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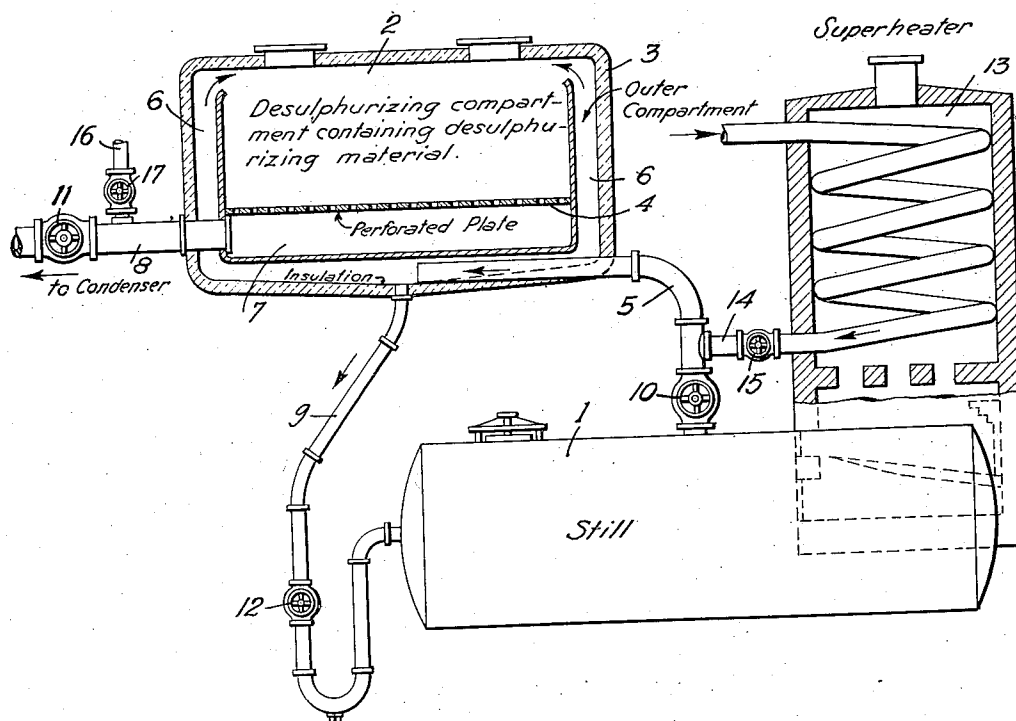
1,622,671

METHOD OF REACTIVATING DESULPHURIZING AGENTS FOR HYDROCARBON OILS

Original Filed April 16, 1924

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Fig. 1.



