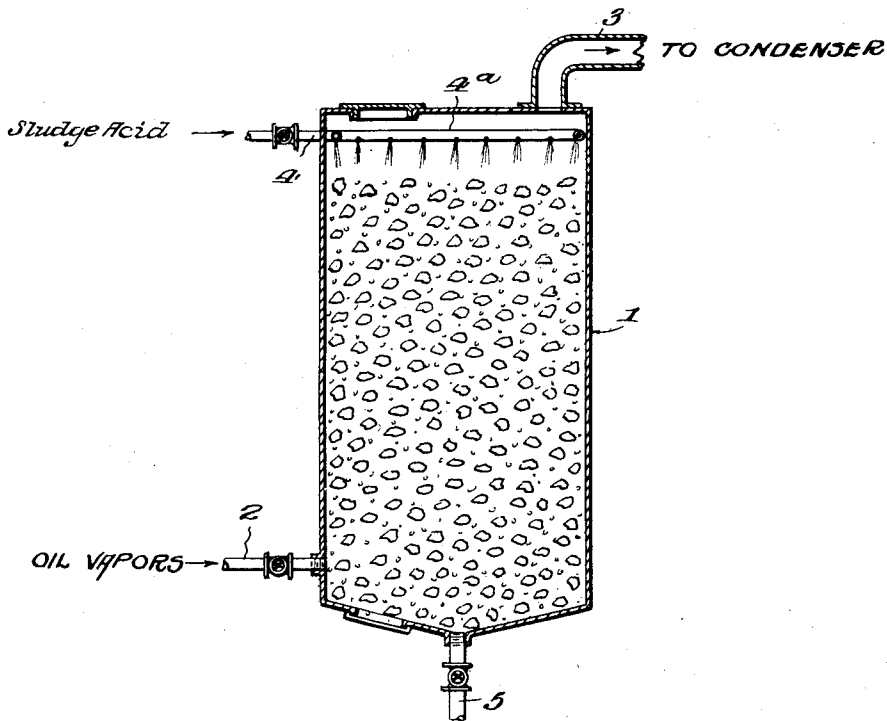


D. T. DAY,
PROCESS FOR TREATING HYDROCARBON OILS.
APPLICATION FILED DEC. 11, 1919.

1,411,237.

Patented Mar. 28, 1922.



INVENTOR.
David T. Day,
Pentti, Stone & Hayden,
ATTORNEYS.

UNITED STATES PATENT OFFICE.

DAVID T. DAY, OF WASHINGTON, DISTRICT OF COLUMBIA.

PROCESS FOR TREATING HYDROCARBON OILS.

1,411,237.

Specification of Letters Patent. Patented Mar. 28, 1922.

Application filed December 11, 1919. Serial No. 344,093.

To all whom it may concern:

Be it known that I, DAVID T. DAY, a citizen of the United States, residing at Washington, District of Columbia, have invented certain new and useful Improvements in Processes for Treating Hydrocarbon Oils, of which the following is a specification.

This invention relates to the extraction of nitrogen bases from oil and oil vapors and particularly those oils and oil vapors obtained in the distillation of shales and coals.

It has been well known that advantageous results were obtained by using sulphuric acid to wash oil distillates to remove the tar.

As a part of the present invention, it has now been found that instead of the usual wash material sulphuric acid, it is of advantage to introduce a spray of sludge acid prepared in accordance with the process described hereinafter.

