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TREATMENT OF HYDROCARBON OILS

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This invention relates to the treatment of hydrocarbon oils, and refers more particularly to the refining of relatively low boiling hydrocarbon distillates at elevated temperatures, especially those resulting from the conversion of relatively high boiling hydrocarbons at elevated temperatures.

In a specific embodiment the invention comprises subjecting hydrocarbon oils to treatment with hydrochloric acid in the presence of a metallic oxide. More specifically, the invention comprises subjecting the hydrocarbon oils to treatment in the liquid phase in the presence of a metallic oxide and hydrochloric acid. Among the metallic oxides which may be employed, and as examples thereof may be mentioned: The oxides of calcium, magnesium, aluminum, zinc, tin, iron, copper, lead, mercury, cobalt, nickel, chromium, manganese, molybdenum, vanadium, tungsten, and the like. Mixtures of the oxides may also be employed.

In applying the process of the invention to practice a metallic oxide, preferably in a finely divided state, is added to the hydrocarbon distillate to be treated in association with hydrochloric acid. The hydrochloric acid is preferably added continuously to the hydrocarbon liquid while undergoing treatment. The hydrocarbon liquid may be refluxed in the presence of the treating reagents or may be subjected to distillation during the process of treatment. It is not essential that all of the hydrocarbon be in the liquid phase during treatment, but it is preferred that it be substantially in the liquid phase. It is usual in the process that excess hydrogen chloride will be contacted with the hydrocarbon vapors and may be removed either before, during or after condensation. An alkaline material or solution of an alkaline material may be employed for the removal of the excess hydrogen chloride. Examples of such alkaline materials are solutions of caustic, soda, ammonia, and the like. The process has shown marked economies over the ordinary methods of treatment such as the use of sulphuric acid and alkaline solutions in various combinations.

As an illustration of the application of the process, the distillate to be treated may contain some of the metallic oxide in suspension and may be fed continuously into a still maintained at a temperature suitable for the vaporization of the desired product; for example, gasoline. Hydrochloric acid may be fed continuously into the body of the liquid, which is subjected to a rate of distillation so that it is simultaneously subjected to the necessary time of treatment with the hydrochloric acid and the metallic oxide.

The temperatures employed will depend upon many factors, such as pressure, necessary time of treatment, properties of the distillate to be treated, and others. Temperatures of from 200–275° F. have been found suitable for the treatment at atmospheric pressure, although lower and higher temperatures have been employed with satisfactory results. At the higher temperatures superatmospheric pressure may be employed, the primary object being to maintain the oil undergoing treatment substantially in the liquid phase. In many cases it is unnecessary to treat the lower boiling portions of the oil undergoing treatment, and this portion may be vaporized rapidly before the treatment becomes effective; for example, in the treatment of a Pennsylvania or Mid-Continent distillate from 20–40%, more or less, may be distilled off before the treatment has become effective. In cases of this kind the treating reagents may be added at the beginning of the operation, or after a portion of the distillate has been removed.

As examples of the results which may be obtained by the application of the invention the following may be cited: A Mid-Continent cracked distillate containing approximately 375 mgs. of gum per 100 ccs. and of a dark yellow color when treated with zinc oxide in the presence of approximately one pound per barrel of hydrogen chloride in the form of a dilute solution will produce a product containing approximately 25 mgs. of gum per 100 ccs. and of a color from 25 to 30 on the Saybolt colorimeter scale and with an appreciable reduction in the sulphur content. The temperature of treatment is approximately 250° F.

A California distillate showing a gum content of 650 mgs. per 100 ccs., a sulphur content of approximately 0.3% and of a dark reddish brown color, may be treated, employing approximately one pound of zinc oxide per barrel of oil treated and approximately one pound of hydrochloric acid in the form of an aqueous solution, and will produce a product of 25–30 Saybolt color with a gum content of approximately 35 mgs. per 100 ccs., more or less, and a sulphur content of approximately 0.2%.

Similar results to those described for zinc oxide may be obtained with tin oxide.

When iron oxide or copper oxide are employed the time and temperature of treatment may have to be extended, for example, with a temperature of 275° F. under a slight superatmospheric pres-

sure, employing approximately one pound per barrel of hydrogen chloride in the form of an aqueous solution, products of satisfactory color, odor and stability are produced, with an appreciable reduction in sulphur content. Additional steam to that produced by the vaporization of the water in the hydrochloric acid may be employed. Direct treatment with gaseous hydrogen chloride has also been employed with satisfactory results.

The above examples are illustrative of the process of the invention only and are not to be construed as limitations thereof.

The treatment herein described may constitute the sole refining action on the oil, or it may constitute one step in a series of refining steps. It may be preceded by the usual treatments with refining agents such as sulphuric acid, caustic soda, plumbite, filtering earth or the like, and may be succeeded by any combination of the above refining agents, followed, if desired, by distillation.

We claim as our invention:

1. A step in a process of refining the gasoline-containing product resulting from the cracking of hydrocarbon oil, which comprises subjecting said product in liquid condition to treatment with added hydrochloric acid and a solid reagent whose major portion consists of a simple metallic oxide or oxides while maintaining said oil at an elevated temperature.

2. A step in a process of refining the gasoline-containing product resulting from the cracking of hydrocarbon oil, which comprises subjecting said product in liquid condition to treatment simultaneously with added hydrochloric acid and a solid reagent whose major portion consists of a simple metallic oxide or oxides while maintaining said oil at an elevated temperature.

3. A process for refining cracked hydrocarbon distillate of motor fuel boiling range which comprises treating such distillate in substantially liquid phase and at elevated temperature with added hydrochloric acid and a finely divided reagent consisting essentially of a simple metal oxide or oxides suspended in the distillate.

4. A process for refining cracked gasoline-containing distillate which comprises heating the distillate in substantially liquid phase in admixture with a solid reagent whose major portion consists of a simple metallic oxide or oxides, and continuously adding hydrochloric acid to the distillate during the heating.

5. A process for refining light cracked hydrocarbon oil which comprises treating the oil, at a temperature above its normal boiling point and under sufficient superatmospheric pressure to maintain the major portion thereof in liquid phase, with added hydrogen chloride in the presence of steam and a zinc oxide.

6. A step in the refining of cracked gasoline-containing distillates, which comprises treating the distillate simultaneously with added hydrochloric acid and a solid reagent whose major portion consists of a simple metal oxide or oxides.

7. A step in the refining of cracked gasoline-containing distillates, which comprises treating the distillate simultaneously with added hydrochloric acid and zinc oxide.

8. A process for refining cracked gasoline-containing distillates which comprises treating the distillate at elevated temperature simultaneously with added hydrochloric acid and a solid reagent consisting essentially of a simple metal oxide or oxides.

9. A process for refining cracked gasoline-containing distillates which comprises treating the distillate at elevated temperature simultaneously with added hydrochloric acid and zinc oxide.

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