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TREATMENT OF MOTOR FUEL

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This invention relates particularly to the treatment of relatively low antiknock value motor fuels such as paraffinic gasolines for improving their antiknock value by cracking reactions. While particularly applicable to treatment of straight-run gasolines, it may also be employed to improve the knock rating of gasolines of intermediate or fair value in this respect or may even be employed to further increase the knock rating of gasolines resulting from the cracking of the heavier portions of petroleum such as the heavy distillates and residual fractions.

In a still more specific sense the invention is concerned with a reforming process involving the use of novel and specially selective catalytic materials which are characterized by the use of special methods for their preparation which will be described in detail in the succeeding specification.

As a result of extended researches by numerous independent investigators it has been established that the worst knocking hydrocarbons are those of a straight-chain paraffinic structure. This knocking tendency is lessened as the structure becomes more condensed as in the branched chain or iso paraffins and is further lessened when any paraffin is dehydrogenated to produce the corresponding mono or di-olefinic compounds, although the latter are not particularly desirable as motor fuel constituents since they have too great a tendency to form gums during storage of gasolines. Cyclic hydrocarbons such as naphthenes or aromatics have relatively low knocking tendencies, but the actual knock rating of individual compounds depends upon the presence of substituent groups which may obviously be either of an alkyl or an alkylene character.

Hydrocarbon motor fuel fractions produced from either the straight run or the destructive distillation of petroleum fractions or by corresponding processes involving destructive distillation of coals or shales and similar materials contain varying proportions of paraffins, olefins, naphthenes, and aromatics although olefinic compounds are substantially absent from straight-run gasolines and aromatic hydrocarbons are ordinarily present only in minor proportions. To improve the anti-knock value of gasolines, thermal cracking without catalysts is frequently resorted to, but in such cases there is a definite practical limit to the improvement in octane number which can be obtained on account of the mixed character of the decomposition reactions which occur in straight cracking. Following primary reactions of dehydrogenation corresponding to the initial stages of cracking there are recombination reactions which result in formation of cyclic compounds and even further decomposition of these secondary products so that as a rule the yields of gasoline-boiling range material are undesirably low when attempts are made to increase the antiknock value beyond a certain point.

A variety of catalytic materials have been tried in cracking of the heavier portions of petroleums and in reforming primary gasolines and some of these have given fairly good results. Catalysts to be suitable for use in reforming must be possessed of a refractory character and show a more or less selective effect in fostering dehydrogenation and isomerization reactions in preference to reactions involving extensive rupturing of the carbon to carbon bonds so that for example butane and butenes are produced by the decomposition of an octane rather than octenes by straight dehydrogenation reactions. Similarly, suitable catalysts should show a selective action in dehydrogenating saturated ring compounds such as napthenes and it is with the use of selective catalysts meeting these general requirements that the present invention is concerned.

In one specific embodiment the present invention comprises a process for catalytically reforming gasolines of inferior antiknock value involving the use of catalysts comprising aluminum oxide, chromium sesquioxide, and reduced nickel, the two last named components being in minor proportions in respect to the alumina and the nickel being present in amounts less than the chromium oxide.

The preferred catalysts are prepared by a special and specific procedure which may be briefly summarized as follows: An aqueous solution containing the nitrates of chromium and aluminum in proper relative proportions for producing a catalyst containing the alumina and chromia in the proper ratio is treated with an alkali metal hydroxide such as sodium hydroxide to first precipitate the hydroxides of aluminum and chromium. These hydroxides are then redissolved in just the requisite excess of alkali to form a clear solution which will then comprise sodium aluminate, and sodium chromite. To this solution a composite solution containing nickel nitrate and ammonium nitrate is added to form a mixed precipitate of nickel, chromium, and aluminum hydroxides. The precipitate is washed with water to the removal of substantially all adsorbed salts and then dried and reduced in a current of hydrogen at gradually increasing temperatures up

to 425–450° C. It has been found that under these conditions substantially all of the chromium oxides are reduced to chromium sesquioxide and that the nickel oxides are substantially all reduced to metallic nickel. By this method of preparation it is obvious that the components of the catalysts are in a state of extremely intimate admixture so that each component is able to best exert its promoting effect upon the other components.