Oil shales have been distilled in Scotland for many years for obtaining oil and ammonia, and as a by-product of nitrogen bases. Nitrogen occurs in practically all oil shales to a varying extent, very much in the proportions in which it is found in coals. When coals or shales are distilled part of the nitrogen goes off as elementary nitrogen, part as ammonia, or ammonium sulphide, and part in the form of various nitrogen bases or substituted ammonias, that is, ammonia in which part of the hydrogen is replaced by an oil radical, or in which an atom of nitrogen takes the place of an atom of carbon in benzol. The proportion of elementary nitrogen ammonia and two nitrogen bases varies with the character of the coal or shale, and with the method of distillation. In Scotland the practice has been so to distill the coal that superheated steam has to break up the nitrogen bases, with the formation of the maximum amount of ammonia at the expense of the nitrogen bases. Nevertheless, the nitrogen bases have been obtained by a simple process and utilized in the manufacture of various medicinal alkaloids, etc. These nitrogen bases are soluble in the oil distillates, and are, as a rule, easily volatile, and accompany the oil vapors. Like ammonia, they are soluble in weak acids, as well as strong. Therefore, when oil distillates in general are washed with strong sulphuric acid for the purpose of taking out tars, the nitrogen bases are also extracted at the same time and are then contained with the tar in the material drawn off, which is generally

known as acid sludge, or acid tar. This acid tar contains sulphuric acid in a somewhat weakened condition. It is frequently thrown away, but various patents have proposed the use of this acid sludge as a material for the preliminary treating of oils for taking out some of the tar, the completion of the refining of the distillate being accomplished with the new sulphuric acid, and when such acid sludge is used in this way it takes out the nitrogen bases as well as some of the tar, and the final sludge acid, which is usually thrown away, takes with it these nitrogen bases, which have recently become of great value.

The object of the present invention is not only to remove the nitrogen bases from oils and vapors, but so to obtain these nitrogen bases as to make them capable of utilization. In this, the fundamental proposition must be borne in mind that nitrogen bases can be extracted by even extremely dilute acid, such as, nitric, hydrochloric, phosphoric, etc. By this invention it has been possible to utilize this acid sludge from oil refining in a new way, which is effective and extremely economical. In order that this matter may be clearly understood, it is perhaps advisable to explain in detail the nature of acid sludge. The tarry acid material which settles when an oil distillate has been agitated with strong sulphuric acid, and then allowed to stand and settle, is variously known as acid tar, sludge acid, etc., and various products are sometimes carelessly spoken of by various names. The material which thus settles out after the agitation of oil with acid is a thick mixture of tar and sulphuric acid and sulphurous acid, which is generally known as acid sludge. Where this acid sludge is further utilized, it is subjected to treatment with steam, which effects the separation of some of the tar and sulphuric acid, much diluted by steam, and so greatly diluted that it is no longer of any value whatever for the refining of oils unless it is put through a subsequent treatment or concentration by distilling off the water by heat and leaving a strong acid. The tar thus obtained from acid sludge by the steam treatment is spoken of as acid tar, because it is still slightly acid in its reaction. The relatively weak acid obtained by the same treatment is spoken of as sludge acid. We have, therefore, three distinct materials, first, acid sludge, the material which

first settles from the oil; second, sludge acid, which is the acid still containing some tar, and third, the acid tar; both acid sludge and acid tar are obtained by the steaming of the acid sludge. It should be remembered that all of the nitrogen bases which may have been extracted by the strong acid in the treatment of the distillates remain in the diluted acid; therefore, if this diluted acid, that is the sludge acid, is used for the further extraction of nitrogen bases from shale oil, vapors, etc., the advantage is gained of obtaining original nitrogen bases contained in the acid, together with the nitrogen content extracted from the oil vapors.

One form of apparatus in which the invention may be operated is illustrated in vertical section in the accompanying drawing, in which 1 illustrates a scrubbing tower filled with coke or some such substance commonly used in scrubbing towers. Oil vapors and gases from stills are introduced into the tower through the pipe 2 and out of the top to a suitable condenser, not shown, through a pipe 3. The sludge acid is introduced into the top of the tower through a pipe 4 and is sprayed from a sprinkler 4^a on to the mass of coke within the tower. The oil vapors in passing upward through the coke come into contact with the sludge acid and the nitrogen contents of the vapors is removed from the vapors and is combined with the sludge acid. The pipe 5 is provided at the base of the tower for the removal of the sludge acid after it has trickled down through the mass of coke.

