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OIL REFINING PROCESS

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9 Claims. (Cl. 196—27)

This invention relates to a process for the improvement or refining of oils and is particularly intended for the improvement of naphtha oils, or oils from coal, brown coal and shale. The improved treatment of the oils has particular reference to the gum, potential gum, sulfur, coloring matter and odorous contents thereof.

Nearly all oils contain organically combined sulfur which is converted into sulfuretted hydrogen during treatment. Thus, earlier processes were unable to work satisfactorily, because the materials used, for example copper, iron, and iron ore, soon became saturated with sulfur and lost their activity.

The principal object of the present invention is to avoid the disadvantages aforesaid and to provide a continuous process which can work without interruption and without deterioration of the catalyser.

The invention consists in conducting oil vapours together with reducing gases, such as hydrogen or carbon monoxide, over the oolitic ore minette, in the presence of steam. The ore should preferably be treated with reducing gases at an elevated temperature before the oil vapours are admitted.

The presence of steam and reducing gases during the treatment keeps the catalytic material permanently clean and active so as to make the process an absolutely continuous one.

Extensive investigation has shown that the oolitic ore makes a particularly fine catalyser. It is necessary, however, to keep it free from deposits and sulfur which it may take up and to do this by continuous removal. This is effected by the addition of steam to the reducing gases accompanying the oil vapours.

The proportion of steam in the reducing gases must be adjusted so that a certain equilibrium is maintained in the state of the minette, for the latter must be neither entirely oxidized nor entirely reduced. It has been found that the amount of steam is best determined by saturating the gases accompanying the oil with moisture at 65° C. to 95° C. The amount of the said gases is preferably 80 to 200 litres per 1 kilogramme of oil, but this largely depends upon the quantity of organically combined sulfur in the oil under treatment.

The working temperature of the process should be about 300° C. to 450° C. At lower temperatures, decomposition of steam and removal of sulfur from the minette might not be sufficiently energetic.

When oils are treated according to the process above described and distilled, it is found that they have lost every kind of objectionable smell and are water white, their sulfur, gum and potential gum being so far reduced as to be well within permissible limits.

The invention is not merely a laboratory procedure. It has been carried out on a large technical scale which has proved that the process can work for considerable periods without deterioration of the catalyser. Hydrocarbons and organically combined sulfur do not affect the working since the sulfur is continuously removed. However, oils often contain mechanical impurities and fractions which do not fully evaporate at a given temperature, and sometimes even tarry matter. In such cases, it is obvious that the catalyser must get coated or clogged so that its full activity will be lost. Also, there may be a slight decomposition of certain bodies with deposition of carbon having the same effect. In this event, the catalyser must be freed from all impurities after a period of working and this can be effected only by oxidation.

To carry out this oxidation in the reaction chamber or tower is not practical because the temperatures rise so high as to smelt the minette or bake it, which naturally renders it unfit for further use. To regenerate the ore by removing it entirely from the tower and burning it outside involves interruption of the process and a serious loss of time, when the many days required for cooling the whole mass and heating up the new charge are taken into consideration.

This difficulty is successfully overcome by removing the catalyser from one end of the reaction chamber in small quantities and replacing the quantity removed by feeding in at the other end a corresponding charge of new or regenerated ore. This is readily accomplished without interruption of the working by an arrangement of valve devices or shutters at the top and bottom of the tower. Such an arrangement can be constructed in many different ways and the particular construction adopted is of no consequence so far as the invention is concerned. The important feature in this regard is the principle of piecemeal renewal of the catalytic mass without interruption of the working.

The charge of fresh ore must be kept in a container wherein it can be preheated before entering the reaction chamber, otherwise condensation of oil and watery vapours would take place inside the reaction chamber due to the introduction of the cold ore. Furthermore, the

fresh charge must be in a reduced state and not oxidized when introduced, otherwise part of the oil vapours would be oxidised upon coming into contact with the oxide. For these reasons, the hopper or storage vessel must be provided with suitable heating means and so devised or adapted that steam or reducing gases can circulate through the ore for the purpose of heating and reducing the same.

