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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 treatment of the lower boiling fractions produced in the cracking of the heavier portions of crude petroleums though corresponding fractions resulting from straight run distilling operations may also be treated.

More specifically the invention has reference to the treatment of cracked hydrocarbon vapors containing undesirable amounts of gum and color-forming compounds and sulphur in higher percentage than is allowable in commercial motor fuels by new and novel means particularly adapted to economically refine them to produce marketable motor fuel therefrom by condensation.

In one specific embodiment the invention comprises treating hydrocarbon vapors, particularly cracked hydrocarbon vapors containing substantial amounts of vapors of gasoline boiling range, with the salts of persulphuric acid which are known as persulphates such as those of sodium, potassium and ammonium. In another embodiment it is contemplated using a mixture of an aqueous solution of a persulphate and sulphuric acid. The use of possible persulphates of the heavy metals is also contemplated.

Though some treating methods for refining cracked vapors are in vogue, these methods operating with greater or less efficiency, it is still common practice to treat the condensed vapors by the following general steps:

1. Treatment with caustic soda to remove dissolved hydrogen sulphide;
2. Treatment with sulphuric acid of commercial grade;
3. Neutralizing with caustic soda;
4. Treatment with plumbite or other sweetening reagents to convert mercaptans to odorless and relatively non-corrosive disulphides;
5. Redistillation to produce an overhead gasoline of proper end point;
6. Final neutralization or sweetening.

The use of sulphuric acid in treating the liquefied distillate is quite universal but it possesses a disadvantage in its lack of perfect selectivity in removing undesirable di- and tri-olefins while leaving substantially unaffected the mono-olefins which add to the antiknock value of the gasoline. Consequently it frequently happens that when sufficient concentrated acid is used to romove the less desirable highly unsaturated hydrocarbons by polymerization or direct chemical action that a portion of the mono-olefins is removed concurrently. Furthermore, if the temperature is allowed to rise to any extent or acid of high strength such as fuming acid containing free sulphur trioxide is used marked oxidation effects are produced which result in extensive polymerization and condensation reactions which yield heavy liquids and tars boiling above the range desired in the finished gasoline and entail a considerable loss of material. Though numerous attempts have been made to utilize sulphuric acid to treat cracked vapors prior to their condensation, I am not aware that any as yet are in practical operation since the relatively high temperature at which these vapors must be treated causes the sulphuric acid to oxidize the hydrocarbons to an undesirable extent. The present invention is concerned with vapor phase treatments utilizing solutions of or solid persulphates to produce refining effects generally equivalent to those produced by sulphuric acid in liquid phase treatments, a major advantage being the production of refined distillates which need substantially no further chemical treatment or rerunning to produce a marketable gasoline.

The persulphates are salts of the hypothetical persulphuric acid $H_2S_2O_8$. The most easily formed persulphate is that of ammonium which is conveniently prepared by the electrolysis of ammonium sulphate in compartment cells, the ammonium persulphate being continuously formed by anodic oxidation, and the anode solution being continuously replenished by the addition of ammonium sulphate. This compound is a white crystalline solid which has a specific gravity of 1.982, decomposes under its melting point and is soluble in water to the extent of 58.2 parts at 0° C. and about 65 parts at room temperature in 100 parts of water. The solutions when moderately heated give off active or ozonized oxygen which assists in the treating effects as will be hereinafter more fully described.

Other persulphates such as, for example, those of sodium or potassium may be prepared by adding their carbonates or hydrates to concentrated solutions of ammonium persulphate whereupon the persulphates of the alkali metals precipitate. These compounds are somewhat less soluble in water but may be employed advantageously in particular cases either alone or in combination with the ammonium salt. Persulphates of the following metals are also available: lithium, cassium, rubidium, calcium, magnesium, strontium, barium, mercury, copper, silver, zinc, cadmium, thallium, lead, manganese, iron and nickel. Obviously the use of particular salts will be governed by the cost as well as by their particular chemical characteristics.

The exact mode of operation employed in conducting vapor phase treatments characteristic of the present invention will depend primarily upon whether the salts are used in aqueous solutions or as solids. When solutions are employed it is convenient to allow them to flow downwardly in towers containing filling or baffling material against rising streams of oil vapors. Towers of the so-called "bubble tray" type may be employed in these counter-flow treatments. The particular persulphate employed and its concentration in the solution will be determined by a large number of factors such as the character of the vapors and of the salt, the extent of treatment desired, the temperature and pressure of the vapors, etc. Concentration of the solution may be maintained by preventing evaporation by the introduction of steam at different levels in the tower, thus maintaining substantially uniform treating conditions. Combination of solutions of persulphates and sulphuric acid in aqueous solution may also be employed. The treatment may be and preferably is a step in a combination of different successive treatments, being preceded by the use of alkaline materials such as solutions of caustic soda to remove free hydrogen sulphide and being followed by alkaline reagents such as caustic soda or ammonia to neutralize residual acidic substances and sometimes by solid contacting, adsorbent or filtering material such as fuller's earth, silica gel, sand, bone black, etc., to effect treatment of reaction products and to produce further effects upon the vapors.