Although, the practice of using acid sludge in a preliminary treatment of oil distillates for a partial extraction of tars from such distillates is already known, the present invention provides for the use of diluted sludge acid, a product formed from acid sludge, which sludge acid frequently contains nitrogen bases, and which may be diluted down to an acid strength of even 1 to 3 per cent. This is novel and its use effects a great economy. It effects a marked improvement, inasmuch as this dilute acid takes out only the nitrogen bases, and does not take out tars from these oil vapors, and by this means sulphuric acid compounds of these nitrogen bases are obtained in solution in water in a condition where the nitrogen bases can easily be obtained in a comparatively pure state by the ordinary processes of neutralization with lime, etc., and the distillation of the bases.

What I claim is:

1. The process of treating hydrocarbon oils to remove the nitrogen content therefrom, which consists in preparing sludge acid by treating hydrocarbon oils with sulphuric acid, and thus forming acid sludge, separating said acid sludge into sludge acid

and acid tar by steam treating said acid sludge, and utilizing said sludge acid thus formed to treat hydrocarbon oils to remove the nitrogen content therefrom by bringing sludge acid into contact with hydrocarbon oils.

2. The process of treating hydrocarbon oils to remove the nitrogen content therefrom, which consists in preparing sludge acid by treating hydrocarbon oils with an acid, and thus forming acid sludge, separating said acid sludge into sludge acid and acid tar by steam treating said acid sludge, and utilizing said sludge acid thus formed to treat hydrocarbon oils to remove the nitrogen content therefrom by bringing sludge acid into contact with hydrocarbon oils.

3. The process of treating hydrocarbon oils to remove the nitrogen content therefrom, which consists in preparing sludge acid by treating hydrocarbon oils with an acid, and thus forming acid sludge, separating said acid sludge into sludge acid and acid tar, and utilizing said sludge acid thus formed to treat hydrocarbon oils to remove the nitrogen content therefrom by bringing sludge acid into contact with hydrocarbon oils.

4. The process of treating hydrocarbon oils to remove the nitrogen content therefrom, which consists in preparing sludge acid by treating hydrocarbon oils with sulphuric acid, and thus forming acid sludge, separating said acid sludge into sludge acid and acid tar, and utilizing said sludge acid thus formed to treat hydrocarbon oils to remove the nitrogen content therefrom by bringing sludge acid into contact with hydrocarbon oils.

5. The process of treating hydrocarbon oils to remove the nitrogen content therefrom, which process consists in preparing sludge acid by treating hydrocarbon oils with sulphuric acid, and thus forming acid sludge, separating said acid sludge into sludge acid and acid tar, and utilizing said sludge acid to remove the nitrogen content from oils by passing oil vapor containing nitrogenous matter into contact with said sludge acid.

6. The process of treating hydrocarbon oils to remove the nitrogen content therefrom, which process consists in preparing sludge acid by treating hydrocarbon oils with sulphuric acid, and thus forming acid sludge, separating said acid sludge into sludge acid and acid tar, and utilizing said sludge acid to remove the nitrogen content from oils by passing oil vapor containing nitrogenous material through a chamber and passing such sludge acid through said chamber in the direction opposite to the path of travel of said oil vapor.

7. The process of treating hydrocarbon oils to remove the nitrogen content there-

from, which consists in preparing sludge acid by treating hydrocarbon oils with sulphuric acid, and thus forming acid sludge, separating said acid sludge into sludge acid and acid tar by steam treating said acid sludge, and utilizing said sludge acid thus formed to remove the nitrogen content from oils, by passing oil vapor containing nitrogenous matter into contact with said sludge acid.

10 8. The process of treating hydrocarbon oils to remove the nitrogen content therefrom, which consists in preparing sludge

acid by treating hydrocarbon oils with sulphuric acid, and thus forming acid sludge, separating said acid sludge into sludge acid and acid tar by steam treating said acid sludge, and utilizing said sludge acid thus formed to remove the nitrogen content from oils, by passing oil vapor containing nitrogenous material through a chamber and passing said sludge acid through said chamber in the direction opposite to the path of travel of said oil vapor.

In testimony whereof I affix my signature. 25
DAVID T. DAY.