Patented Apr. 18, 1933 1,904,173

UNITED STATES PATENT OFFICE

REGINALD K. STRATFORD AND WILLIAM P. DOOHAN, OF SARNIA, ONTARIO, CANADA, ASSIGNORS TO STANDARD OIL DEVELOPMENT COMPANY, A CORPORATION OF DELAWARE

METHOD OF REMOVING CORROSIVE SULPHUR FROM HYDROCARBON OILS

No Drawing. Application filed May 21, 1928. Serial No. 279,620.

This invention relates to improvements in treating petroleum crude oils or distillates containing corrosive constituents, especially corrosive sulphur. The invention in a preferred form comprises treating the oil with a solution containing one or more alkali or alkaline earth metal hydroxids, associated with a substance which tends to promote contact between the oil and the solution. Such substances are especially naphthenic acid soaps, sulphonic acid soaps, fatty acid soaps, or mixtures of any of the foregoing. Other contact-promoting bodies, such as rosin, sulphonated oleic acid, Turkey red oil, or the like, may be used.

It is well known that corrosive sulphur, when existing as elementary sulphur and in certain compounds, cannot be successfully removed from oil by treating with caustic alkali unless the oil is heated to a relatively high temperature. Alkali sulphids, however, under certain conditions are known to have the power of fixing elementary sulphur at lower temperature. In the U. S. patent to Cobb, No. 1,300,816, granted April 15, 1919, removal of corrosive sulphur by specially prepared solutions containing such sulphids is described and claimed.

By means of our invention, it is possible to use with advantage the so called "spent" caustic solutions which contain sulphids produced by contact with sulphur-containing oils. While the utility of this invention is chiefly in connection with such solutions, we have found that the action of even fresh caustic solutions is promoted by the presence of soaps and other compounds of the type mentioned.

The present invention will be fully understood from the following description:

Mid-Continent natural or first-run naphtha is agitated under pressure of about 100 lbs. per square inch at about 212° F. for 15 minutes with a 30° Baumé "spent" absorption lye containing 1% by weight of naphthenic acid soap, preferably sodium naphthenate. About 35% of the sodium hydroxid originally present in the lye had been converted into salts, mostly sodium sulphid. About 65% of the sodium hydroxid remained as such. After the treatment, the naphtha was tested by shaking repeatedly with metallic mercury at room temperature. The mercury remained bright, showing that corrosive sulphur had been eliminated from the naphtha.

We prefer a naphthenic acid soap prepared from lye used in treating Colombian or Peruvian gasoline. This lye contains substantial amounts of naphthenic acid soaps, which may be separated and then dissolved in the proper amount in the "spent" lye to be used for treating. Alternatively, a portion of the lye containing the soaps may be added directly to the "spent" lye treating solution. Ordinarily, the naphthenic soap lye referred to does not contain enough sodium sulphid and caustic to be used satisfactorily alone. We have found that about 0.1 to 5.0% of the naphthenic soap is satisfactory; around 1% being best in many cases. The permissible upper limit is determined largely by the tendency of the oil to form objectionable emulsions with the oil. The amount of soap should not be large enough to induce this.

Instead of naphthenic acid soaps, we may use alkali and ammonium salts of the higher fatty acids or mixtures of these soaps; also other soaps, such as oleates and/or stearates of aluminum, iron and calcium. The amount of these may be varied widely, but in general should be between 0.1 and 5.0%.

The invention is not limited to any particular method of treating. We prefer to use a continuous mixer of the type shown in the United States patent to Charles Leaver, No. 1,635,718, granted July 12, 1927, and in the copending United States application of Stratford, McIntyre, and Moor, Serial No. 239,656, filed December 13, 1927. The lye

may be used in any suitable way, preferably at temperatures between 220 to 300° F. and pressure sufficient to prevent undesirable vaporization. A relatively large volume of lye is used, preferably about equal to the volume of oil. When treating gasoline, the inlet pressure in the treater may average about 100 to 150 pounds per square inch and the outlet pressure about 60 to 100 pounds. Although caustic soda lyes have been particularly referred to herein, it will be understood that the invention is equally applicable to other alkaline treating agents, such as caustic potash lyes. The invention may also be applied in connection with fresh or "spent" treating lyes containing lead or other heavy metals.

As stated above, soaps and the like also facilitate the action of fresh lye on corrosive sulphur present in oil. In working with fresh lye, we prefer to use the treating method described in Serial No. 239,656, just mentioned.

Various changes and alternative procedures may be adopted within the scope of the appended claims in which it is our intention to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. The method of removing corrosive sulphur from hydrocarbon oils, consisting of bringing the oil into intimate contact at a temperature between 212° and 300° F. with an alkaline solution containing a substance adapted to promote contact between the oil and treating solution.

2. The method of removing corrosive sulphur from hydrocarbon oils, comprising bringing the oil into intimate contact at a temperature between 212–300° F. with a large volume of a solution of caustic soda containing a small percentage of soap adapted to promote contact between the oil and the treating solution.

3. The method of removing corrosive sulphur from hydrocarbon oils, comprising bringing the oil into intimate contact at a temperature between 212–300° F. with a large volume of a caustic soda solution containing a small percentage of a naphthenic acid soap.

4. The method of removing corrosive sulphur from hydrocarbon oils, comprising agitating the oil under pressure and at a temperature between 212° and 300° F. with a caustic soda solution containing a small percentage of a soap adapted to promote contact between the oil and the treating solution.

5. Method according to claim 4, in which the soap adapted to promote contact is derived from lye which has been used in treating Colombian or Peruvian gasoline.

6. Method according to claim 4, in which the contact-promoting substance is about 1% by weight of a naphthenic acid soap.

7. Method according to claim 4 in which the soap adapted to promote contact is introduced into the treating solution in the form of lye containing soaps produced by treatment of Colombian or Peruvian gasoline.

8. The method of removing corrosive sulphur from gasoline, consisting of agitating the gasoline under pressure and at elevated temperature with a "spent" lye containing residual caustic soda, together with a substance adapted to promote contact between the caustic soda and the gasoline.

9. The method of removing corrosive sulphur from hydrocarbon oils, comprising bringing the oil into intimate contact at a temperature between 212° F. and 300° F. with an alkaline solution containing rosin.

10. The method of removing corrosive sulphur from hydrocarbon oils, comprising bringing the oil into intimate contact at a temperature between 212° F. and 300° F. with sulphonated oleic acid.

REGINALD K. STRATFORD.
WILLIAM P. DOOHAN.