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TREATMENT OF HYDROCARBON OILS

Jacque C. Morrell, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of South Dakota

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This invention relates to the treatment of hydrocarbon oils and refers more particularly to the treatment of the lower boiling distillates produced in the cracking of the heavier portions of crude petroleums though corresponding distillates resulting from straight run distilling operations may also be treated.

More specifically the invention has reference to the treatment of distillates 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 the distillates to produce marketable motor fuel therefrom.

In one specific embodiment the invention comprises treating hydrocarbon distillates, particularly cracked hydrocarbon distillates containing substantial amounts of gasoline boiling range, with the salts of persulphuric acid which are known as persulphates.

The steps most commonly used to reduce the gum and sulphur content and improve the color stability of cracked distillates may be in general outlined as follows:

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.

While the use of sulphuric acid is quite universal, it possesses a disadvantage in its lack of selectivity in removing undersirable di- and triolefins while leaving substantially unaffected the monoolefins which add to the antiknock value of the gasoline so that when sufficient acid is used to remove the undesirable highly unsaturated hydrocarbons a portion of the less highly unsaturated are 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 intensive 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. The present invention is concerned with the treatments constituting an improvement over the sulphuric acid treatment in that the reactions produced by the reagents used are more selective and may be stopped short of excessive polymerization with resulting increase in yield of finished product. Further advantages will appear hereinafter.

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 which is conveniently prepared by the electrolysis of ammonium sulphate in compartment cells, the ammonium persulphate being continuously formed by anodic oxidation, 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 sulphate 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, caesium, 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.

It is characteristic of the present invention that the persulphates may be used either in aqueous solution or as finely divided solids. When solutions are used practical operations may be conducted generally in the same manner and in the same types of equipment used with sulphuric acid. For example, treatments may be conducted at approximately atmospheric temperatures by circulating the solution of persulphate from the bottom cone of a batch agitator commonly used in oil refineries back into the top thereof through sprays or other distributing means, the circulation being continued until the solution is spent and the desired treating effect has been produced. Similarly the persulphate solutions

may be used in lieu of sulphuric acid in continuous treating plants of the alternate mixer and settler type, the solution being injected into the suction side of centrifugal pumps and being subjected to mixing with the oils during passage therethrough and through lines containing baffling material.

Treatments may also be conducted by agitating oils with solid persulphates, either by chemical stirring devices or by blowing with air, the amounts used depending upon the particular salt employed, the characteristics of the oil to be treated and the degree of refinement desired. 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, 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.

Temperatures employed, while conducting treatments, may be varied over a wide range from temperatures substantially sub-atmospheric in the neighborhood of 20° F. to elevated temperatures as high as 200° F. or higher, this condition being adjusted to suit the needs of the particular stock under treatment and being determined in a large measure by the type of persulphate employed and the degree of refining effect desired. Pressures may also be varied though atmospheric or slightly super-atmospheric pressures are preferred.

The chemical effects produced by the use of persulphates upon hydrocarbon distillates in place of sulphuric acid are in general of the same nature though the extent of polymerization, oxidation and miscellaneous side reactions resulting in the formation of sulfoxy compounds may be better controlled. As an example of treating results obtainable by the use of persulphates as treating agents, a cracked distillate produced from heavy California residuum may be treated with a saturated solution of ammonium persulphate at the rate of approximately six pounds of solid salt per barrel of oil. 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 practiced upon California cracked distillates, that the acid equivalent employed is substantially less.

The results obtained by using ammonium persulphate in the amount mentioned and redistilling to produce gasoline may produce a product having the following properties:

Gravity	55.4 A. P. I.
Color	+30 Saybolt
Sulphur	0.1%
Gums	25 mgs.

The persulphates may be used alone or in combination with other treating reagents and as sulphuric acid, plumbite solution, solution of copper salts, adsorbent earths, neutralization agents. Mixed solutions of persulphates and sulphuric acid are particularly effective. Solutions of persulphates may be used effectively in the treatment of end point cracked distillates requiring no redistillation. Preferably such treatment is followed by treatment with adsorbent earths. It will be evident from the foregoing disclosure and example that by the use of the process of the present invention cracked hydrocarbon distillates 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 oils either as a single treatment or a step in combination with other treatments.

I claim as my invention:

1. A process for refining hydrocarbon distillate which comprises, subjecting said distillate in liquid condition to agitation in the presence of an aqueous solution of ammonium persulphate.

2. A process for refining hydrocarbon distillate which comprises, subjecting said distillate in liquid condition to agitation in the presence of an aqueous solution of ammonium persulphate and sulphuric acid.

JACQUE C. MORRELL.