Patented Feb. 21, 1928. 1,660,295

UNITED STATES PATENT OFFICE.

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TREATMENT OF HYDROCARBON RESIDUES AND PRODUCT OBTAINED THEREBY.

No Drawing. Application filed April 25, 1925. Serial No. 25,941.

This invention relates to improvements in processes of treating heavy hydrocarbon residues of the type of pressure still tar, cracking coil tar, and the like, to fit them for use as fuel oil or for other purposes. The invention also includes the compositions so prepared. A novel and advantageous method of regulating cracking processes, and treating the residues therefrom, constitutes another feature of the invention.

In the operation of refinery cracking equipment there are produced heavy oil residues or tar, the value of which is impaired by their tendency to form solid or semi-solid carbonaceous matter on more or less prolonged standing. This carbonaceous matter may form a precipitate, or a suspension, or both. For convenience it may be referred to as a sediment.

For example, the pressure tar obtained from pressure stills is ordinarily made substantially unsalable as a fuel oil because of this characteristic, and is frequently not well adapted even for fuel use in the refinery. The deposited carbon may clog the pipes or burners, or cause other difficulties. Similar trouble is experienced with cracking coil tar and analogous materials. The expedients heretofore proposed for correcting this, such as blending with a lighter oil, distilling and fluxing back a portion of the distillate, settling, filtration, and the like, fail to remove the real source of difficulty and do not give complete satisfaction.

In accordance with the present invention, heavy residues are substantially freed from sediment-forming bodies by treatment with an acidic material, preferably a dilute water solution of an acid.

Ordinarily a small percentage of acid, one-half to one percent by volume of the oil treated, is sufficient. However, larger proportions of acid may be used without disadvantage. Sulfuric acid is most economical, but other acids having the property of precipitating the sediment may be used, for example, dilute hydrochloric acid, dilute acetic acid, and dilute solutions of salts, such as sodium acid sulfate or aluminum sulfate, which hydrolyze to form acids. Sulfuric acid of 30°–60° Bé. is suitable. Weaker acids sometimes fail to act completely, and stronger acids may give trouble by the formation of sludge which interferes with the subsequent treatment. The acid used may be diluted treating acid, such as is ordinarily sent to the acid recovery plants operated in connection with refineries. When the oil to be treated contains water, a more concentrated acid may be used so as to allow for dilution when added to the oil.

Heating facilitates the process, but it is not an essential feature. It is frequently desirable to treat the tar while it retains some or all the heat acquired in the still or coil. Temperatures up to 800° F. or more are not excessive. Agitation is desirable to bring the acid and oil rapidly into intimate contact. The oil may be treated with the acid at ordinary pressure; sometimes, however, it is advantageous to use superatmospheric pressure.

In a preferred form of the invention, when working with cool tar, about one-half per cent by volume of 37° Bé. sulfuric acid is added and the mixture is heated to about 200°–275° F. Carbonaceous sediment settles out rapidly, leaving an upper layer of tar substantially free from solids and B. S. I term this material "stabilized" tar, as it does not produce substantial amounts of sediment even after long standing. This tar, after removal of the sediment, will ordinarily pass specification requirements for Bunker C fuel oil, and some tars treated in the manner described will pass specifications for higher grades. Besides its use as a fuel oil, the product may be disposed of to advantage in other ways, for example as a stock for cracking when suitably blended with gas oil or the like. Heretofore, pressure tar has not been considered suitable for cracking on account of the large amount of carbon deposited. This difficulty is substantially avoided by the treatment in accordance with this invention. Various other blends may be prepared from the pressure tar.

A particularly important advantage of the invention is in connection with the operation of cracking equipment. In present practice, the necessity of obtaining a residue which can be practically disposed of imposes a serious limitation upon the operation. In pressure distillation, if an amount of pressure distillate approaching the maximum is taken off, the residue ordinarily contains an excessive quantity of coke-like material, either as such or in the form of carbonaceous-

sediment-producing bodies. A similar limitation is encountered in the operation of cracking coil and drum equipment and the like.

In accordance with the present invention, cracking is regulated to produce objectionable residues of the type just described and these are treated with dilute acid, thereby fitting them for use as a fuel, or otherwise. This procedure enables me to reduce the stock farther than in prior practice; as a result, I obtain an important increase in the amount of pressure distillate or cracked stock and a correspondingly increased production of gasoline. There is no appreciable loss by the formation of sludge as an incident of the acid treatment. The acidic reagents in the concentration used are precipitants, not sludge-forming compounds.

Referring, for example, to the operation of my process in connection with pressure stills, after the desired amount of pressure distillate has been taken off, the pressure tar may be run through a cooler to reduce its temperature to about 250–275° F. The proper amount of acids may then be introduced into the tar line. The tar and acids are mixed, for example in a mixing column. The treatment with acid may take place under the pressure prevailing in the distillation apparatus. The mixture of oil and acid is run to a settling or thickening device, and after a suitable period the greater portion of the tar may be drawn off as a clean product. The remaining portion containing solids may be substantially completely clarified by filtration, preferably through a rotary continuous vacuum filter. Other forms of filter may be used. The whole of the treated residue may be filtered or it may be allowed to settle and the liquid separated by decantation, siphoning off or the like.