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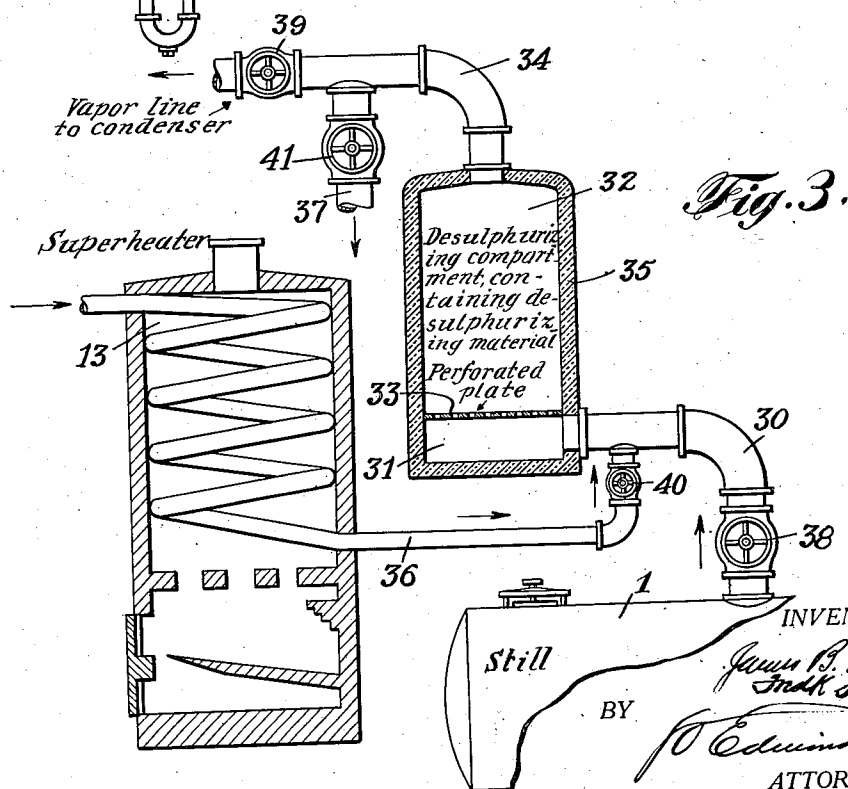
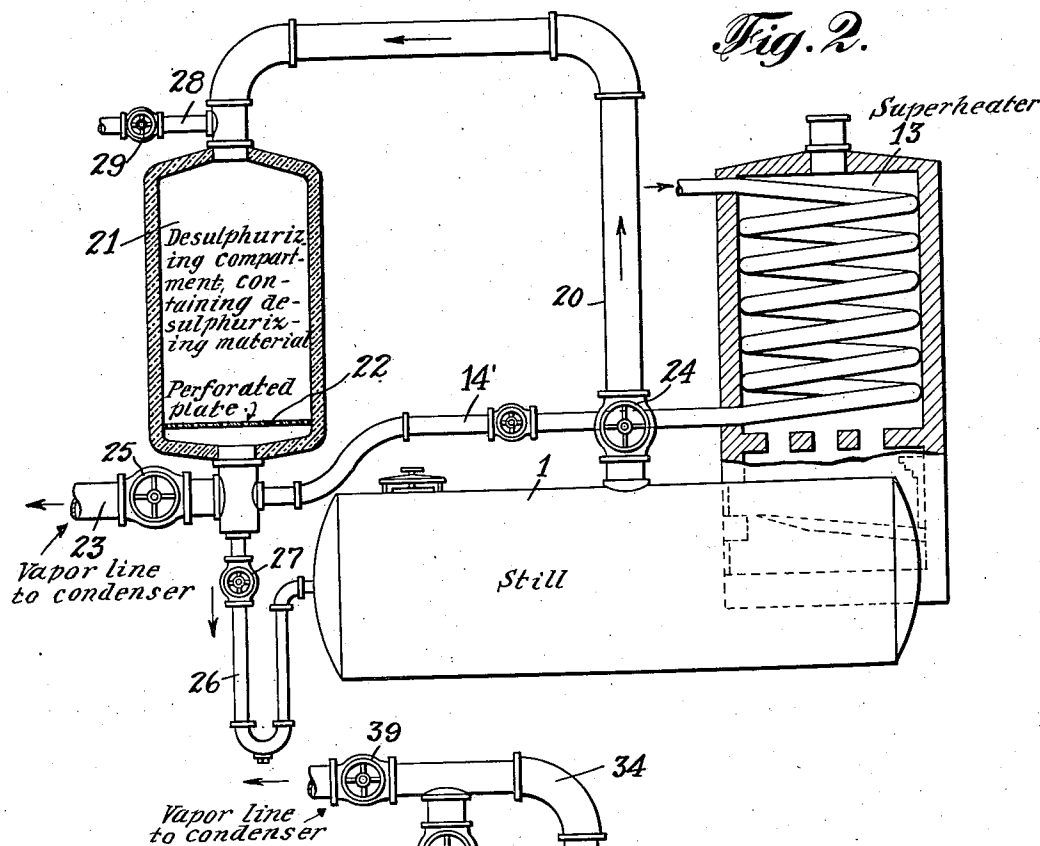
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2 Sheets-Sheet 2



UNITED STATES PATENT OFFICE.

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METHOD OF REACTIVATING DESULPHURIZING AGENTS FOR HYDROCARBON OILS.

