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OXIDATION OF PETROLEUM FRACTIONS

Archibald P. Stuart, Media, Pa., assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

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This invention relates to the preparation of valuable products from cracked petroleum fractions containing dicyclic hydrocarbons.

In the catalytic cracking of high molecular weight petroleum materials to produce lower molecular weight products, principally gasoline, the products include in addition to gasoline certain higher boiling fractions, generally known as catalytic gas oil, which contain dicyclic hydrocarbons. These higher boiling fractions can be recycled to the cracking operation to obtain gasoline from some of the hydrocarbons therein, but some of the hydrocarbons are refractory to cracking and remain in the higher boiling range after the second pass through the cracking operation. Catalytic gas oils are often used only for fuel, and it would be highly desirable to obtain more valuable products from catalytic gas oils obtained after either one or two passes through a catalytic cracking operation.

According to the present invention, valuable products are obtained from catalytic gas oils by hydrogenation thereof and partial oxidation of dicyclic hydrocarbons in the hydrogenation products, which hydrocarbons have one cycloaliphatic ring in the molecule and one aromatic ring in the molecule. The products of the oxidation are believed to be ketones, the carbon atom of the carbonyl group of which is a member of the cycloaliphatic ring.

The oxygenated compounds which are formed in the partial oxidation are useful as petroleum additives, resin intermediates, etc. They can be removed from the unoxidized hydrocarbons by various methods, such as by extraction of the oxygenated compounds by means of a polar solvent, e.g. ethanol, acetone, furfural, phenol, liquid SO_2, etc., by selective adsorption of the oxygenated compounds on an adsorbent such as silica gel, etc.

The partial oxidation according to the invention is not applicable to catalytic gas oils as obtained directly from cracking operations, since such catalytic gas oils generally contain too small amounts of dicyclic compounds containing a cycloaliphatic ring. It is therefore necessary to subject the catalytic gas oil to a hydrogenation prior to the oxidation according to the invention, thereby to convert compounds containing two aromatic rings to dicyclic hydrocarbons containing one aromatic ring and one cycloaliphatic ring. Such hydrogenations are known in the art as such, and any suitable hydrogenation procedure for bringing about this result can be employed.

The oxygenated compounds which are prepared according to the invention are used, in one embodiment, as additives for gasoline or motor oil, for the purpose of reducing combustion chamber deposits in internal combustion engines. Preferably the amount of oxygenated compounds employed for such use is within the approximate range from 0.05 to 5 weight percent based on the hydrocarbon fraction to which it is added, more preferably 0.1 to 2 weight percent.

Alternatively, the oxygenated compounds can be reduced, by catalytic hydrogenation or reduction with sodium and alcohol or other known procedures, to obtain

oxygenated dicyclic compounds in a lesser stage of oxidation, believed to be dicyclic compounds having a hydroxyl group attached to the cycloaliphatic ring. Such compounds may be employed as additives for gasoline or motor oil, for the purpose of reducing combustion chamber deposits, in proportions similar to those described previously.

Alternatively these oxygenated compounds in a lesser stage of oxidation can be chemically dehydrated according to known procedures in order to form dicyclic hydrocarbons which differ from the original dicyclic hydrocarbons in having an olefinic double bond in the 1,2 position in the cycloaliphatic ring. These ultimate dicyclic hydrocarbons can be polymerized or copolymerized with other monomers such as butadiene to form synthetic plastics or rubber-like materials.

The oxidation according to the invention is performed by contacting a suitable fraction containing dicyclic hydrocarbons with a free-oxygen containing gas at a temperature within the approximate range from 150° F. to 300° F. in the presence of a metallic catalyst of the well known drier type, e.g. compounds of manganese, cobalt, copper, lead, iron, etc., e.g. oxides or acetylacetonates of such metals, salts of such metals with carboxylic acids such as acetic acid, benzoic acid, petroleum naphthenic acids, etc. Any known oxidation catalyst of this well known type can be employed. Air is the preferred free-oxygen containing gas, although substantially pure oxygen can be employed if desired. Any known diluent for oxygen can be employed if desired in the oxidation.

The charge stock for the oxidation according to the invention is a hydrogenated petroleum fraction containing at least 5 weight percent based on charge of dicyclic hydrocarbons containing one aromatic ring and one cycloaliphatic ring. Preferably the charge stock contains at least 10 percent of such dicyclic hydrocarbons, e.g. 10 to 50 percent. A major proportion of the charge stock boils within the approximate range from 480° F. to 600° F. Preferably, at least 10 percent of the charge boils below 500° F., and at least 10 percent above 550° F.

