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## BENZINE HYDROCARBONS OF INCREASED KNOCK-PROOF

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This invention relates to a method of increasing the knock-proof of benzine hydrocarbons and to benzine hydrocarbons having a correspondingly increased knock-proof.

It is known to liberate benzine hydrocarbons, with the aid of fuller's earths and other substances having a large inner surface, of impurities which tend to the formation of resinous substances. This refining process, which is mostly intended to replace the hitherto usual treatment with sulfuric acid, is carried out at relatively low temperatures of about 100-150° C. if normal pressure is employed and the hydrocarbons are treated in liquid phase. Higher temperatures were not employed, since under these conditions the purifying efficacy of the fuller's earth does not appear or drops too rapidly.

We have now discovered that fuller's earths, more particularly those activated by a treatment with an acid or containing small additions of aluminium chloride or polymerising catalysts of similar effect, such as zinc chloride, boron fluoride, phosphoric acid or iron chloride, are capable of materially increasing the knock-proof, if higher temperatures are used. Instead of fuller's earths other natural substances of large surface which contain silica or even silica gel or alumina may be employed.

With the aid of this new process the most various hydrocarbons may successfully be treated, for instance cracked benzenes obtained from natural or synthetic hydrocarbons, benzenes obtained by a polymerisation or benzenes extracted from hydrocarbon gases by activated coal. The process is on principle designed for hydrocarbon mixtures which contain aliphatic olefines with straight chains. It is more particularly suitable for the treatment of hydrocarbons produced by the catalytic conversion of carbon monoxide and hydrogen. In this case the application of our new method is of great importance and its success very surprising, since the synthetic benzenes produced by such a conversion, for instance according to the method of Fischer and Tropsch, mostly show a too low octane number. The process is of course not required for purely aromatic hydrocarbons since these substances possess already a satisfactory knock-proof.

The manner in which our new process may be carried out will now be illustrated more in detail by some examples which are not intended, however, to limit the scope of our invention in any way.

*Example 1.*—A primary benzine, which has been obtained by absorption with activated coal

from hydrocarbon gases resulting in a catalytic conversion of carbon monoxide with hydrogen under a pressure of 7 atms. at a temperature of about 190° C., and which showed a specific weight of 0.692 and an octane number of 40 was passed at a temperature of 180-200° C. in a quantity of 30 liters hourly over 100 kgs. of fuller's earth activated by hydrochloric acid. The content in olefines of the starting material amounted to 41%. A benzine clear as water was obtained as end product which showed the same density of 0.692 and an octane number of 54.

By "primary benzine" we mean benzenes which have been recovered by physical methods, for instance by a distillation or a stabilization, from the material indicated.

*Example 2.*—A stabilized primary benzine recovered by a hydrogenation of carbon monoxide under normal pressure at 190° C. was used as starting material. It showed a density of 0.691 and an octane number of 44, while it started boiling at 35-40° C. and had a boiling limit of 200° C. This material was passed at 180-200° C. with a velocity of hourly 40 liters in contact with 100 kgs. of an activated fuller's earth. An end product clear as water with an octane number of 51 was obtained in continuous operation.

*Example 3.*—A cracked benzine recovered from those primary products of a hydrogenation of carbon monoxide, which boiled between 200 and 233° C., by a thermic cracking treatment carried out under a pressure of 8 atms. at about 520° C. with a cracking period of about half a minute was used as starting material. This cracked benzine had a density of 0.720 and an octane number of 58, it had a light yellow color and contained about 80% olefines. 50 liters of this cracked benzine were hourly led at 300° C. over 100 kgs. of fuller's earth activated by sulfuric acid. A benzine clear as water and having an octane number of 78 was obtained as end product.

*Example 4.*—As starting material served a benzine obtained similarly as explained with reference to Example 3 by the cracking of primary products obtained in a benzine synthesis according to Fischer and Tropsch. This benzine showed a light yellow color, a specific weight of 0.724 and an octane number of 61.5. The cracked benzine was passed at a temperature of 180-200° C. in a quantity of hourly 25 liters over 100 kgs. of a silica gel to which some aluminium chloride was added. A product clear as water was obtained which possessed an octane number of 73.5.

*Example 5.*—A cracked benzine which showed an upper boiling limit of 200° C. and which con-

tained 70% olefines was treated at 250° C. with an activated fuller's earth recovered from Bavarian bleaching clays by means of sulfuric acid. The octane number was thus improved from 65 to 77. After some time the capability of the fuller's earth to increase the octane number dropped so that the octane number of the starting material was increased only to about 70 when about 100 kgs. of the cracked benzine had been treated per kilogram of the fuller's earth.

*Example 6.*—A cracked benzine obtained in a similar manner as the starting material mentioned in Example 4 was treated at 200° C. with silica gel. An end product clear as water having a specific weight of 0.725 and an octane number of 70 was obtained.

