Patented Sept. 6, 1932 1,876,270

UNITED STATES PATENT OFFICE

HERMANN ZORN, OF MANNHEIM, GERMANY, ASSIGNOR TO I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, OF FRANKFORT-ON-THE-MAIN, GERMANY

CONVERSION OF HYDROCARBONS OF HIGHER BOILING POINT INTO THOSE OF LOWER BOILING POINT

No Drawing. Application filed April 14, 1930, Serial No. 444,354, and in Germany April 18, 1929.

The present invention relates to an improved process for the conversion of hydrocarbons of higher boiling point into those of lower boiling point.

I have found that the conversion of hydrocarbons such as mineral oils, tar oils, oils obtained in the destructive hydrogenation of carbonaceous materials, distillation or conversion products thereof and the like into hydrocarbons of lower boiling point by thermal treatment, such as cracking with or without the employment of elevated pressure or by destructive hydrogenation can be carried out so as to furnish particularly good yields, by employing complex organometallic compounds (see Paul Pfeiffer, "Organische Molekülverbindungen" 1927, pp. 231 et seq.) as catalysts, the organometallic compounds which are soluble in the hydrocarbons to be converted being especially applicable according to this invention. Particularly suitable for the process according to the present invention are the metal compounds soluble in hydrocarbon oils of substances of the type of 1.3-diketones, such as acetylacetones, or homologues thereof such as propenyl and butyryl acetone, as for example chromium acetylacetone, $Cr(C_5H_7O_2)_3$, or vanadylacetylacetone, $VO(C_5H_7O_2)_2$, and the like. The said compounds are very resistant to elevated temperatures, their decomposition taking place only at temperatures at which the hydrocarbons treated are split up. The metals thereby set into the free state have a strong catalytic action on the said hydrocarbons. The metal constituent of said catalysts capable of forming complex compounds is usually a heavy metal and is preferably selected from groups 3 to 7 of the periodic system, although the invention is not limited to the employment of these metals. Examples of the said metals are tungsten, molybdenum, chromium, vanadium, manganese,, uranium, niobium, zirconium, cerium, tin, titanium or aluminum. Copper, zinc, cobalt or nickel are also metals very suitable for the production of the said compounds. The said organometallic compounds may be employed singly or mixed together, or in conjunction with other substances having a catalytic action. In many cases it is advantageous to operate by first preparing a solution of the organometallic compound in the starting material to be converted, and then subjecting this solution, if desired after the addition of other substances, to heat treatment, under ordinary or elevated pressure, in the presence or absence of gases or vapours, such as hydrogen or gases or substances which contain or supply hydrogen, nitrogen, ammonia, water vapor and the like.

The catalytic effect of the metallic salts of acetyl acetone is apparently due to the metals set free in very finely divided state by the thermal decompositon of said salts of acetyl acetone, though I do not wish to confine myself to this theory. The said salts have a splitting action and therefore may be made use of both in cracking and destructive hydrogenation processes. Many of them promote also the hydrogenating action, such as the salts of chromium or vanadium or of tungsten or molybdenum or the like and thus have a double effect. The hydrogenating activity of some of the salts of acetylacetone, such as the nickel salt is somewhat reduced if initial materials containing sulphur are employed, probably on account of the fact that nickel in this respect is not immune to sulphur poisoning. The splitting activity of such salts, however, is not impaired even when employing initial materials containing sulphur.

The conversion of hydrocarbons of high boiling point into others of lower boiling point may according to the present invention be carried out at temperatures of between about 300° and 600° centigrade and preferably between about 350° and 450° centigrade. Higher or lower temperatures also come into question. Pressures suitably em-

ployed in the destructive hydrogenation range from 20 to 500 atmospheres or even 1000 atmospheres or more but also higher or lower pressures may be employed.

The following examples will further illustrate the nature of this invention, but the invention is not restricted to these examples. The parts are by weight.

Example 1

2.7 parts of vanadylacetylacetone and 2.6 parts of nickel acetylacetone are dissolved in 100 parts of an American gas oil boiling at from 200° to 300° centigrade. This solution is subjected to destructive hydrogenation, in the presence of hydrogen, at 425° centigrade and under a pressure of 200 atmospheres. In addition to gaseous hydrocarbons 31.1 parts of benzine hydrocarbons, boiling up to 180° centigrade and 57.1 parts of middle oils are obtained.

Example 2

A solution of 3.5 parts of chromium acetylacetone in 100 parts of an oil obtained by the destructive hydrogenation of brown coal under pressure and boiling at from 200° to 350° centigrade is destructively hydrogenated at 425° centigrade under a pressure of 200 atmospheres. In addition to gaseous hydrocarbons, 42 parts of benzine hydrocarbons, boiling up to 180° centigrade, and 47 parts of middle oils are obtained.