Application filed April 16, 1924, Serial No. 706,858. Renewed August 12, 1926.

When certain materials, such as metallic oxides, are used as desulphurizing agents for desulphurizing hydrocarbon oils, their activity becomes impaired after a while on account of taking up sulphur from the treated oil. A process for desulphurizing hydrocarbon oils, using such materials as desulphurizing agents, is disclosed in a copending application filed by James B. Rather, Leslie C. Beard, Jr., and Thomas M. Berry on even date herewith, Serial No. 706,815.

The present invention relates to a method of reactivating, or restoring to their original oxide condition and activity, metallic oxides after their activity has been impaired as a result of their use as desulphurizing agents for hydrocarbon oils.

Prior processes for desulphurizing hydrocarbon oils require desulphurizing materials in particles not larger than 200 mesh, and leave the desulphurizing materials mixed with a considerable amount of the oil residuum, at the end of a run, and in order to reactivate the desulphurizing materials, the oil must be pressed out, leaving a cake of the desulphurizing material which must be burned to remove the sulphur compounds, and must be subsequently ground to 200 mesh before it is suitable to be used in such process for another run. These methods of reactivating the desulphurizing materials have required separate apparatus, such as filters, retorts, grinders, etc., and the removal of the materials to such apparatus for treatment, with consequent losses, expense and delay. After reactivation they must be replaced in the oil desulphurizing apparatus. Much handling and moving about of the materials has been required, as well as cumbersome and expensive apparatus.

The principal object of our invention is to provide a method of reactivating certain metallic oxides after they have been used as desulphurizing agents for desulphurizing hydrocarbon oils, and to provide a method which is safe and simple to follow, which does not require dangerously complicated apparatus, and which may be carried out quickly, inexpensively and efficiently.

A further object of our invention is to provide a method of reactivating desulphurizing materials, such as metallic oxides after use as desulphurizing agents for hydrocarbon oils, which does not require the removal

of the desulphurizing materials from the apparatus in which they are contained while acting as desulphurizing agents for hydrocarbon oils, and which does not require the desulphurizing agents to be moved about or removed to separate apparatus.

A further object of our invention is to provide a process for desulphurizing hydrocarbon oils by means of desulphurizing materials, such as metallic oxides, and to provide a method of reactivating the desulphurizing materials after they have been used in carrying out such process, which process and method may be carried out in the same apparatus without necessitating any handling or removal of the desulphurizing materials, and a further object of our invention is to provide an apparatus adapted for use in carrying out both the process of desulphurizing hydrocarbon oils and the method of reactivating the desulphurizing materials used in the process.

Other objects of our invention will be in part obvious and in part pointed out hereinafter.

The invention accordingly consists in the several steps and the relation to each of the others thereof which will be exemplified in the hereinafter disclosed method, and the scope of the application of which will be indicated in the claims that follow.

In order that a clearer understanding of our invention may be had, attention is hereby directed to the accompanying drawings, forming a part of this application and illustrating diagrammatically certain apparatus adapted for use in carrying out our process for desulphurizing hydrocarbon oils and also in carrying out our method of reactivating the desulphurizing materials used in the oil desulphurizing process. Referring to the drawings, Fig. 1 is a diagrammatic layout of such an apparatus; Fig. 2 is a diagrammatic layout of such an apparatus in a modified form; and Fig. 3 is a diagrammatic layout of such an apparatus in still another form.

Similar reference characters refer to similar parts throughout the several views of the drawings.

With a preferred form of apparatus (Fig. 1) we carry out our process by vaporizing the oil to be treated in a still of conventional design, and conducting the oil vapors

from the still through a conduit 5 into a closed receptacle 2, such as a tower, which comprises a closed outer shell, insulated as at 3, and an inner shell, having its bottom 5 and walls spaced from the outer shell, forming an outer compartment 6 between the shells. The conduit 5 leads to the vapor inlet located between the bottoms of the two shells of the cabinet. Preferably a perforated plate 4 is mounted in the inner shell, and the vapor outlet from the tower is situated between the plate 4 and the bottom of the inner shell and communicates with exit pipe 8 which leads to a suitable condenser. The desulphurizing agents, which may be copper oxide or other metallic oxides, and which are preferably in the form of particles larger than 100 mesh, are supported in a mass on the plate 4 within the inner 20 shell of the tower. The desulphurizing material is preferably substantially dry, and it may or may not be distributed over or mixed with inert material serving as a framework. Such inert material may be 25 fuller's earth, pumice, or any other porous substance.