The charge stock can be a hydrogenated cracked petroleum fraction containing for example 15 to 50 weight percent of aromatic hydrocarbons, i.e. hydrocarbons containing at least one aromatic ring per molecule. Alternatively, it can be a hydrogenated aromatic concentrate from cracked petroleum containing up to 100 percent aromatic hydrocarbons and obtained by extraction with a selective solvent for aromatics, e.g. furfural, or selective adsorption on a selective adsorbent for aromatics, e.g. silica gel, or by other known methods. Charge stocks having high aromatic contents are preferred.

The charge stock contains a large proportion of dicyclic hydrocarbons having alkyl side chains in the molecule. The conditions employed in the oxidation as disclosed previously are such that the principal oxidation involves carbon atoms in the cycloaliphatic ring, rather than carbon atoms in alkyl side chains. The carbonyl group formed in the oxidation is formed primarily at the alpha carbon atom of the cycloaliphatic ring in the dicyclic molecule, except in cases where that carbon atom has an alkyl radical attached thereto.

Any suitable hydrogenation procedure can be employed prior to the oxidation according to the invention. Preferably, the hydrogenation is performed by passing the charge stock downwardly through a bed of solid hydrogenation catalyst at a space rate within the approximate range from 0.25 to 5.0 volumes of charge per volume of catalyst bed per hour, and at a temperature within the approximate range from 500° F. to 650° F. and pressure within the approximate range from 500 to 2000 p.s.i.g. Any suitable hydrogenation catalyst can be employed, preferred catalysts being metals such as cobalt, molyb-

denum, nickel, etc., or oxides or sulfides thereof, associated with a suitable carrier, e.g. alumina, bauxite, silica-alumina composites. Hydrogenation catalysts for partial hydrogenation of dicyclic aromatic hydrocarbons are well known in the art, and any suitable known catalyst can be employed

The hydrogenation should be performed at conditions which produce a maximum amount of dicyclic compounds containing one aromatic ring and one cycloaliphatic ring and a minimum amount of compounds containing two cycloaliphatic rings. Thus the temperature in the hydrogenation should not be substantially greater than 650° F. and the liquid hourly space velocity is preferably at least 1. In the light of the present specification a person skilled in the art can select proper hydrogenation conditions to bring about the desired result in a given instance.

The following examples illustrate the invention:

Example I

A hydrogenated first pass catalytic gas oil containing 64 weight percent of saturated hydrocarbons and 36 weight percent of aromatic hydrocarbons, of which 15 weight percent are dicyclic hydrocarbons containing one cycloaliphatic ring and 2 percent are dicyclic hydrocarbons containing two cycloaliphatic rings, which hydrogenated gas oil has refractive index n_D^{20} of 1.4879, specific gravity d_4^{20} of 0.8689 and the following Engler distillation in ° F.:

Initial	440	50	524
5	467	60	536
10	479	70	551
20	492	80	574
30	504	90	614
40	514	End (94)	628

is contacted in liquid phase with 5 standard cubic feet of air per liter of charge per hour at a temperature of 250° F. and pressure of 100 p.s.i.g. in the presence of 0.5 weight percent of manganese benzoate based on charge for a period of 5 hours. The product contains oxygen-containing dicyclic compounds, which are extracted from the unoxidized hydrocarbons by means of ethanol.

The previous hydrogenation was performed at 608° F., 800 p.s.i.g., and liquid hourly space velocity of 0.9 volume per volume of catalyst bed per hour, using a catalyst comprising about 20 percent molybdenum disulfide on alumina. The original first pass catalytic gas oil contained about 62 percent saturates and 38 percent aromatics, of which 3 percent based on charge were dicyclic hydrocarbons containing one cycloaliphatic ring.

The oxygen-containing compounds are separated from the extracting solvent, e.g. ethanol, by dilution of the ethanol solution with water in order to precipitate the oxygen-containing dicyclic compounds.

The recovered oxygen-containing dicyclic compounds are in one embodiment employed as additives for gasoline, e.g. a 90–400° F. commercially available leaded gasoline, for the purpose of reducing combustion chamber deposits, using for example 0.1% of additive material, or as additives for motor oil, e.g. a commercially available SAE 10W30 oil, for the same purpose and using for example 0.1% of additive material.

In one embodiment, the oxygen-containing dicyclic compounds are reduced to dicyclic compounds having a hydroxyl group attached to a cycloaliphatic ring by suitable procedure for converting cyclic ketones to cyclic hydroxyl compounds. Thus for example the carbonyl compounds can be contacted with hydrogen at 190° F. to 230° F. in the presence of a catalyst comprising copper oxide and chromium oxide for a period sufficient to convert the carbonyl oxygen to a hydroxyl group. Alternatively, known methods of reduction by hydrogenation with a Raney nickel catalyst can be employed to convert the carbonyl compounds to hydroxyl compounds. The resulting hydroxyl compounds can be employed as additives for gasoline or motor oil in a manner generally similar to that previously described with reference to the carbonyl compound.

