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PROCESS FOR PRODUCING AROMATIC HYDROCARBONS

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This invention relates to the improved method of segregating the aromatic hydrocarbons and their derivatives in the treatment of hydrocarbon oils.

In the refinement of gasoline, kerosene, or the like, a polar solvent is often used to extract impurities such as aromatic, hydroaromatic and unsaturated hydrocarbons. The separation of the saturated aliphatic hydrocarbons—which are called raffinat, or refined petroleum products—from the aromatic, hydroaromatic and unsaturated hydrocarbons—which are called the extract—is only a moderately efficient one. Since the extract is the starting point of this process, the incomplete separation in this treatment, namely, the presence of the saturated aliphatic hydrocarbons therein, presents a serious problem.

Therefore, the object of this invention is to eliminate the saturated aliphatic hydrocarbons from the extract and thereby obtain a maximum amount of aromatic hydrocarbons in their purest form.

Certain crude petroleums and pressure distillates contain large quantities of aromatic hydrocarbons and it is with these that this process deals primarily. These aromatic hydrocarbons are generally objectionable and are eliminated by reason of their solubility in a polar solvent, such as liquid sulphur dioxide, liquid ammonia, or liquid hydrogen chloride. Such polar solvents are referred to herein as those of the "liquefied gas type." In the treatment of hydrocarbon materials with a polar solvent, such as liquid sulphur dioxide, the attention of those interested in the art has heretofore been directed to the raffinat, which contains the saturated aliphatic hydrocarbons, while the extract has been used for a cheap fuel, or was discarded. It has been found that this extract contains many valuable products, but the presence of the saturated aliphatic hydrocarbons in such extract has prevented their economical recovery and utilization prior to my invention.

Ordinarily, in order to assure the elimination of all of the impurities, such as aromatic, hydroaromatic and unsaturated hydrocarbons, from the raffinat, the separation has been carried on at temperatures high enough so that some of the saturated aliphatic hydrocarbons are lost in the extract. The presence of a relatively small proportion of saturated aliphatic hydrocarbons when mixed with aromatic, hydroaromatic and unsaturated hydrocarbons interferes materially with the satisfactory utilization of the aromatic constituents, in that they affect the distillation and nitration steps that follow. I have found that these saturated aliphatic hydrocarbons in the extract are practically eliminated by retreatment with liquid sulphur dioxide at low temperatures. This is highly important, because the separation of the various groups of aromatic hydrocarbons is best accomplished by fractional distillation, and as there are saturated aliphatic hydrocarbons and aromatic, hydroaromatic and unsaturated hydrocarbons boiling at the same temperature, it is practically impossible to separate them by fractional distillation alone, and this has militated against the commercial use of the extract.

In the extract are concentrated the aromatic, hydroaromatic and unsaturated hydrocarbons, together with a small quantity of saturated aliphatic hydrocarbons. The liquid sulphur dioxide is washed out with water and the remainder of the extract is treated with sulphuric acid, which eliminates the unsaturated hydrocarbons. Sulphuric acid of approximately 85% purity is used because the reaction between certain hydrocarbons and strong sulphuric acid is so vigorous as to polymerize or change them, causing loss of valuable materials, whereas if an acid of less strength is used these relatively reactive hydrocarbons are not attacked. By this elimination of the liquid sulphur dioxide and the unsaturated hydrocarbons, a smaller volume of extract, consisting of aromatic, hydroaromatic and the objectionable saturated aliphatic hydrocarbons, remains. In accordance with the invention this material is then treated with a polar solvent of the liquefied gas type to separate the non-polar hydrocarbons. In the preferred

practice of the invention the thus-treated extract is treated with a large proportion of sulphur dioxide at approximately 0° F. to reduce the saturated aliphatic hydrocarbons to a minimum. It has been found necessary in this additional treatment with liquid sulphur dioxide to use an amount nearly equal to the volume of hydrocarbon material to be treated, but preferably a very considerable excess of the liquid sulphur dioxide should be used. The extract from this second extraction is washed with water and then neutralized. This extract is steam distilled and fractionated, and the various fractions are nitrated, or otherwise treated to obtain the desired aromatic hydrocarbon products. The step of nitration, for example, may be carried out by mixing with equal volumes of nitric and sulphuric acid.

To demonstrate the utility of this process, the following run was made:

500 gallons of gasoline from California crude was washed with 20° Bé. caustic soda to remove certain sulphur compounds, then dried and treated with 250 gallons of liquid sulphur dioxide at 0° F. four times in succession. 79.38% raffinat, or saturated aliphatic hydrocarbons, and 19.29% of extract, or aromatic, hydroaromatic and unsaturated hydrocarbons, were recovered, with 1.33% loss. 42 gallons of the extract obtained from this treatment was treated with 55 pounds of 85% sulphuric acid, applied in three charges, drawing off the acid sludge after each change. The remainder was then washed with water and neutralized with weak caustic soda, and 38⅔ gallons remained to be treated. This was extracted with 150% liquid sulphur dioxide at 0° F. and 38.88% saturated aliphatic hydrocarbons separated out in the upper layer, and 61.12% of extract was drawn off. The extract had a gravity of 40° A. P. I. before the second extraction, and the saturated aliphatic hydrocarbons from the second extraction had a gravity of 47.2° A. P. I. The extract from the second extraction was neutralized with weak caustic soda and washed with water. This material was then ready for the fractional distillation and subsequent nitration as heretofore described.