Inert granular material, for example powpered coke, may be added to secure more efficient filtration. The solid material separated in the filter or otherwise may be used as a fuel, with or without briquetting. When coke is used as a filter aid, especially good fuel briquettes may be made from the material collected in the filter.

Heavy oils, such as crude still bottoms, may be blended with pressure tar and the mixture then treated with acid in accordance with this invention. Crude still bottoms and the like ordinarily contain more or less cracked material that gives rise to objectionable deposits. Acid treatment tends to accelerate the formation of sediment, but the bottoms are of such high viscosity that settling of the sediment is slow. However, I have found that if the bottoms are diluted with pressure tar or the like, and then treated, good results are obtained. The acid causes sediment to separate from both the bottoms and the tar. The treated mixture is valuable as a fuel oil, since its specific gravity and viscosity are relatively low, and sediment and water are substantially removed.

In some cases it is desirable to blend the pressure tar or the like with a light oil prior to treatment with the acid, or to use a blending agent to facilitate the filtration of the tar after treatment. The treated tar, after separation of solids and acid solution, ordinarily contains a trace of acid. This may be neutralized or removed, but it is ordinarily unobjectionable.

In my application for United States patent, Serial No. 3,595, filed January 20, 1925, I have described and claimed the stabilization of pressure tar or the like by treatment with acid oil.

Various details of the procedure described in connection with this invention may be modified within the scope of the appended claims, in which it is my intention to claim all novelty inherent in the invention as broadly as the prior art permits.

I claim:

1. Process of treating a heavy hydrocarbon oil residue derived from a cracking process, and normally characterized by formation of carbonaceous sediment on standing, comprising bringing the said residue into contact with a small amount of an acidic body in non-sludge-forming concentration, whereby relatively rapid formation of sediment is obtained, and separating the sediment.

2. Process of treating a hydrocarbon oil residue of the type of pressure tar, comprising bringing the residue into contact with a small amount of a dilute acidic body in non-sludge-forming concentration, whereby a relatively rapid formation of sediment is obtained, adding an inert granular material to the mixture, and separating the oil from the sediment and added solids.

3. Process for stabilizing pressure tar, comprising treating the tar with a dilute aqueous solution of sulfuric acid in non-sludge-forming concentration at an elevated temperature, whereby a relatively rapid precipitation of sediment is obtained, and separating the sediment.

4. Process for stabilizing pressure tar, comprising treating the tar with about one-half to one percent by volume of sulfuric acid of 30°–60° Bé., heating to 200°–275° F., whereby relatively rapid precipitation of sediment is obtained, and separating the sediment.

5. The invention according to claim 4, in which the treatment with acid is carried on under superatmospheric pressure.

6. Process of preparing a commercially valuable heavy hydrocarbon oil, comprising subjecting an oil to cracking conditions, continuing the cracking treatment until a residue characterized by a tendency to form

large amounts of carbonaceous sediment on standing is produced, treating the residue with a dilute acid in non-sludge-forming concentration, whereby sediment is formed relatively rapidly, and separating the clarified heavy oil from the sediment.

7. Process of preparing heavy hydrocarbon residues, comprising subjecting an oil to cracking conditions, continuing the cracking treatment until a residue characterized by a tendency to precipitate large amounts of carbonaceous sediment is produced, withdrawing the residue from the cracking zone, introducing a dilute acid in non-sludge-forming concentration into the stream of residue, mixing the acid and residue, and separating the sediment.

8. Process of preparing heavy hydrocarbon residues, comprising subjecting an oil to cracking conditions, withdrawing the residue from the cracking zone, mixing a dilute solution of an acid in non-sludge-forming concentration with the residue while the same remains at substantially the temperature of the cracking operation, settling and removing separated sediment, and withdrawing the substantially clear supernatant liquid.

9. Process of preparing heavy hydrocarbon residues, comprising subjecting an oil to cracking conditions, withdrawing the residue from the cracking zone, treating the residue without substantial loss of temperature with a dilute acid in non-sludge-forming concentration, whereby a relatively rapid precipitation of sediment is obtained, separating the sediment, withdrawing the substantially clear supernatant liquid, and filtering the residual liquid containing solids.

10. Process of preparing heavy hydrocarbon residues, comprising subjecting an oil to cracking conditions, mixing a small amount of a dilute water solution of acid in non-sludge-forming concentration with the hot residue, whereby a relatively rapid formation of sediment is obtained, and separating the liquid from the sediment.

11. A heavy hydrocarbon oil prepared by treating pressure tar with a small amount of acid in non-sludge-forming concentration.

12. A heavy hydrocarbon oil prepared by treating a mixture of pressure tar and crude still bottoms with a dilute acid in non-sludge-forming concentration.

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