Patented Sept. 22, 1936 2,055,416

UNITED STATES PATENT OFFICE

2,055,416

METHOD OF REFINING MINERAL OILS

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No Drawing. Application October 8, 1934, Serial No. 747,419. In the Netherlands October 17, 1933

8 Claims. (Cl. 196—36)

This invention relates to a process of manufacturing refined hydrocarbon oils and is more particularly concerned with a treating process whereby high grade light fuel oils are obtained from hydrocarbon mixtures rich in unsaturated or aromatic components, such for example as cracked, and especially vapor phase cracked distillates.

It is known that the conventional sulfuric acid treatment, when applied to such distillates, causes a considerable amount of losses, resulting in decreased yields and in the absence in the final products of various compounds, such as aromatic and unsaturated hydrocarbons, which are highly desirable therein, since they tend to impart to the fuel oil high antiknock properties.

It is therefore an object of this invention to provide a process which would desulfurize, reduce the gum formation and improve the color of the distillates treated in a manner comparing favorably with that of the sulfuric acid treatment, while giving at the same time considerably higher yields and better octane ratings.

Briefly stated, this process consists in treating the desired distillate with a small quantity of a mono- or poly-sulfonic acid of an aliphatic and/or aromatic hydrocarbon, either substituted or not, or with a mixture of such acids. The hydrocarbons to be refined are contacted in vapor phase with a solution or suspension of the sulfonic acid in an organic substance inert at the operating temperature, which makes it possible to carry out the process in the presence of steam.

The sulfonic acids which have been found especially suitable for this purpose are the benzenesulfonic acid, the β-naphthalene-sulfonic acid, the methane-disulfonic acid, and the sulfonic acids of toluene and xylene. The organic radicles of these acids may be substituted hydrocarbon groups. It was found that the substituents exert a definite influence on the process; thus, sulfonic acids with a negative substituent, such as a halogen (for example, parachlorobenzene sulfonic acid) are usually more suitable than those with a positive substituent such as the amino groups. These sulfonic acids differ somewhat in the action which they exert on the oil being treated. For example, some of them have an especially favorable influence on the color of the distillate, while others exert a specific desulfurizing action, or may increase the anti-knock stability of the hydrocarbons. By selecting a certain sulfonic acid, or by applying a mixture of such acids, the character of the treating action may be controlled in any desired manner. The sulfonic acids must be however, substantially free of sulfuric acid, since the latter is easily reduced at the temperatures of the process, and the conversion products thus obtained unfavorably affect the final product.

According to this invention, it is possible to apply the sulfonic acid treatment to petroleum distillates in the vapor phase and in the presence of steam. Such method, while very advantageous for commercial scale operations, since in the petroleum industry distillation is usually carried out with the aid of steam, was until now considered impracticable, as it was believed that a continuous supply of steam would completely hydrolize the sulfonic acids and render them ineffective. It has however now been found that substantially no such hydrolysis occurs if the sulfonic acids are dissolved or suspended, in not too great a concentration, in a liquid organic solvent inert at the working temperature, which is probably due to the fact that the organic solvent protects the dissolved sulfonic acid from the action of the steam. The concentration of the acids should preferably be below 5%, while the allowable upper limit is approximately 10%. Moreover, it is advantageous to work at a temperature at which there is no substantial hydration, since it has been found that an intensive hydration tends to reduce the solubility of the sulfonic acid in the organic solvent. The temperature consequently has to be fixed for each acid separately, although temperatures of about 100 to 250° C. have been generally found very satisfactory.

The desired inert organic solvent may be selected from pressure distillate residues, lubricating oils, gas oils, stove oils, Edeleanu extracts, etc. Since it has been found that it is preferable to use the least possible amount of the organic solvent capable to protect the sulfonic acid from the hydrolizing effect of steam, and since sulfonic acids dissolve more easily in light fractions, it may sometimes be advisable to dissolve these acids, for example, in a relatively light Edeleanu extract, and then to admix the solution in desired proportions with a heavier oil, such as lubricating oil or a stove oil.

A preferred form of apparatus in which this process is carried out may, for example, take the form of a treating column filled with Raschig rings providing a large contact surface. It is known that the light fractions obtained by cracking, the so-called pressure distillates, usually require a redistillation in order to conform to some desired boiling range specifications. In practice, such distillation is generally carried out with the aid of steam, and the mixture of steam and hydrocarbon vapors thus obtained may, before being passed to the condensing apparatus, be led through the treating column countercurrent to the treating agent. The treating agent dissolved or suspended in an organic inert solvent may be recirculated, and a certain amount of fresh sulfonic acid or the solvent continuously added in order to maintain the desired degree of concentration. It is also possible to use several treat-

ing units in series and to pass the hydrocarbon vapors and the treating agent consecutively and countercurrently through all of them.

