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PROCESS FOR PRODUCING DIESEL OILS

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Up to the present no successful attempt has been made to replace the gas oils used for driving Diesel engines, by distillation or extraction products of carbonaceous substances such as pit-coal or brown-coal, as no one has succeeded in producing the ignition of such substances in a Diesel engine. Only in Diesel engines working under particularly high compression is it possible to make use of the products of the distillation of brown coal or pit-coal tar. However it has been proposed to mix tar oils, such as pit-coal tar oil with gas oil, but here again there has been no satisfactory result. On the one hand the asphaltic and resinous constituents dissolved in the pit-coal tar oil produce in the combustion chamber of the Diesel engine deposits of carbon, and on the other hand the ignition properties of such a mixture of fuels are unsatisfactory. The gas oil added favourably affects the readiness of the mixtures to ignite to such an extent that there is ignition in the Diesel engine, but the delay in ignition peculiar to gas oil, when gas oil is used in admixture with tar oils, is insufficient, so that the mixture injected into the Diesel engines gives an extremely short burning period. The sharp increase of pressure produced by the high speed of combustion of the mixture is the cause of the considerable knocking when such difficultly ignitable fuels are used in Diesel engines.

It is known that those middle and heavy oils boiling at temperatures lying between 200-320° C. which are obtained by the catalytic conversion of carbon monoxide and hydrogen into synthetic hydrocarbons, are suitable for use in Diesel engines. These oils excel by reason of their readiness to ignite, and in their behaviour in the engine cylinder resemble very closely the gas oils used up to the present in Diesel engines. It would therefore be logical to assume that the use in Diesel engines of mixtures of tar oils and the synthetic oil hereinbefore referred to would lead to the same unsatisfactory results.

It has been found that the tar oils, such as pit-coal tar oils, brown coal tar oils, low temperature distillation tars, shale oils, wood tar and the like, which are obtained during the high or low temperature coking of carbonaceous bituminous substances such as pit-coal, brown coal, shale, wood, peat and the like, are so improved by the addition of synthetic oil that by such addition to them a fuel is produced that is suitable for use in Diesel engines. Those constituents of paraffin hydrocarbons obtained by the catalytic hydrogenation of carbon monoxide at

ordinary or slightly altered pressure which boil at over 200° C. have proved particularly suitable for this purpose.

By the use of the hydrocarbon oils obtained by the catalytic hydrogenation of carbon monoxide it is possible, as with the tar oils before referred to, to improve other hydrocarbons poor in hydrogen, such for example as the extraction products of pit coal and brown coal; products of a mild hydrogenation—and hydrocarbons that are solid under normal conditions can also be treated in this manner.

If these solid hydrocarbons are insoluble in the paraffinic oils, dissolving agents are also used, the effect of which is to dissolve the solid bodies or to distribute them in a very fine state of division. The paraffinic oils are added to the products poor in hydrogen in such quantity that the resulting mixture is one which will readily ignite in the Diesel engine. The proportions which are suitable depend upon the nature of the substances used, and the best conditions under which the mixing is effected are in every case determined by simple experiment.

Whereas hitherto for the purpose of converting any hydrogenation oil into a usable Diesel oil it has been essential to increase by expensive means the hydrogen content to about 12-13%, according to the present invention the simple mixing together of the hydrocarbon oils rich in hydrogen and a hydrogenation product with a considerably smaller content of hydrogen produces a very good usable Diesel oil. The possibility of avoiding large additions of hydrogen is of very great practical importance because it is precisely the addition of hydrogen in large quantities—that is to say the carrying out of considerable hydrogenation—that necessitates the use of particular agents such as catalysts, or requires high pressures or considerable losses of gaseous constituents. When using the products poor in hydrogen which are hereinbefore referred to, it is necessary however to ensure that the content of hydrogen is at least so high that the added hydrocarbon oils rich in hydrogen such as are obtained by the catalytic hydrogenation of carbon monoxide, do not cause excessive quantities of hydrocarbons to be separated out as a flocculent precipitate from the products poor in hydrogen. Occasionally it has proved to be advantageous to precipitate from the products poor in hydrogen the substances which are capable of precipitation by means of the hydrocarbons rich in hydrogen, with a small quantity of another hydrocarbon rich in hydrogen, such as gas

oil. The products from which the precipitated substances have been removed by filtration give an extremely good Diesel oil when mixed with the hydrocarbon oils rich in hydrogen produced from a mixture of carbon monoxide and hydrogen. By this means substances such as extracts from coal to which only a little hydrogen has been added can be employed in a very useful manner. The insoluble constituents obtained by previous precipitation can if required be converted by a further addition of hydrogen into a substance which likewise gives a very valuable Diesel fuel when mixed with hydrocarbons rich in hydrogen. If conditions are suitable, the hydrocarbon oils which have a relatively very low content of hydrogen and which have been separated out from the insoluble substances are first subjected to a further weak hydrogenation before they are mixed with the products rich in hydrogen. Hydrogenation can be carried out under particularly simple reaction conditions.