The subject of promoter catalysis is one which is difficult to analyze and most of the knowledge thereof is on an empirical basis. In the present instance the experimental evidence indicates that the effect of small additions of nickel greatly accentuates the selective properties of alumina-chromia mixtures so that reforming of gasolines to improve their antiknock value is accomplished more effectively than when employing chromium oxides alone, alumina-chromia catalysts alone, or reduced nickel alone on supports such as alumina.

The present types of catalyst may be employed in any of the ordinary process flows common to commercial reforming plants or special types of plant equipment may be used. The majority of reforming plants in operation at the present time are of the coil and chamber type wherein the oil to be cracked is passed through a continuous tubular element and brought more or less quickly up to a temperature at which the rate of cracking is high enough for commercial purposes. The heated products are then admitted to an enlarged reaction zone in which the conversion reactions are substantially completed. Following this chamber or zone, the remainder of the elements of the plant are concerned with the fractionation of products with removal of light distillates as an overhead, the recycling of intermediate and partially converted cuts and the removal of heavy and readily carbonizable residue. In plants of this character a catalyst is more conveniently placed in the reaction chamber as a filler, commonly in the form of cylinders or granules of about 6 to 10 mesh diameter.

While the catalysts of the present process are utilizable in the ordinary run of refinery equipment, they are better employed in parallel tubular heaters composed of tubes of relatively small diameter so that heat necessary for the endothermic reactions of reforming is more easily supplied. Such arrangements will take the place of ordinarily large diameter reaction chambers and are usually best preceded by a vaporizer and preheater to bring the gasoline to a suitable temperature for reforming treatment. It is comprised within the scope of the invention to utilize the method of operation in which the catalysts are employed alone or with other refractories as filling materials in regenerative furnaces which are alternately heated by the passage of flue gas and then used as a means of heating and reforming gasoline vapors.

Owing to the generally high catalytic potency and selectivity of the present types of catalysts the range of temperatures which are employed when they are used in reforming is somewhat lower than that employed in ordinary thermal or other catalytic reforming processes and is comprised within the approximate range of 400–500° C. though somewhat higher temperatures may be employed in the case of certain refractory stocks. There is ordinarily no necessity of using pressures materially above atmospheric since the selectivity of the reactions leading to the formation of high antiknock value hydrocarbons may even be somewhat reduced by this practice although a balance must ordinarily be struck between the quality and yield of the reformed gasoline products obtained and the capacity of commercial equipment.

The following examples are given to indicate the commercial value of the process although not with the intention of limiting the scope of the invention in strict accordance with the data presented.

A catalyst typical of those utilizable according to the present invention was prepared as follows. An aqueous solution containing 175 parts by weight of chromium nitrate, $Cr(NO_3)_3.9H_2O$, and 375 parts by weight of aluminum nitrate, $Al(NO_3)_3.9H_2O$, was treated with an aqueous solution of sodium hydroxide to primarily precipitate the hydroxides of aluminum and chromium and then redissolve the primary precipitate to form a solution of sodium aluminate and sodium chromite. To the clear solution, 35 parts by weight of nickel nitrate and 400 parts by weight of ammonium nitrate in joint solution were added slowly with stirring to form a mixed precipitate of nickel, chromium, and aluminum hydroxides. The precipitate was washed by decantation and mechanical filtration, dried at a temperature of 110° C. and finally reduced in a current of hydrogen at gradually increasing temperatures from about 200 to 450° C. The granulation of the material was effected after the drying stage and before reduction.

The above catalyst was employed in reforming a Mid-Continent straight-run gasoline having an octane number of 44 by the motor method. A temperature of 450° C. and substantially atmospheric pressure was employed. An 85% yield of 65 octane number gasoline was obtained having the same boiling range as the original charge. At a temperature of 500° C. the octane number was raised to 71 with a 75% yield.