The hydroxyl compounds can in one embodiment be dehydrated, for example by contact with alumina at 750° F., to convert the hydroxyl compounds into dehydration products thereof containing a cyclohexene ring and an aromatic ring. These dehydration products have an olefinic double bond in the cycloaliphatic ring in the 1,2 position. They are capable of undergoing vinyl-type addition polymerization at the olefinic double bond. Any suitable known means of bringing about such polymerization can be employed to produce dimers or higher molecular weight vinyl polymers from these unsaturated hydrocarbons. Thus for example they can be polymerized, e.g. at minus 40° F., in dimethyl ether with a sodium naphthalene ($C_{10}H_8Na_2$) catalyst to produce high molecular weight polymers. The polymer can be recovered from the product mixture by adding water to hydrolyze the sodium compounds and filtering the precipitated polymer. The unsaturated hydrocarbons can also be copolymerized with olefins such as propylene or isobutylene, e.g. at minus 150° F., in butane with 0.5 gram of an aluminum chloride or other Friedel-Crafts catalyst per 100 ml. of monomers.

Such polymers of the unsaturated hydrocarbons can be employed, e.g. in 1% concentration, as viscosity index improving additives for petroleum lubricating oil, e.g. a mixed base oil having Saybolt Universal viscosity at 100° F. of about 100 and viscosity index of about 80 prior to addition of the additive.

Example II

In a manner generally similar to that described in Example I, a hydrogenated second pass catalytic gas oil containing about 58 weight percent of saturated hydrocarbons and 42 weight percent of aromatic hydrocarbons of which 20 weight percent are dicyclic hydrocarbons containing one cycloaliphatic ring is partially oxidized in liquid phase to produce oxygen-containing dicyclic compounds which are extracted from the unoxidized hydrocarbons by means of ethanol. The products thus obtained can be further employed in a manner similar to that described in Example I.

The invention claimed is:

1. Process for producing valuable products from petroleum which comprises: contacting a petroleum fraction containing at least 5 weight percent of dicyclic hydrocarbons containing one aromatic ring and one cycloaliphatic ring and containing alkyl substituents on nuclear carbon atoms, a major proportion of which fraction boils within the range from 480° F. to 600° F., in liquid phase with free-oxygen containing gas at a temperature of 150° F. to 300° F. in the presence of a metallic oxidation catalyst, thereby to convert said dicyclic hydrocarbons to dicyclic ketones, said fraction having been previously prepared by hydrogenation of a cracked petroleum fraction to convert dicyclic hydrocarbons containing two aromatic rings into dicyclic hydrocarbons containing one aromatic ring and one cycloaliphatic ring.

2. A petroleum fraction selected from the group consisting of gasoline and motor oil for use in internal combustion engines containing from 0.05 to 5 weight percent of dicyclic ketones produced according to claim 1, said ketones having one aromatic ring and one cycloaliphatic ring, and having alkyl substituents on nuclear carbon atoms.

3. Process for producing valuable products from petroleum which comprises: contacting a petroleum fraction containing at least 5 weight percent of dicyclic hydrocarbons having one aromatic ring and one cycloaliphatic ring and having alkyl substituents on nuclear carbon atoms, a major proportion of which fraction boils within the range from 480° F. to 600° F., in liquid phase with free-oxygen containing gas at a temperature of 150° F. to 300° F. in the presence of a metallic oxidation catalyst,

thereby to convert said dicyclic hydrocarbons to dicyclic ketones, and subsequently reducing said dicyclic ketones to dicyclic hydroxyl compounds, said fraction having been previously prepared by hydrogenation of a cracked petroleum fraction to convert dicyclic hydrocarbons containing two aromatic rings into dicyclic hydrocarbons containing one aromatic ring and one cycloaliphatic ring.

4. A petroleum fraction selected from the group consisting of gasoline and motor oil for use in internal combustion engines, containing from 0.05 to 5 weight percent of dicyclic hydroxyl compounds produced by contacting a petroleum fraction containing at least 5 weight percent of dicyclic hydrocarbons having one aromatic ring and one cycloaliphatic ring and having alkyl substituents on nuclear carbon atoms, a major proportion of which fraction boils within the range from 480° F. to 600° F., in liquid phase with free-oxygen containing gas at a temperature of 150° F. to 300° F. in the presence of a metallic oxidation catalyst, thereby to convert said dicyclic hydrocarbons to dicyclic ketones having one aromatic ring and one cycloaliphatic ring and having alkyl substituents on nuclear carbon atoms, and subsequently reducing said dicyclic ketones to dicyclic hydroxyl compounds, said fraction having been previously prepared by

hydrogenation of a cracked petroleum fraction to convert dicyclic hydrocarbons containing two aromatic rings into dicyclic hydrocarbons containing one aromatic ring and one cycloaliphatic ring.

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