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PAUL McMICHAEL, OF FLUSHING, NEW YORK, ASSIGNOR TO HYDROCARBON REFINING PROCESS CO., INC., OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

REFINING HYDROCARBON OILS.

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This invention relates to an improved method for refining petroleum hydrocarbons, and more particularly relates to a method for refining light petroleum oils and distillates, especially gasoline containing cracked oils and pressure distillates. The method of the invention is particularly applicable to the treatment of cracked oils produced from crude petroleum oils having an asphaltic base.

For many commercial purposes gasoline is considered satisfactory if it passes certain tests as to color, corrosive properties and sulfur content. Gasoline intended for use as motor fuel is usually considered to be of satisfactory merchantable quality if in color it is equal to or better than +22 on the Saybolt Universal chronometer scale (A. S. T. M. tentative method of test—serial designation D 156—23T), if it does not discolor a strip of mechanically polished pure sheet copper after being heated therewith for three hours at 122° F. (A. S. T. M. tentative method of test—serial designation D 130—22T), and if on being shaken thoroughly with a strongly alkaline solution of sodium plumbite neither it nor the solution is discolored, and on being further shaken thoroughly with the solution after the addition of flowers of sulphur neither it nor the solution nor the sulphur is discolored (Doctor test for gasoline—page 605 Bulletin No. 17 of the Kansas City testing laboratory).

Hitherto, the general practice in the refining of petroleum oils has involved treatment of the oil with sulphuric acid. The methods of acid treatment commonly employed have several disadvantages. For example, the acid treatment as usually carried out tends to introduce sulphur into the oil in a form which it is difficult to remove and which makes it difficult to bring the oil to a quality where it will pass the copper strip test. Likewise, in the treatment of oils containing large amounts of unsaturated constituents such as cracked oils, treatment with strong sulphuric acid tends substantially to denude the oil of unsaturated constituents. Unsaturated compounds such as the olefines constitute an excellent and advantageous constituent for motor fuel, and their removal introduces an unnecessary loss. Difficulties in disposing of waste acid and acid sludges are also encountered, and the number of distillations frequently required is also a disadvantage.

According to the present invention, the oil is subjected to treatment with an alkaline aqueous solution of a reducing agent and a heavy metal compound, and is thereafter subjected to treatment with a dilute aqueous solution containing a free acidic constituent.

The process of the invention may be carried out in two or three steps. The oil may be initially treated with an alkaline aqueous solution of a reducing agent and then successively treated with an alkaline aqueous solution of a heavy metal compound and finally with a dilute aqueous solution containing a free acidic constituent, or the treatment with the heavy metal compound and the reducing agent may be combined and the oil initially treated with an alkaline aqueous solution containing a reducing agent and a heavy metal compound subsequently treated with a dilute aqueous solution containing a free acidic constituent.

As the reducing agent, it is particularly advantageous to employ sodium hyposulphite ($Na_2S_2O_4$). Other reducing agents soluble in aqueous alkaline solution are also useful in carrying out the invention. The aqueous solution may be alkaline with an alkali hydroxide such as sodium hydroxide.

Metallic salts in which a heavy metal constituent is present as a base constituent or as an acid constituent and oxides or hydroxides of heavy metals are useful in carrying out the invention. For example, aqueous solutions containing sodium hydroxide and sodium chromate, or sodium hydroxide and sodium plumbite (a solution of litharge in sodium hydroxide solution), may be used, or an aqueous solution of copper sulphate with an excess of sodium hydroxide may be employed.

Following the alkaline treatments, the oil may be subjected to treatment with acidulated water or with a solution of acid sodium carbonate. Where acidulated water is employed, the acid concentration may range from in the neighborhood of 0.02% up to 1% or somewhat higher. Hydrochloric acid may be employed with advantage for acidulating the water employed, but other acids such as sulfuric acid and acetic acid are also useful.

The reducing solution may be prepared by dissolving the commercial sodium hyposulphite in a 15° Bé. caustic soda solution to saturation. It is, however, advantageous to employ freshly prepared solutions of the reducing agent, and such solutions may be prepared by dissolving zinc dust in a solution of sodium bi-sulphite, precipitating the zinc compound formed by the addition of milk of lime, and decanting the solution containing the sodium hyposulphite from the precipitate. An excess of the sodium salt may be used and free alkali introduced into the solution by the causticizing treatment, or a solution of caustic alkili may be added to the decanted solution.