*Example 7.*—A gas oil fraction of the primary products of the synthesis of benzine from carbon monoxide and hydrogen, which had a boiling range of 200–330° C. was cracked under gentle conditions, viz. in a pipe furnace under a pressure of about 8 atms. above normal and at a temperature of 520° C. in such manner that the material remained for 30 seconds in the reaction zone. A benzine of the specific weight of 7.20 which contained preponderably mono-olefines and possessed an upper boiling limit of 200° C. and an octane value of 58, was obtained in a yield of 75%. This cracking benzine was treated at 250–400° C. with fuller's earth. The octane number was thereby increased to about 78, while only about 25% were converted into gases, i. e. into products which were gaseous under normal conditions of temperatures (20° C.) and pressure. When the same gas oil fraction was cracked under severe conditions, for instance under a pressure of 8 atms. above normal, at 540° C. and with a reaction period of 300 seconds, the yield amounted only to 65%, while 35% were converted into gases.

The following general conditions of operation may be given, which show the manner in which our invention can be put into practice.

The highest value is approximately attained when about 50–60 kgs. benzine have passed one kg. of the fuller's earth or the other active material employed. When about 100 kgs. benzine have passed 1 kg. fuller's earth, we may attain about 40% of the highest value. These figures show approximately in which manner the efficacy of the fuller's earths drops in the course of the operation.

The treatment with fuller's earth for the improvement of the octane number may also be carried out at temperatures which exceed the temperature limits mentioned in the examples given above.

The operating temperature will advantageously be increased more particularly when the effect of the fuller's earth used with respect to the improvement of the octane number diminishes. Temperatures of 300–400° C. may be employed after a more extended use of the fuller's earth.

It is advantageous to perform the increase of temperature which is required by the drop of the effect of the fuller's earth in improving the octane number, only gradually and from batch to batch. In this case no cracking worth speaking of occurs nor is any remarkable quantity of the material lost by the formation of gases. If the temperature is increased too rapidly, the fuller's earth would have so high an activity in the individual treating stages that a substantial part of the hydrocarbons would be cracked so that a large quantity of hydrocarbons would be formed which

are gaseous under normal conditions of temperature and pressure.

Even if the operating temperature is increased only slowly and carefully, it cannot always be avoided with certainty that the benzines recovered in the treatment with the fuller's earth are slightly discolored. These discolored products may subsequently be subjected to a refining treatment.

Not all known fuller's earths are suitable for increasing the octane number to the same extent. We have found that the earths activated by hydrochloric acid or sulfuric acid are most useful. We have found excellently suited for instance those fuller's earths which are recovered from Bavarian clay products by a treatment with acids, such as the products which are on the market under the trade names "Granosil" or "Tonsil".

The operating temperature must be adjusted within the range specified above to the specific fuller's earth or the other specific active material employed as well as to the time during which this material has already been used and to the starting benzine under treatment.

The effect of the fuller's earths and the similar materials mentioned above is not bound to a specific limit of the pressure. We are therefore enabled to even operate under any optional pressure above normal, but generally operate in gaseous phase.

The lower limit of the velocity with which the hydrocarbons under treatment are contacted with the active material may be determined merely in accordance with economic considerations, since we succeed in the improvement of the knocking qualities of the various starting materials, and may thus obtain therefrom highly knock-proof benzine, even if very low velocities are employed. The velocity can advantageously be increased to such an extent that for instance 30–40 liters of the starting benzine are hourly contacted with 100 kgs. of the fuller's earth. We may, however, pass even as much as 90 liters or more of the starting benzine hourly with 100 kgs. of the contact substances.

The following modification, amongst others, is of great practical importance.

Hitherto when it was intended to produce highly knock-proof fuels from hydrocarbon mixtures mainly containing saturated paraffinic hydrocarbons, one was compelled to conduct the cracking operation in such manner that a large proportion of aromatic hydrocarbons was formed in order to attain the high knock-proof required. This aim could be reached only by the use of rigorous or severe cracking conditions which, however, led to the formation of large quantities of methane and other hydrocarbons which are gaseous under normal conditions of pressure and temperature. When gentle cracking conditions are employed, in order to reduce these losses caused by the formation of gaseous hydrocarbons, the cracked benzines produced are not satisfactorily knock-proof. According to the present invention it is however possible to employ gentle cracking conditions, which lead in dependency on the boiling range of the starting material for instance to the formation of 75–80% or even more than 90% olefines, and thus to materially reduce the losses suffered by the formation of the gaseous hydrocarbons mentioned, while nevertheless a satisfactory octane value may be obtained. To this end we subject the products obtained in cracking under gentle conditions, of a mixture

mainly consisting of paraffinic hydrocarbons, to an additional subsequent treatment with fuller's earth or similar materials in the manner described above.

Even the benzines recovered by the cracking, under rigorous conditions, of such mixtures mainly comprising paraffinic hydrocarbons may be improved with regard to their octane value by a treatment in accordance with the present invention. The benzines obtained in a cracking treatment carried out under gentle conditions contain, however, a considerably larger percentage

of constituents which are capable of being improved so that the yield is materially better when gentle cracking conditions are employed, as shown by Example 7 mentioned above.

5 Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

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