15 1. In a process of removing sulphur from mineral oil distillates, the step of contacting the distillate in liquid condition with magnesium oxide

in nascent form at elevated temperature not below 300° F. nor sufficiently high to vaporize the liquid.

2. In a process of removing sulphur from mineral oil distillates, the step of contacting the distillate in the presence of steam with magnesium oxide in nascent form at elevated temperature not below 300° F. nor sufficiently high to vaporize the liquid. 5

3. In a process of removing sulphur from mineral oil distillates, the steps of passing the distillate through a mass of magnesium oxide in nascent form at elevated temperature not below 300° F. nor sufficiently high to vaporize the liquid, and then contacting the liquid with a caustic alkali solution. 10 15

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