Where the treatments with the reducing agent and the heavy metal compound are carried out together, a suitable salt or an oxide or hydroxide of a heavy metal may be added to a sodium hyposulphite solution prepared from the commercial material as described. Or the hyposulphite solution may be freshly prepared as described and the resulting suspension, before separation of the precipitate, employed directly in the treatment of the oil. In this latter method of procedure, the hyposulphite solution containing calcium hydroxide and zinc hydroxide may be thoroughly agitated to form an emulsion or suspension and a caustic soda solution added before use in the refining operation.

The invention will be further illustrated by the following examples, but it will be understood that they are employed to illustrate the invention and that the invention is not limited thereto.

A cracked petroleum distillate made from a crude petroleum having an asphaltic base was agitated for about 1 hour with about 10% by volume of 15° Bé. caustic soda solution saturated with sodium hyposulphite. After separation of the hyposulphite solution the oil was agitated for a period of from about 6 to 12 hours with about 10% by volume of an aqueous solution containing about 10% by weight of sodium chromate and 1% by weight of free caustic soda. The treatment was stopped when a test sample gave a satisfactory Doctor test. After separation of this solution, the oil was agitated with water acidulated with less than about 1% of hydrochloric acid until a test sample showed the desired color. The period of agitation was from about 2 to 6 hours. The separation of the various treating solutions from the oil was accompanied by an intermediate washing with water to remove remaining traces of the preceding treating solution.

Before treatment, the oil gave positive results in each of the four tests previously described. After treatment with the hyposulphite solution, the corrosion test and the Doctor test without the addition of flowers of sulphur were satisfactory but the Doctor test with the addition of flowers of sulphur was positive and the color was still unsatisfactory. After treatment with the chromate solution, satisfactory tests were obtained except as to color. Following the final treatment, an oil was obtained which was satisfactory in each of the four tests.

The hyposulphite and heavy metal compound solutions may be reused in the process until they are no longer active in the refining operation, either with or without the addition, between successive operations, of fresh refining agents.

As a further example, a cracked petroleum distillate made from a crude petroleum having an asphaltic base was agitated for about 1 hour with about 10% by volume of an emulsion prepared by slowly adding about 35 parts by weight of zinc dust to about 400 parts by weight of a 38° Bé. solution of acid sodium sulphite with agitation at a temperature between about 86° and 104° F, after standing about two hours adding about 22 parts by weight of calcium oxide as milk of lime with agitation, allowing the mixture to stand in a closed container for about 6 hours or more and then agitating the resulting mixture to the form of an emulsion, and adding from about ⅓ to ¼ of its own volume of a 40° to 45° Bé. solution of caustic soda before use. After this treatment the oil was satisfactory except as to color, and it was then agitated for from about 2 to 6 hours with water acidulated with less than 1% of sulphuric acid. Following this treatment, the oil was satisfactory in each of the four tests.

It will be apparent that the process of the present invention enables a satisfactorily refined product to be obtained without redistillation. Treatment with strong sulphuric acid is avoided so that the olefines and similar constituents desirable as components of the finished product are retained therein, and losses incurred by the removal of such constitutents are substantially eliminated. By avoiding treatment with strong sulphuric acid, the necessity of disposing of strongly acid solutions or of acid sludges is also eliminated. At the same time, the process of the invention enables the production of refined products satisfactory as to the four tests above enumerated.

I claim:

1. A method of refining petroleum oils and distillates, which comprises subjecting the oil to treatment with sodium hyprosulphite and a heavy metal compound in alkaline aqueous solution, and thereafter subjecting the treated oil to treatment with a dilute aqueous solution containing a free acidic constituent.

2. A method of refining petroleum oils and

distillates, which comprises subjecting the oil to treatment with sodium hyposulphite and a heavy metal compound in alkaline aqueous solution, and thereafter subjecting the oil to treatment with acidulated water.

3. A method of refining petroleum oils and distillates, which comprises subjecting the oil to treatment with an alkaline aqueous solution containing sodium hyposulphite, then to treatment with an alkaline aqueous solution containing a heavy metal compound, and thereafter to treatment with a dilute aqueous solution containing a free acidic constituent.

4. A method of refining petroleum oils and distillates, which comprises subjecting the oil to treatment with an alkaline aqueous solution containing sodium hyposulphite and thereafter to treatment with an alkaline aqueous solution containing a heavy metal compound.

In testimony whereof I affix my signature.

PAUL McMICHAEL.