It is of particular advantage to the present process that when the two components are mixed together there is not only an improvement in the quality of the mixture for engines but also a refining of the components poorer in hydrogen. Thus it is already known that the added synthetic paraffin hydrocarbons separate out from the hydrocarbons poor in hydrogen the constituents which in the Diesel engine lead to the deposition of carbon. The separated substances may be very simply removed from the mixture of oils, the refining agent, namely the synthetic paraffin hydrocarbons, preferably remaining in the hydrocarbons poor in hydrogen, to be burnt in the Diesel engine. Thus the addition of these synthetic paraffin hydrocarbons renders possible the use of the crude tar oils directly instead of being obliged to commence with the much more expensive distillation products.

The mixture of oils together with the substances separated out may be treated first with lye and then with fuller's earth or alternatively it may be treated with fuller's earth alone.

By mixing an oil whose specific gravity is near to 1, with a synthetic hydrocarbon oil which has a specific gravity of approximately 0.75, a mixture is obtained which has a specific gravity of about 0.84 to 0.86 just as have the Diesel oils hitherto used.

It is desirable to favourably influence the solidification point. Whereas the tar oils have a very low solidification point and the synthetic paraffin hydrocarbons employed according to the process of the invention have a high solidification point, the Diesel oil produced by mixing together the two components has a solidification point, normal for Diesel oils, of for example -20°C .

The process is hereinafter explained by means of examples.

Example 1.—75 parts by weight of crude heating oil obtained from pit-coal tar and having a specific gravity of 1.09, which oil will not ignite in a Diesel engine, are intimately mixed at ordinary temperature with 100 parts by weight of a paraffin oil of a specific gravity of 0.76, an initial boiling point of about 200°C ., and a solidification point of $\pm 0^{\circ}\text{C}$. obtained from carbon monoxide and hydrogen. On admixture black insoluble substances and liquid impurities are removed from the pit-coal tar oil. The mixture of oils is treated at a slightly raised temperature first with a 30% solution of caustic soda and then

with fuller's earth. After filtration 170 parts by weight of a clear unvarying Diesel oil having a specific gravity of 0.85 is obtained. This Diesel oil ignites very readily and has an excellent solidification point, which lies at -20°C .

Example 2.—70 parts of brown coal tar boiling at temperatures lying between 200 and 300°C ., whose specific gravity is 0.907 and which has a solidification point of -23.5°C ., are mixed with 30 parts by weight of a paraffin oil obtained from carbon monoxide and hydrogen whose specific gravity is 0.77 and which boils at temperatures lying between 200 and 310°C . After the removal of the constituents separated out, a Diesel oil is obtained which has a specific gravity of 0.866 and a solidification point of -16.5°C . This oil was found to be very satisfactory when tested in a Diesel engine.

Example 3.—65 parts of a pit-coal distillate boiling at temperatures lying between 215 and 360°C ., having a specific gravity of 1.07 and a solidification point of -29°C ., are mixed with 35 parts of the same synthetic oil as used in Example 2. After the removal of the constituents separated out and after treatment of the mixture of oils with caustic soda and fuller's earth, a Diesel oil is obtained which has a specific gravity of 0.96 and a solidification point of -18°C . and which ignites very readily.

Example 4.—65 parts of a fraction, boiling at between 200 and 320°C . of a tar obtained from pit-coal by low temperature distillation and which has a specific gravity of 0.991 and a solidification point of -27.5°C . is mixed with 35 parts of the same synthetic oil as used in Example 2. After the removal of the constituents separated out by treatment of the mixture of oils with fuller's earth, a Diesel oil is obtained which has a specific gravity of 0.912 and a solidification point of -20.5°C .

Example 5.—70 parts of a fraction, boiling at between 200 and 320°C . of a dephenolated tar obtained from pit-coal by low temperature distillation, which fraction has a specific gravity of 0.966 and a solidification point lying below -50°C . are mixed with 30 parts of the same synthetic hydrocarbon as used in Example 2. After the constituents separated out have been removed, a Diesel oil is obtained which has a specific gravity of 0.707 and a solidification point of -23°C .