The oil vapors from the still 1 enter the tower at the conduit 5, flow upward through the compartment 6, then downward through 30 the desulphurizing material in the inner shell, into the space 7 below the plate 4, and out of the tower through the conduit 8, for treatment and disposal in the well known manner. The vapors leaving the tower are 35 in satisfactory desulphurized condition. Preferably, there is a return conduit or pipe 9 leading from the bottom of chamber 6 to the still 1, whereby liquid products, formed by the condensing of the oil vapors or otherwise, are led back into the still. The various conduits may be provided with the usual valves, such as 10, 11 and 12.

For the purpose of revivifying or reactivating the desulphurizing material contained 65 in the tower 2, we provide a superheater 13, of conventional design, which has an outlet pipe 14 communicating with the pipe 5. Pipe 14 has a suitable valve 15, which is normally closed during a run. When it is 70 desired to revivify the desulphurizing agents, it is not necessary to remove these agents from the tower to a separate apparatus, as has been the practice heretofore, but they may be left in the tower and may 75 be reactivated by proper treatment without removal therefrom. When it is desired to carry out this step of the process, the valve 10 of the conduit 5 is closed, as is also the valve 12 of the pipe 9, and the valve 11 of 80 the pipe 8. An exhaust pipe 16 leads from the pipe 8 and has a valve 17, which is normally closed during a run, but which is now open for the reactivating step. Valve 15 is now opened and steam is passed from the 85 superheater into the compartment 6 of the

tower, from which it flows downwardly through the tower and the desulphurizing agents therein, and out at the pipe 16. This flow of steam is continued until the last traces of oil vapor are removed from the 70 tower. Then superheated steam is passed from the superheater through the tower until the temperature of the contents of the tower compartment are about 500 degrees Fahrenheit. Then superheated air at ap- 75 proximately the same temperature is passed from the superheater through the tower. By this process the desulphurizing agents in the tower, which after a run are sulphides, give up their sulphur components in the form of 80 sulphur dioxide, which passes from the tower with the air. After the removal of the sulphur dioxide, the passage of superheated air is continued from the superheater 13 until any reduced copper or other metal 85 is converted to the original condition of the oxide.

The use of superheated steam is not essential, though preferable, and superheated air alone may be used. The superheating of the 90 steam or air, or both, may be accomplished in any suitable manner, either by heating the tower or by heating the steam or air, or both, before they reach the tower.

Referring to Fig. 2, instead of leading oil 95 vapors from a still into the bottom of an outer compartment, such as 6, in a tower 2, as shown in Fig. 1, the oil vapor may be directed through a conduit 20 directly into the top of a closed receptacle 21 so as to 100 flow downwardly through the desulphurizing agents contained therein, and past the perforated plate 22 and out at the outlet pipe 23. Pipe 20 has a valve 24, and pipe 23 has a valve 25. A run-back pipe 26 is 105 adapted to return liquids formed in the tower 21 to the still 1. This pipe has a valve 27. The superheater 13 may have its outlet pipe 14' leading into the bottom of the tower so that superheated steam and air 110 may be passed from the superheater 13 upwardly through the tower 21 and out at the exhaust pipe 28 which leads from the pipe 20. Pipe 28 has a valve 29 which is normally closed during a run. The valve 115 24 of pipe 20 and the valve 25 of pipe 23 and the valve 27 of pipe 26 are all closed during the step of reactivating the desulphurizing material in the tower 21 after a run. The revivifying or reactivating step 120 of the process is carried out in the manner described heretofore by means of steam and air, or air alone, passed from the superheater through the tower until all traces of oil vapor and sulphur dioxide are removed from 125 the tower and the desulphurizing materials are restored to their original condition.