Example 3

A solution of 2.5 parts of nickel acetylacetone and 2.5 parts of chromium acetylacetone in 100 parts of an American gas oil boiling between 200° and 300° C. is subjected in an autoclave to a temperature of 450° C., while under a pressure of 20 atmospheres. 38.0 parts of hydrocarbons of the nature of benzine boiling at about 180° C. and 49.1 parts of middle oil are obtained in addition to gaseous products.

What I claim is:—

1. In the thermal decomposition of hydrocarbons of high boiling point into those of lower boiling point, the step which comprises employing a metal compound of a 1.3-diketone soluble in the hydrocarbons to be converted, as a catlyst.

2. In the thermal decomposition of hydro carbons of high boiling point into those of lower boiling point, the step which comprises employing a metal compound of acetylacetone, soluble in the hydrocarbons to be converted, as a catalyst.

3. In thermal decomposition of hydrocarbons of high boiling point into those of lower boiling point at a temperature between 300° and 600° centigrade, the step which comprises employing a metal compound of a 1.3-diketone soluble in the hydrocarbons to be converted, as a catalyst.

4. In the thermal decomposition of hydrocarbons of high boiling point into those of lower boiling point at a temperature between 350° and 450° centigrade, the step which comprises employing a metal compound of a 1.3-diketone soluble in the hydrocarbons to be converted, as a catalyst.

5. In the conversion of hydrocarbons of high boiling point into those of lower boiling point by destructive hydrogenation, the step which comprises employing a metal compound of a 1.3-diketone, as a catalyst.

6. In the conversion of hydrocarbons of high boiling point into those of lower boiling point by destructive hydrogenation at a temperature between 350° and 450° centigrade and at a pressure between 50 and 500 atmospheres, the step which comprises employing a metal compound of a 1.3-diketone soluble in the hydrocarbons to be converted, as a catalyst.

7. In the conversion of hydrocarbons of high boiling point into those of lower boiling point by destructive hydrogenation at a temperature of about 425° centigrade and at a pressure of about 200 atmospheres, the step which comprises employing as a catalyst an acetylacetonete of a metal selected from the group consisting of vanadium, nickel and chromium.

8. In the thermal decomposition of hydrocarbons of high boiling point into those of lower boiling point, the steps which comprise preparing a solution in the said hydrocarbons of high boiling point of a metal compound of a 1.3-diketone, and subjecting this solution to a heat treatment.

9. In the thermal decomposition of hydrocarbons of high boiling point into those of lower boiling point, the steps which comprise preparing a solution in the said hydrocarbons of high boiling point of a metallic compound of acetylacetone, and subjecting this solution to a heat treatment.

10. In the conversion of hydrocarbons of high boiling point into those of lower boiling point by destructive hydrogenation, the steps which comprise preparing a solution in the said hydrocarbons of high boiling point of a metallic compound of a 1.3-diketone, and subjecting this solution to said destructive hydrogenation.

11. In the conversion of hydrocarbons of high boiling point into those of lower boiling pint by destructive hydrogenation at a temperature of about 425° centigrade and at a pressure of about 200 atmospheres, the steps which comprise preparing a solution in the said hydrocarbons of high boiling point of an acetylacetone of a metal selected from the group consisting of vanadium, nickel and chromium, and then subjecting this solution to said destructive hydrogenation.

12. In the thermal decomposition of hydrocarbons of high boiling point into those

of low boiling point at a temperature of between 300 and 600° C., the step which comprises employing as a catalyst a 1.3-diketone of a metal selected from groups three to seven of the periodic system, which compound is soluble in the hydrocarbons to be converted.

13. The process as defined in claim 12 wherein the metal combined with the diketone is a heavy metal.

14. In the thermal decomposition of hydrocarbons of high boiling point into those of low boiling point at a temperature of between 300 and 600° C., the step which comprises employing as a catalyst an acetylacetone of a metal selected from groups 3 to 7 of the periodic system, said acetylacetone being soluble in the hydrocarbons to be converted.

15. In the conversion of hydrocarbons of high boiling point into those of lower boiling point by destructive hydrogenation at a temperature of about 425° C. and a pressure of about 200 atmospheres, the steps which comprise preparing a solution in the said hydrocarbons of high boiling point of an acetylacetone of chromium and then subjecting this solution to destructive hydrogenation.

In testimony whereof I have hereunto set my hand.

HERMANN ZORN.