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TREATMENT OF CRACKED PETROLEUM RESIDUE

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In cracking petroleum for increased yields of gasoline, such as is now very prevalent, there remains a residual material which cannot be economically cracked further into the desired gasoline product, and which is substantially waste, being used only for burning or road-oiling and the like. In accordance with the present invention however, it now becomes possible to obtain from this material products which are of particular utility, and in some instances of a character not approachable by products heretofore known.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

Residual material from cracking, as for instance cracking coil residue or tar may be treated in accordance with the invention, or such material as cycle gas oil which is in effect a distillate from residual material and which is now returned with the feed stock to the cracking zone or is sometimes employed in furnace oil blends, etc.; the choice of the material in any instance depending somewhat upon conditions, desired products in view, etc. The materials which I prefer are highly unsaturated in their hydrocarbon form, and on fractionally distilling cracking coil tar the first or lightest fraction may show unsaturation and aromatics to the extent for instance of 45 per cent by the Kattwinkel method, and a high boiling fraction may show unsaturation and aromatics to the extent of over 80 per cent, and a cycle gas oil may show unsaturation of 40–50 per cent. Carbon muck is first to be eliminated, in a suitable manner. Particularly conveniently this may be accomplished by distillation, thereby leaving such matter as bottoms. The overhead condensate taken off cracked residual petroleum in cracking plant operation where of the character corresponding to cycle gas oil, is in effect a distillate freed from carbon muck, and is available directly for treatment in accordance with the invention for obtaining valuable products, instead of as at present being disposed of by mixing in with fresh feed in the cracking cycle or being used as fuel or such like disposal. The material which is to be treated may however in any case desired be subjected to distillation. Of the overhead distillate taken off, the fractions may be of course cut as closely as may be desired in view of particular circumstances. And from heavier residual materials there may be taken off for instance fractions corresponding generally to gas oil range and fractions corresponding generally to lubricating range, and these may be cut as closely or be sub-divided as finely as may be desired in any given instance. The overhead so obtained, or such selected portions of it as desired, may be advantageously subjected to the action of a small amount of an agent of the characteristics of maleic anhydride in amount sufficient to react with diolefins e. g. five per cent, at a temperature of 200–225° F., for 1 to 4 hours (usually about 2½ to 3 hours), and the product is then washed with an alkali solution, such as 5–20 per cent NaOH, and generally about 10 per cent, and then the oil is further washed with water, and residual water is eliminated in any suitable way, as for instance by blowing with air, at about 200–225° F. The oil from this treatment, or otherwise where this operation is not desired, is now subjected to the action of a small amount of a catalyst, such as of halide character. This may be a halide such as aluminum chloride, or desirably, boron fluoride. The amount of such catalyst may be 2–5 per cent. Usually 3 per cent is satisfactory, and the treating temperature is about 212° F., or in the range 60–250° F. for several hours, as four to twelve. During catalytic treatment, the oil is of course sufficiently agitated to insure thorough contact and action. The oil is now advisably washed with water or alkaline solutions and then water, and any traces of water remaining may be suitably eliminated, as by heat or heat and vacuum or by blowing with air at a temperature about 200–225° F. until clear. The oil may now be treated if desired with sulphuric acid in rather small amount, for instance 1–5 per cent, and a further treatment with clay, in amount for instance 2–5 per cent is advantageous, and at a temperature above 250° F. or up to around 325° F. The oil product finally may be distilled to adjust to desired boiling point. Where wax is present in appreciable amount this is advisably removed at some suitable stage in the procedure, generally after the catalytic operation, and for instance desirably before treating with sulphuric acid or clay. The removal of the wax may be effected by usual measures, or preferably by subjecting to the action of an anti-solvent mixture, as for instance benzol and acetone or the like. Thus, the oil may be mixed with about 3 volumes of a composition of 35 per cent acetone, 52 per cent benzene and 13 per

cent toluene, and be chilled to around 0° F. and wax be filtered or centrifuged.

Unsaturated hydrocarbons initially predominant in the raw material so treated are changed by the treatment, with production of larger saturated or polymerized molecules. And a particularly important characteristic of the products, whether in lighter or heavier range, is their remarkably high gum-solvent action. Thus, a fraction of lubricating oil range so prepared has such high solvent power that where employed as a crankcase lubricant for instance in an internal combustion engine it is not only an excellent lubricating oil but is of particular value in avoidance of ring-sticking. Such oil may also be blended with other lubricating stocks or lubricating oil addition agents if desired, as for instance viscosity improving polymers, pour inhibitors, e. p. agents, etc. Products which are fractionated to a range lighter than corresponding to lubricating oil, as for instance in ranges on the order of gas oil, likewise have this very high gum-solvent property and may be advantageously employed as additions to motor fuel where it is desired to raise the gum-solvent action of the fuel in order to avoid valve-sticking and the like. Kauri-butanol numbers of above 40 are readily obtained in accordance with the present invention.

As an example: A cycle gas oil taken off from the fractionating zone in a cracking coil installation is subjected to the action of boron fluoride in amount of about 3 per cent (conveniently introduced as an ether solution), for 6 hours at 212° F. The product, of boiling range 405–680° F. has a kauri-butanol number 42.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:

1. A process of making lubricating and solvent oils from cracked residual petroleum, which comprises distilling from cracked residuum petroleum fractions corresponding generally to gas oil range and to lubricating range, subjecting a desired fraction thereof to the action of a small amount of maleic anhydride at a temperature of 200–225° F. for a few hours, washing the resultant material with a caustic alkali solution then with water, blowing with air at about 200–225° F., then subjecting the resultant material to the action of a small amount of boron fluoride at 60–250° F. for several hours, washing the resultant material with water, and blowing with air at around 200–250° F.

2. A process of making lubricating and solvent oils from cracked residual petroleum, which comprises distilling from cracked residuum petroleum fractions corresponding generally to gas oil range and to lubricating range, subjecting a desired fraction thereof to the action of a small amount of maleic anhydride at a temperaure of 200–225° F. for a few hours, washing the resultant material, blowing with air at about 200–225° F., then subjecting the resultant material to the action of a small amount of boron fluoride at 60–250° F. for several hours.

3. A process of making lubricating and solvent oils from cracked residual petroleum, which comprises distilling from cracked residuum petrolum fractions corresponding generally to gas oil range and to lubricating range, eliminating diolefines, then subjecting the resultant oil to the action of a small amount of boron fluoride at 60–250° F. for several hours.

4. A process of making lubricating and solvent oils from cracked residual petroleum, which comprises distilling from cracked residuum petroleum fractions corresponding generally to gas oil range and to lubricating range, eliminating diolefines from a desired fraction thereof, then subjecting the resultant oil to the action of a small amount of a halid catalyst at 60–250° F. for several hours.

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