Referring to Fig. 3, instead of passing the oil vapors downwardly through a tower containing the desulphurizing materials, these 130

oil vapors may be passed upwardly through the tower containing such materials. To this end, the apparatus, as shown in Fig. 3, includes a pipe 30 leading from the still 1 into a vapor chamber 31 formed in the bottom of a tower 32 below a suitably mounted perforated plate 33 therein, so that oil vapor may flow from the still upwardly through the desulphurizing agents in the tower and out through the outlet pipe 34 to a suitable condenser. The tower 32 is preferably insulated, as at 35. This apparatus is also adapted to be used to revivify or to reactivate the desulphurizing agents in the tower 32. To this end, the superheater 13, by means of pipe 36, communicates with the conduit 30 and the outlet pipe 34 has an exhaust pipe 37. The steam and air, or air alone is passed upwardly through the tower, first to remove all traces of the oil vapor, and then to produce sulphur dioxide from the copper or other sulphides and to convert any reduced copper or other metal to the original condition of the oxide. The valve 38 of pipe 30 and the valve 39 of pipe 34 are open for a run of oil and are closed during the reactivating step. The valve 40 of pipe 36 and the valve 41 of pipe 37 are closed during a run of oil and are open for the reactivating step.

It will be readily apparent from the above that the process is safe, simple, economical and fast, and may be carried out with a simple apparatus, without requiring mechanical stirrers, and without requiring removal or transference of the desulphurizing material to condition the apparatus for another run.

As many changes could be made in the construction of apparatus described, and as many apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that the matter contained in the above description or shown in the accompanying drawings be interpreted as illustrative and not in a limiting sense.

The above disclosed process for desulphurizing hydrocarbon oils is claimed in an application filed by James B. Rather, Leslie C. Beard, Jr., and Thomas M. Berry on even date herewith, Serial No. 706,815.

What we claim is:—

1. The process of desulphurizing metallic sulphides carrying oil, which includes re-

moving the oil from the sulphides without burning the oil, and then converting the metallic sulphides to metallic oxides.

2. The process of desulphurizing metallic sulphides carrying oil, as obtained by subjecting metallic oxides to sulphurous oil vapors, which consists of first removing the oil from said sulphides, and then subjecting the metallic sulphides to a current of air at a temperature sufficiently high to remove the sulphurous elements of the sulphides in the form of sulphur dioxide.

3. The process of desulphurizing metallic sulphides carrying oil, as obtained by subjecting metallic oxides to sulphurous oil vapors, which consists of first removing the oil from said sulphides, and then subjecting the metallic sulphides to a current of air, while maintaining the sulphides and air at a temperature of about 500 degrees Fahrenheit, to remove the sulphurous elements of the sulphides in the form of sulphur dioxide.

4. The process of desulphurizing metallic sulphides carrying oil, as obtained by subjecting metallic oxides to sulphurous oil vapors, which consists of first removing the oil from said sulphides by subjecting the metallic sulphides to a current of superheated steam, and then subjecting the sulphides to a current of air, while maintaining the sulphides and air at a temperature of about 500 degrees Fahrenheit, to remove the sulphurous elements of the sulphides in the form of sulphur dioxide.

5. The process of desulphurizing metallic sulphides carrying oil, as obtained by subjecting metallic oxides to sulphurous oil vapors, which consists of first removing the oil from said sulphides by subjecting the metallic sulphides to a current of superheated steam, and then subjecting the sulphides to a current of air, while maintaining the sulphides and air at a temperature of about 500 degrees Fahrenheit, to remove the sulphurous elements of the sulphides in the form of sulphur dioxide, and continuing the current of air at a sufficiently high temperature to convert any resulting metal to metallic oxide.

This specification signed this 14th day of April, 1924.

JAMES B. RATHER.
FREDERICK S. SHEPARD.