Using a Pennsylvania straight-run gasoline at a temperature of 500° C., the octane number was increased from 44 to 78 with a 75% yield.

The character of the present invention is apparent from the foregoing specification and limited numerical data introduced, although neither section is intended to be unduly limiting.

I claim as my invention:

1. A process for reforming hydrocarbon distillates of approximate motor fuel boiling range which comprises subjecting said distillate at temperatures adequate to effect the reforming thereof to contact with catalytic material comprising essentially a major proportion of alumina and minor proportions of chromium sesquioxide and nickel.

2. A process for reforming hydrocarbon distillates of approximate motor fuel boiling range which comprises subjecting said distillate at temperatures of the order of 400–500° C. to contact with catalytic material comprising essentially a major proportion of alumina and minor proportions of chromium sesquioxide and nickel.

3. A process for reforming hydrocarbon distillates of approximate motor fuel boiling range which comprises subjecting said distillate at temperatures of the order of 400–500° C. to contact with catalytic material comprising essentially a major proportion of alumina and minor proportions of chromium sesquioxide and nickel, the weight of said sesquioxide being greater than the weight of said nickel.

4. A process for reforming hydrocarbon dis-

tillates of approximate motor fuel boiling range which comprises subjecting said distillate at temperatures of the order of 400–500° C. under substantially atmospheric pressure to contact with catalytic material comprising essentially a major proportion of alumina and minor proportions of chromium sesquioxide and nickel, the weight of said sesquioxide being greater than the weight of said nickel.

5. A process for reforming hydrocarbon distillates of approximate motor fuel boiling range which comprises subjecting said distillate at temperatures of the order of 400–500° C. under substantially atmospheric pressure to contact with granular catalytic material comprising approximately 65% by weight of alumina, 30% by weight of chromium sesquioxide, and 5% by weight of nickel.

6. A process for reforming hydrocarbon distillates of approximate motor fuel boiling range which comprises subjecting said distillate at temperatures of the order of 400–500° C. under substantially atmospheric pressure to contact with granular catalytic material produced by jointly precipitating aluminum and chromium hydroxides from aqueous solution by the addition of alkali metal hydroxides thereto, redissolving the precipitate in an excess of alkali hydroxide, adding a joint solution of nickel nitrate and ammonium nitrate in proportions adequate to the formation of a mixed precipitate of nickel, chromium, and aluminum hydroxides in which the aluminum hydroxide constitutes the major proportion, washing, drying, and granulating the composite precipitate and subjecting said precipitate to the action of hydrogen at temperatures not exceeding 450° C. to effect the production of chromium sesquioxide from chromium hydroxide and nickel from nickel hydroxide.

7. A process for reforming hydrocarbon distillates of approximate motor fuel boiling range which comprises subjecting said distillate at temperatures of the order of 400–500° C. under substantially atmospheric pressure to contact with granular catalytic material produced by jointly precipitating aluminum and chromium hydroxides from aqueous solution by the addition of alkali metal hydroxides thereto, redissolving the precipitate in an excess of alkali hydroxide, adding a joint solution of nickel nitrate and ammonium nitrate in proportions adequate to the formation of a mixed precipitate of nickel, chromium, and aluminum hydroxides in which the aluminum hydroxide constitutes the major proportion, washing, drying, and granulating the composite precipitate and subjecting said precipitate to the action of hydrogen at temperatures not exceeding 450° C. to effect the production of chromium sesquioxide from chromium hydroxide and nickel from nickel hydroxide.

8. A process for increasing the anti-knock value of hydrocarbons boiling in the gasoline range which comprises contacting the same at reforming temperature with a catalyst comprising a major proportion of alumina and minor proportions of chromium sesquioxide and nickel.

9. A process for increasing the anti-knock value of hydrocarbons boiling in the gasoline range which comprises contacting the same at reforming temperature with a catalyst comprising a major proportion of alumina and minor proportions of chromium sesquioxide and nickel, the weight of the chromium sesquioxide being greater than that of the nickel.

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