In effect, the invention as above described provides an absolutely continuous process with the contact mass showing always an equal purity and composition. Consequently, the finished product also has at all times an equally high quality.

A further important object of the invention is a process which enables all other additional treatments of the product, apart from the usual distillation, to be eliminated. For example, there is elimination of the washing with acid or sodium hydroxide which causes considerable loss of substance. The invention therefore further provides for the removal of any noxious substance contained in the oil after the treatment hereinbefore described. As already stated, the organically combined sulfur of the oils leaves the reaction chamber in the form of sulfuretted hydrogen which may be partly retained in the condensate. The oil also may retain some moisture from the steam present during the process. Neither of these bodies must be allowed to remain in the oil product. The employment of sodium hydroxide for the removal of water and sulfuretted hydrogen is rather expensive. Consequently, the invention provides for conducting the condensate from the reaction chamber first through a medium which absorbs moisture from oil, for example lime or common salt, and secondly through a medium which absorbs sulfuretted hydrogen. For the second medium, it is very advantageous to use the very fine part of the minette which has been crushed for use in the reaction chamber and which is to fine for that purpose. This fine material, which otherwise would have to be wasted, forms an ideal filtering medium so far as sulfuretted hydrogen is concerned. Any suitable sieving or separating means may be employed for grading the minette so that an appropriate grade is used in the tower, the fines being available for filtering, as indicated.

Salt used for removal of moisture from the condensate can easily be recovered by evaporation of the absorbed water.

We claim:

1. Continuous process for treating oils consisting in conducting oil vapours with reducing gases over the oolitic ore minette in the presence of steam and at a temperature of 300° C. to 450° C., the proportion of reducing gases and steam being so adjusted that released sulfur escapes from the reaction chamber in the form of sulfuretted hydrogen and does not form permanent sulfide of iron in the chamber.

2. Continuous process for treating oils comprising conducting oil vapours with reducing gases over the oolitic ore minette in the presence of steam and at a temperature of 300° C. to 450° C.

3. Continuous process for treating oils comprising conducting oil vapours with reducing gases over the oolitic ore minette at a temperature of 300° C. to 450° C., the reducing gases being saturated with water vapour at a temperature of 65° C. to 95° C.

4. Continuous process for treating oils comprising conducting oil vapours with reducing gases over the oolitic ore minette at a temperature of 300° C. to 450° C. and in the presence of an adjusted quantity of steam, and gradually removing the charge of ore and replacing it with fresh ore.

5. Continuous process for treating oils comprising conducting oil vapours with reducing gases over the oolitic ore minette at a temperature of 300° C. to 450° C. and in the presence of an adjusted quantity of steam, removing portions of the charge of ore during the working and replacing such portions by preheated portions in a reduced condition.

6. Continuous process for treating oils comprising conducting oil vapours with reducing gases over the oolitic ore minette at a temperature of 300° C. to 450° C. and in the presence of an adjusted quantity of steam, removing portions of the ore during the working and replacing such portions by pre-heated portions from which a removal of oxygen has been effected.

7. Continuous process for treating oils comprising conducting oil vapours with reducing gases over the oolitic ore minette at a temperature of 300° C. to 450° C. and in the presence of an adjusted quantity of steam, and conducting the oil condensate from the reaction through a water absorbent and through a sulfur remover.

8. Continuous process for treating oils comprising conducting oil vapours with reducing gases over the oolitic ore minette at a temperature of 300° C. to 450° C. and in the presence of an adjusted quantity of steam, and conducting the oil condensate from the reaction through a water absorbent and through a filtering medium containing iron oxide.

9. Continuous process for treating oils comprising conducting oil vapours with reducing gases over crushed and graded oolitic ore minette at a temperature of 300° C. to 450° C. and in the presence of an adjusted quantity of steam, and conducting the oil condensate from the reaction through a water absorbent and through the fines resulting from the crushing and grading of the oolitic ore.

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