Example 6.—70 parts of a hydrogenation oil obtained from brown coal in the first hydrogenation stage, having thus been only incompletely hydrogenated, whose solidification point is 17.5°C . having a specific gravity of 0.901 and a boiling range of 200 to 320°C . is mixed with 30 parts of the same synthetic oil as used in Example 1. After the removal of the separated off constituents by treatment of the mixture of oils with fuller's earth, a Diesel oil is obtained whose specific gravity is 0.861 and which has a solidification point of -15°C . This oil when tested on an engine proved to be excellent Diesel oil which can be stored indefinitely without deterioration.

Example 7.—A hydrogenation oil obtained from pit-coal in the first hydrogenation stage, and which has a boiling range of from 200 to 320°C ., a specific gravity of 0.974 and a solidification point lying below -40°C . was used as the component poor in hydrogen. The content of acidic constituents of this hydrogenation oil which had been incompletely saturated with hydrogen, amounted to 16.0%. 60 parts of this hydrogenation oil were mixed with 40 parts of the same

synthetic oil as used in Example 2. After the removal of the separated-off constituents a Diesel oil was obtained having a specific gravity of 0.895 and a solidification point of -20°C . This mixture likewise can be stored without deterioration.

Example 8.—70 parts of a liquefied extract of pit-coal which has been obtained by mild hydrogenation and which boils at between 200 and 320°C , while having a specific gravity of 1.028 and a solidification point of -43.5°C ., are mixed with 30 parts of the same synthetic oil as used in Example 2. When the constituents separated-off are removed a Diesel oil is obtained which has a specific gravity of 0.946 and a solidification point of -22.5°C .

Example 9.—80 litres of a heavy anthracene oil are mixed at ordinary temperature with 20 litres of a gas oil having a content of hydrogen of about 8%. There is at once a heavy precipitation of asphaltic substances, which are filtered off. The filtrate is mixed with the same volume of a mixture of hydrocarbons which boil at between 200 and 310°C ., and which have been obtained by the catalytic hydrogenation of carbon monoxide, the product being a mixture which is excellent as a fuel for Diesel engines.

We claim:

1. A fuel for driving Diesel motors, consisting of paraffinic oils obtained by the catalytic reduction of carbon monoxide to hydrocarbons and having boiling points ranging from 200°C . to 320°C . and of carbonaceous products poor in hydrogen in simple admixture.

2. A fuel for driving Diesel motors, consisting of paraffinic oils rich in hydrogen obtained by the catalytic hydrogenation of carbon monoxide having boiling points ranging from 200°C . to 320°C ., and of liquid carbonaceous products poor in hydrogen in simple admixture.

3. A fuel for driving Diesel motors, consisting of paraffinic oils rich in hydrogen obtained by the catalytic hydrogenation of carbon monoxide and having boiling points ranging from 200°C . to 320°C . and of solid carbonaceous products poor in hydrogen in simple admixture.

4. A fuel for driving Diesel motors, consisting of paraffinic oils rich in hydrogen obtained by the catalytic hydrogenation of carbon monoxide and having boiling points ranging from 200°C . to 320°C . and of tar oils obtained by the distillation of carbonaceous materials in simple admixture.

5. A fuel for driving Diesel motors, consisting of paraffinic oils rich in hydrogen obtained by the catalytic hydrogenation of carbon monoxide and having boiling points ranging from 200°C . to 320°C . and of extraction products from carbonaceous materials in simple admixture.

6. A fuel for driving Diesel motors, consisting of paraffinic oils rich in hydrogen obtained by the catalytic hydrogenation of carbon monoxide and having boiling points ranging from 200°C . to 320°C . mixed with hydrogenation products of carbonaceous materials of nature differing from and poorer in hydrogen than the paraffinic oils.

7. A fuel for driving Diesel motors, consisting of paraffinic oils obtained by the catalytic reduction of carbon monoxide to hydrocarbons and having boiling points ranging from 200°C . to 320°C . and of carbonaceous products poor in hydrogen, in such proportions that the mixture has the same specific gravity as ordinary Diesel oils.

8. A fuel according to claim 7, for driving Diesel motors, which contains, in addition, solvents for the carbonaceous substances that are poor in hydrogen and are insoluble in the paraffinic oils rich in hydrogen.

9. A fuel for driving Diesel motors, according to claim 6, wherein the hydrogenated products of carbonaceous materials are obtained by hydrogenation of the said materials to such an extent that no appreciable quantities of hydrocarbons flocculate on admixture with the paraffinic oils rich in hydrogen.

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