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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.

More specifically, the invention comprises subjecting hydrocarbon oil vapors to treatment with mixtures of sulfur dioxide, oxygen-containing gases and steam in the presence of solid salts of metals such as, for example, the salts of aluminum, zinc, tin, copper, lead, iron. mercury, cobalt, nickel, chromium, manganese, molybdenum, vanadium, tungsten, cadmium. and others, individual salts being used alone or mixed with others in various combinations which have been found suitable for producing particular treating effects. As examples of salts of metals which may be used may be mentioned sulfites, sulfates, acetate nitrates, chlorides, bromides, iodides, phosphates, hypochlorites. chlorates, perchlorates, permanganates, chromates, dichromates, et cetera. As examples of oxygen-containing gases, air, oxygen, or ozone, alone or in combination, may be mentioned ozonized air having been found to be particularly efficacious in some instances.

In some cases it may be found preferable to space the finely divided salts by supporting them on or mixing them with relatively inert materials of a non-metallic nature such as fuller's earth, clays, bentonite, beauxite, crushed firebrick, pumice stone, et cetera, this expedient serving to expose more surface and prevent the agglomeration of the salts into masses too large for effective action. The function of the salts or mixtures thereof employed may be of a true chemical nature or they may function merely as catalysts.

The usual method of refining cracked distillates is to subject them to treatment with sulfuric acid and alkaline solutions including plumbite solutions consisting of litharge dissolved in alkaline solutions in various combinations of treatment and subsequently to subject the acid treated product to redistillation usually in the presence of steam. The present invention permits the direct treatment of the hydrocarbon vapors from the cracking process, reducing the cost of reagents and eliminating the redistillation or re-running operation, although it is within the scope of the invention to revaporize the product in a subsequent operation and subject the vapors to treatment as described.

The invention is more particularly directed to the treatment of vapors of lower boiling cracked distillates though straight run distillates may also be treated within the scope of the invention.

In applying the process of the invention to practice any suitable equipment may be employed which will permit the contacting of the hydrocarbon vapors and the treating gases employed with the solid contacting or polymerizing materials; for example, a suitable tower or chamber packed with a selected mixture of contact materials may be employed following the fractionator of a cracking system, the gaseous reagents being introduced at a suitable point or points along the line of flow of the ascending or descending vapors, thus permitting contact with the solid materials of the mixture of hydrocarbon oil vapors and the gaseous treating mixtures. Similarly any device which permits the efficient contacting of the hydrocarbon vapors undergoing treatment with the gases and solids may be employed. The solid contacting materials may sometimes be employed in successive strata of varying composition, or may be supported on superimposed plates designed to produce intimate contact.

It has been found desirable to neutralize the vapors before or after condensation and to this end the vapors may be treated with ammonia gas or pass counterflow to solutions of alkalis in auxiliary neutralizing equipment, or the condensed vapors may be treated with liquid alkalis such as solutions of caustic soda, ammonia or the like, the traces of reagents and reaction products remaining being washed out with water when found necessary.

The reactions involved in treatments conducted within the scope of the invention have been observed to produce effects comparable with those produced by sulfuric acid of varying strength used after the customary methods of treatment. The amounts of reagent used will vary with the character of the vapors treated from a fraction of a percent to as high as 10% by weight of the oil vapors treated in cases where relatively heavy treatments are desired. The proportions of sulfur dioxide, oxidizing gas and steam may also be varied to produce a wide variety of treating effects.

The effects produced upon oil vapors, particularly those produced from the cracking of heavy hydrocarbon oils by the use of gases and solid contact substances characteristic of the invention are in general those of polymerization or condensation of relatively highly unsaturated hydrocarbons or their derivatives, particularly

their sulfur derivatives. The net result is the controllable elimination of groups of compounds which are readily polymerized under oxidizing conditions to form substances of a gummy or resinous nature which are undesirable in motor fuel.

Various temperatures of treatment may be employed, for example, from 250–600° F., more or less, and the pressures may be subatmospheric, atmospheric or superatmospheric. While the results may vary with the conditions employed, the pressures and temperatures are chosen so that the hydrocarbons are treated substantially in the vapor phase.

As specific examples of the operation of the process of the invention and of the results obtained, a California cracked distillate of approximately motor fuel boiling range may be vaporized and subjected to treatment with a mixture of sulfur dioxide, oxygen and steam during the passage of the vapors in a downward direction through a stationary contact mass consisting of a mixture of a finely divided zinc sulfate supported on fuller's earth, the weight of the earth being approximately four times that of the salt. The sulfur dioxide may be used in an amount equivalent to approximately four pounds per barrel with oxygen slightly in excess of that necessary for its complete oxidation to sulfur dioxide. Steam is used at the rate of approximately two pounds per barrel. The untreated product may show a gum content of approximately 500 mgs. per 100 ccs. and have a reddish brown color, with a sulfur content of approximately 0.35%. The treated product after suitable separation from spent reagents, neutralizing with alkalis and washing with water, may show a gum content of approximately 30 mgs. and a color of +25 on the Saybolt scale. The sulfur content may be found to be as low as 0.1%.

In the case of a mixed Mid-Continent and West Texas cracked distillate treated with approximately the same amounts of reagents, the gum content may be reduced from 300 mgs. to 25 and the color raised from a light amber to approximately 30 on the Saybolt scale. The sulful content may be reduced from 0.4% to approximately 0.15%.

The process of the invention is particularly suitable to the treatment of cracked distillates produced from California oils. In some cases the untreated distillates may contain 600 mgs. of gum and have a dark reddish color while the treated distillates may have a gum content of only 50 mgs. and a color of 25 to 30 on the Saybolt scale. The sulfur content may be reduced from 0.5% to 0.1%.

The foregoing description and examples have disclosed a process applicable to the treatment of hydrocarbon oil vapors which has a wide applicability and is capable of great variations in the methods of operation and the amounts of reagents employed. Therefore, the specific cases cited are not to be construed in a limiting sense upon the broad scope of the invention as many other modifications can be used and examples of results therefrom given.

We claim as our invention:

1. A step in the process of refining the overhead products of hydrocarbon oil cracking, which comprises subjecting said products in heated vaporous condition to the action of a mixture of sulphur dioxide and steam in the presence of discrete particles of a solid metallic salt.

2. A step in the process of refining the overhead products of hydrocarbon oil cracking, which comprises subjecting said products in heated vaporous condition to the action of a mixture of sulphur dioxide, free oxygen and steam in the presence of discrete particles of a metallic salt.

3. A process for refining hydrocarbon vapors which comprises passing the same with sulphur dioxide and steam through an earthy contact material containing discrete particles of a metallic salt.

4. A process for refining hydrocarbon vapors which comprises treating the same with sulphur dioxide in the presence of zinc sulphate.

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