The treating column should preferably be constructed of a material that does not oxidize easily. Although the metals themselves are not attacked by the sulfonic acids, metal oxides are dissolved by them so that corrosion takes place, which is not only detrimental to the apparatus, but also affects unfavorably the treating process. Stainless steel may be advantageously used for the construction of treating columns, while enamel or clay linings also give excellent results.

According to the invention, the treatment may be carried out at atmospheric, super-atmospheric or sub-atmospheric pressures, and may also be combined with any of the other known methods of treating, which may be applied before as well as after the sulfonic acid treatment. For example, the oil may be pre-treated with dilute acid, lye, or an absorbent material to remove certain constituents such as nitrogen bases, phenols, mercaptans, etc. In such cases, it is possible to use a concentration of sulfonic acids even lower than stated above.

This invention may further be illustrated by the following example, without limiting its scope to any of the specific substances or steps used.

A vapor phase cracked gasoline with the following properties: octane number 69, color Saybolt indeterminable, specific gravity 0.753, bromine number 162, gum 300 mg., was distilled with steam, and the vapor mixture, containing about 10% steam, and the vapor were passed consecutively through two columns filled with Raschig rings, held at a temperature of about 200° C. A 2% solution in lubricating oil of a benzene-sulfonic acid, free of water and of sulfuric acid, was passed through the second column countercurrent to the vapors, after which the partly spent reagent was mixed with 1% of fresh benzene-sulfonic acid, and passed through the first column.

After condensation, a gasoline with the following properties was obtained: octane number 71, color Saybolt 25, specific gravity 0.752, bromine number 150, gum 7 mg. The treating losses were very small.

From the above figures it will be clear that the process gives very satisfactory results. Attention is particularly drawn to the octane number, which is even somewhat higher in the final product than in the original gasoline. The relatively small decrease of the bromine number shows that the unsaturates had not been affected by the treatment, while the gum-forming components were effectively removed from the distillate.

It may be added that it is sometimes of advantage to neutralize the acid treated distillate with an aqueous solution of sodium carbonate instead of sodium hydroxide. This may have a particularly favorable effect on the gum stability. A cracked distillate treated according to the invention and subsequently condensed, was washed in one case with sodium carbonate, and in the other case with sodium hydroxide. The gum stability of both gasolines was determined according to the Voorhees and Eisinger method described in A. P. I. Refinery Technology, Sec. II, 169, Jan. 3, 1929, and was found to be 1300 in the first case and only 20 in the second.

I claim as my invention:

1. In the process of treating hydrocarbon oils the steps of vaporizing a hydrocarbon oil, bringing the resulting vapors at a non-cracking temperature in contact with an effective quantity of hot liquid organic sulfonic acid substantially free from sulfuric acid and separating the treated vapors from the liquid sulfonic acid.

2. In the refining of a petroleum distillate in the vaporous state the step of subjecting the vapors at a non-cracking temperature to the action of an effective quantity of hot liquid organic sulfonic acid which is substantially free from sulfuric acid.

3. In the refining of a petroleum distillate in the vaporous state, the step of subjecting the vapors at a temperature between 100° C. and 250° C. to the action of an effective quantity of hot liquid organic sulfonic acid which is substantially free from sulfuric acid.

4. In the process of treating a petroleum distillate in the vaporous state the step of subjecting the vapors at a non-cracking temperature to the action of a hot liquid solution of organic sulfonic acid in an organic solvent which is substantially inactive under the conditions of the treatment, said solution being substantially free from sulfuric acid.

5. In the process of treating a petroleum distillate in the vaporous state the step of subjecting the vapors at a non-cracking temperature to the action of a hot liquid solution of organic sulfonic acid, said solution containing not more than 10% sulfonic acid in an organic solvent which is substantially inactive under the conditions of the treatment and is substantially free from sulfuric acid.

6. In the refining of a petroleum distillate in the vaporous state the step of subjecting the vapors at a non-cracking temperature in the presence of steam to the action of an effective quantity of hot liquid organic sulfonic acid, which is substantially free from sulfuric acid, and under conditions to prevent the condensation of steam.

7. In the refining of a petroleum distillate in the vaporous state the step of subjecting the vapors at a non-cracking temperature of said distillate to the action of an effective quantity of hot liquid organic sulfonic acid, which is substantially free from sulfuric acid, and under conditions to prevent the formation of metal sulfonates.

8. In the process of treating a hydrocarbon distillate of the type of gasoline in the vaporous state to produce a stable gasoline of good color and low gum content the steps of subjecting the vapors at a temperature between 100° C. and 250° C. to the action of an effective quantity of a liquid solution of an organic sulfonic acid, substantially free of sulfuric acid, said solution containing not more than 10% of sulfonic acid in an organic solvent which is substantially inactive under the conditions of the treatment, and under conditions to prevent formation of metal sulfonates, separating the vapors from the treating solution, condensing the treated vapors, and treating the resulting condensate with an aqueous solution of sodium carbonate, whereby a gasoline is produced possessing an octane number which is higher than that of the original distillate.

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