Patented Nov. 7, 1933 1,933,748

UNITED STATES PATENT OFFICE

1,933,748

PROCESS FOR TREATING HYDROCARBON OILS

Jacque C. Morrell, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of South Dakota

No Drawing. Application November 15, 1929 Serial No. 407,373

1 Claim. (Cl. 196—29)

This invention relates to the treatment of hydrocarbon oils such as petroleum distillates and more particularly to cracked hydrocarbon oils.

In the ordinary refining of such petroleum distillates various modifications of sulphuric acid treatment are usually employed, consisting of treating with sulphuric acid, caustic soda, and plumbite solution in separate steps and in varying order. While the ordinary sulphuric acid treatment and other treatments, such as with clays, suffice for some kinds of cracked distillates, they are not satisfactory for the treatment of distillates containing high percentages of sulphur compounds. Sulphuric acid is a suitable reagent for removing ordinary sulphur compounds from petroleum distillates, but the composition of cracked distillates is such that enormous losses are entailed when it is attempted to both refine with respect to color, odor and stability, and also with respect to removal of sulphur compounds by treatment with sulphuric acid.

The removal of sulphur compounds is included in refining but is handled separately here because for the ordinary treatment of cracked distillate to produce a product of satisfactory color and odor, a relatively small amount of sulphuric acid is required, while to remove a substantial percentage of sulphur compounds in addition a very large quantity of sulphuric acid is required.

Cracked distillates are composed of several primary groups of hydrocarbons which include the important unsaturated and aromatic hydrocarbons, both of which react with sulphuric acid, in particular the unsaturated hydrocarbons. The aromatic and unsaturated hydrocarbons are particularly important in motor fuels because of their anti-knock properties permitting the operation of motors at greater efficiency, either in ordinary operation or in the operation of high compression type. In ordinary refining, only sufficient amount of acid is used to remove the highly unsaturated hydrocarbons such as the diolefines, but with a large amount of sulphuric acid, which is required for desulphurizing, a higher percentage of the desired unsaturated hydrocarbons, and a substantial percentage of the aromatic hydrocarbons are removed along with sulphur compounds. In addition to this removal and direct loss of material, low boiling unsaturated hydrocarbons within the gasoline range are converted into higher boiling hydrocarbons in the gas oil range by acid treatment owing to a reaction known as polymerization.

It is the purpose of the present invention to cut down materially the amount of sulphuric acid required for desulphurization by treating separately with reagents which remove or assist in removing the sulphur compounds without accompanying serious losses due to acid treatment. The present invention is directed particularly to the use of the acids and the oxides of nitrogen and complex compounds of the latter, specifically nitric and nitrous acid, nitrous oxide, nitric oxide, nitrogen dioxide, nitrogen trioxide, nitrogen tetroxide and nitrogen pentoxide in the refining of cracked distillates. At elevated temperature, for example between 150° and 350° F., more or less, the oxides are preferably diluted with inert gases such as carbon dioxide, nitrogen, flue gas containing little or no oir, etc. The reason for this is the very explosive nature of the oxides of nitrogen and hydrogen vapors. In treating the distillates with the acids, they may be simply refluxed and given a subsequent treatment which will be hereinafter described. In treating the distillates with the oxides of nitrogen, all of which are gases, the temperature is very carefully regulated while the gases are bubbled through the body of oil in one modification of the process. Low temperatures, i. e. considerably below atmospheric e. g. 10–20° F. are desirable in some cases. In order to prevent too great a loss of oil vapors, the oil container should be connected with a reflux condenser if the temperature is in any way elevated. The unused gases may be recirculated back through the liquid body by means of a suitable pump or compressor. As an alternative method of treatment the distillate may be vaporized and the highly diluted oxide of nitrogen passed directly into the vapor zone.

Preferably the container is so arranged that the gases have to be passed through the longest path of travel, for example, in a vertical container, or through suitably arranged baffles in a horizontal container. As the temperature of treatment should not be excessive, the oil may be heated when desired by means of heating coils placed within the oil body as an alternative to external heating, or the oil may be circulated through a coil obtaining heat from any source. When treating with the acids directly, proper precautions, well known in the art, should be used to prevent corrosion.

The oil which has been treated as described for from one to several hours, more or less, is then subjected to further treatment with caustic solutions after which the caustic is withdrawn.

While this caustic treating step is not absolutely necessary, it is desirable, as it facilitates subsequent operations. The oil is then treated with sulphuric acid using from 10 to 30 pounds, more or less, per barrel of distillate. The acid is preferably concentrated, for example, from 90 percent up to the concentrations of fuming acid, for example, so-called 130 percent. The acid treatment is applied in the usual manner by proper mixing and contacting with the oil and the sludge from the treatment withdrawn. The oil may then be water washed or treated with the caustic solutions. The caustic is removed and the oil distilled in the presence of steam. The treatment with the acids or oxides of nitrogen or derivatives thereof, is the principal step in the process although the benefits of the invention depend, in a large measure, on the combination of such treatment with the subsequent treatments described. The said sulphur removal compared with ordinary sulphur treatment is increased and the losses by reaction, solution and polymerization are greatly decreased by the application of this process.

My invention, therefore, results in the production of superior products, entailing much smaller losses of the distillates undergoing treatment when compared with ordinary sulphuric acid treatment, and especially saving those hydrocarbon groups in the distillate which are desirable for motor fuel uses, particularly for anti-knock purposes. In one method of applying the process and as an alternative, the oxides of nitrogen may be combined to form relatively loose or unstable compounds with other substances, for example, nitrogen dioxide with sulphuric acid to form the well known nitrosyl sulphuric acid and also with ferrous sulphate to form a brownish complex compound. The latter may also be made by treating nitric acid direct with ferrous sulphate. In applying the latter reagents various combinations and temperatures are used.

As an example a pressure distillate of 54 Bé. gravity and a sulfur content of 0.8% produced a gasoline with an initial boiling point of 102° F. and end point of 437° F. and sulphur content of 0.12% when treated as described by a mixture of oxides of nitrogen followed by treatment with sulphuric acid and caustic in the steps described. The sulphur content of the finished product by ordinary treatment was 0.2%. The gasoline possessed good color, odor and stability.

I claim:—

A process for desulphurizing hydrocarbon oils containing unsaturated hydrocarbons and sulphur which comprises treating such oil at elevated temperature with a gaseous oxide of nitrogen diluted with inert gas and then subjecting the thus treated oil to the action of sulphuric acid.

JACQUE C. MORRELL.