To illustrate the difference in yields obtained, or, in other words, the superiority of the above described process from what could be accomplished from utilizing an extract obtained in the usual way, the following example is given:

The original extract was nitrated with a mixed acid composed of 100% by volume of concentrated nitric acid and 100% by volume of concentrated sulphuric acid, and 62% of the volume of the extract was nitrated. After subjecting this same extract to the above process, the final concentrated extract upon nitration by the same method gave 81% by volume of nitrated material, thus showing a higher concentration of aromatic hydrocarbons in a second extract, resulting in an increased yield of 19% of nitrated material.

It must be understood that there is practically no additional cost to this re-treatment with liquid sulphur dioxide, as the sulphur dioxide is recovered and used again, thereby operating in a continuous cycle.

The term "hydrocarbon material", as used herein, is intended to include all the distillates of crude petroleum such as gasoline, kerosene, lubricating distillates and the like, or any mixture thereof.

What I claim is:

1. A process of treating a mixture of saturated aliphatic hydrocarbons and aromatic, hydroaromatic and unsaturated hydrocarbons, comprising treating such mixture with a polar solvent of the liquefied gas type to form a solution containing said aromatic, hydroaromatic and unsaturated hydrocarbons together with a minor proportion of said saturated aliphatic hydrocarbons, separating said solution from the undissolved saturated aliphatic hydrocarbons, recovering the extracted material from said solution, treating said extracted material with a polar solvent of the liquefied gas type and thereby dissolving said aromatic, hydroaromatic and unsaturated hydrocarbons and separating them as a solution in the solvent from the minor proportion of saturated aliphatic hydrocarbons contained in said extracted material, separating the last-named solution from the residual undissolved saturated aliphatic hydrocarbons, and recovering the purified extract from said last-named solution.

2. A process of treating a mixture of saturated aliphatic hydrocarbons and aromatic, hydroaromatic and unsaturated hydrocarbons, comprising treating such mixture with a polar solvent of the liquefied gas type to form a solution containing said aromatic, hydroaromatic and unsaturated hydrocarbons together with a minor proportion of said saturated aliphatic hydrocarbons, separating said solution from the undissolved saturated aliphatic hydrocarbons, recovering the extracted material from said solution, treating said extracted material with a polar solvent of the liquefied gas type, and thereby dissolving the aromatic, hydroaromatic and unsaturated hydrocarbons and separating them as a solution in said solvent from the minor proportion of saturated aliphatic hydrocarbons contained in said extract, the volume of said further amount of said polar solvent being at least equal to the volume of the extract, separating the last-named solution from the residual undissolved saturated aliphatic hydrocarbons, and recovering the purified extract from said last-named solution.

3. A process according to claim 2, said

polar solvent of the liquefied gas type comprising liquefied sulfur dioxide.

4. A process of treating a mixture of saturated aliphatic hydrocarbons and aromatic, hydroaromatic and unsaturated hydrocarbons, comprising treating such mixture with a polar solvent of the liquefied gas type to form a solution containing said aromatic, hydroaromatic and unsaturated hydrocarbons together with a minor proportion of said saturated aliphatic hydrocarbons, separating said solution from the undissolved saturated aliphatic hydrocarbons, recovering the extracted material from said solution, treating the extracted material with sulfuric acid to remove unsaturated hydrocarbons and separating the residual aromatic and hydroaromatic hydrocarbons from said minor proportion of saturated aliphatic hydrocarbons by treatment with a polar solvent of the liquefied gas type in an amount such that the volume of said solvent is at least equal to that of the extract being treated, and thereby dissolving said aromatic and hydroaromatic hydrocarbons and separating them as a solution in said solvent from said minor proportion of saturated aliphatic hydrocarbons, separating the last-named solution from the residual undissolved saturated aliphatic hydrocarbons, and recovering the aromatic and hydroaromatic hydrocarbons from said last-named solution.

5. A process of treating a mixture of saturated aliphatic hydrocarbons and aromatic, hydroaromatic and unsaturated hydrocarbons, comprising treating said mixture with liquefied sulfur dioxide to form a solution containing the aromatic, hydroaromatic and unsaturated hydrocarbons together with a minor proportion of said saturated aliphatic hydrocarbons, separating said solution from the undissolved saturated hydrocarbons, recovering the extracted material from said solution, treating said extracted material with sulfuric acid to remove unsaturated hydrocarbons and treating the residual extract with a volume of liquefied sulfur dioxide substantially in excess of that of said residual extract to dissolve said aromatic and hydroaromatic hydrocarbons and separate them as a solution in the sulfur dioxide from said minor proportion of unsaturated aliphatic hydrocarbons, separating the last-named solution from the residual undissolved saturated aliphatic hydrocarbons, and recovering the purified extract from said last-named solution.

In testimony whereof I sign my name.

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