When the solid persulphates are used in vapor phase treatments they may be incorporated or mixed with relatively inert siliceous spacing materials such as fuller's earth, clays, bentonite, etc., and the treatments may be conducted by passage of the vapors either in an upward or downward direction through such composite masses. When excessive sludge formation causes clogging or channeling of the contact masses parallel arrangements of treaters may be employed with clean-out of chambers being conducted while others in parallel are being used. Treatments may also be effected by injecting or atomizing finely divided composite solid particles into vapors rising through towers containing no filling material. For example, minor amounts of solid persulphates such as ammonium or sodium persulphate may be incorporated in amounts up to 20% by weight with diatomaceous earth and the particles forced through sprays or nozzles into the ascending vapors counterflow thereto.

It is to be noted here that owing to the fact that the basicity of the persulphates may be regulated by employing salts of different metals, that a wide variety of treating effects is possible. Furthermore, oxidation effects appear to be produced by small amounts of ozone or active oxygen rather than by oxygen in combination with sulphur as in the case of sulphuric acid so that there is in general a reduced tendency toward the formation of sulfoxy compounds which are both difficult to remove from the oil when they remain dissolved therein and are difficult to decompose to regenerate the acid when present in the sludge resulting from acid treatments.

The temperatures employed in conducting treatments are commonly those of the vapors as they come from the fractionating equipment of the cracking unit and are usually comprised within the approximate range of 250 to 500° F. depending upon the pressure and the mean boiling range of the vapors. Similarly treatments may be conducted under a pressure corresponding to the pressure upon the fractionating tower or the pressure may be reduced to atmospheric or even subatmospheric. It will be obvious that the concentration and amount of the particular salt employed in the treatment may be suitably adjusted to compensate for temperatures and pressures which may be most convenient to use.

The treating effects produced upon cracked vapors by the use of persulphates either in solution or as solids are in general equivalent to those produced by the use of sulphuric acid in the liquid phase though the extent of polymerization, oxidation and miscellaneous side reactions resulting in the formation of sulfoxy and other compounds are more controllable. The use of combinations of solutions of persulphates and sulphuric acid is contemplated in the present invention. As an example of results obtainable by treating cracked vapors in a manner and by means typical of the process of the present invention, the vapors from the final fractionating tower of a cracking unit operating upon California gas oil may be admitted to the bottom of a tower filled with Raschig rings to rise countercurrent to a down-flowing solution of ammonium persulphate containing approximately 20% of the solid salt, the concentration being maintained by adding steam to the tower to maintain required partial pressures. The amount of solid salt used per barrel of condensate of approximate gasoline boiling point range may be approximately five pounds. At this point it may be noted that ammonium persulphate has a molecular weight of 228 and contains approximately 35% sulphur trioxide by weight while sulphuric acid, considered as monohydrate, contains 81.6% sulphur trioxide. From this it will be seen that while an amount of persulphate is used corresponding in weight to the usual sulphuric acid treatment of approximately six pounds per barrel commonly practised upon California cracked distillates, that the acid equivalent employed is substantially less. The gasoline produced from such a distillate refined by the combination of sulphuric acid, ammonium and persulphate in solution, may have the following properties:

Gravity	55° A. P. I.
Color	30 Saybolt
Sulphur	0.2%
Gums	25 mgs.

By using the solution of ammonium persulphate in the amount and in the manner mentioned the condensed gasoline may then have the following properties:

Gravity	55.4 A. P. I.
Color	28 Saybolt
Sulphur	0.25%
Gums	30 mgs.

Similar and improved results may be obtained with cracked distillates from Mid-Continent and other charging stocks. It will be evident from the foregoing disclosure and example that by the use of the process of the present invention cracked hydrocarbon vapors may be efficiently treated to produce finished gasoline conforming to commercial requirements. The scope of the invention is not, however, to be limited to the specific descriptive material and example given since it is aimed to cover broadly the use of persulphates in the treatment of hydrocarbon oil vapors either as a single treatment or a step in combination with other treatments.

I claim as my invention:

1. A process for refining hydrocarbon distillates which comprises, subjecting said distillate in heated vaporous condition to the action of an aqueous solution of a persulphate.

2. A process for refining hydrocarbon distillates which comprises, subjecting said distillate in heated vaporous condition to the action of an aqueous solution of a persulphate containing sulphuric acid.

3. A process for refining hydrocarbon distillates which comprises, subjecting said distillate in heated vaporous condition to the action of an aqueous solution of ammonium persulphate.

4. A process for refining hydrocarbon distillates which comprises, subjecting said distillate in heated vaporous condition to the action of an aqueous solution of a persulphate of an alkali metal.

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