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AMENDED SPECIFICATION

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PATENT SPECIFICATION



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COMPLETE SPECIFICATION

Improvements in and relating to Processes for the Manufacture of Diesel Fuels

We, FRIEDRICH UHDE, of Doggingstrasse 12, Dortmund, Germany, and THEODOR WILHELM PRIERMANN, of Castrop-Rauxel, Germany, both German citizens, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 The content of hydrogen in crude oils or fuel oils which are obtained by distillation of petroleum or by hydrogenation of brown coal, oil shale or the like, should according to the present day standards, not be substantially less than 12%. Oils which contain a considerably smaller proportion of hydrogen, such as are obtained, for example, by coking or distillation of mineral coal or brown coal, are not directly suitable for driving Diesel engines. It is however, possible to make such oils which are poor in hydrogen more or less suitable for driving Diesel engines. Thus, by employing 25 high compression pressures and by making considerable structural alterations to the cylinder head and combustion chamber, tar oil, for example, can be satisfactorily used in Diesel engines, but a special priming oil is then necessary for starting and when idling.

Processes are known by which oils which are poor in hydrogen and have the same boiling limits as Diesel oil can be economically manufactured. For example, by hydrogenating various kinds of coal, if suitable contact catalysts are used and the supply of hydrogen is suitably regulated, synthetic liquid hydrocarbons can be manufactured in which the hydrogen content is considerably below the above indicated standard of 12%. These oils which are poor in hydrogen can also be made, for example, 45 by further hydrogenation of primary bitumens with condensing contact cata-

lysts. These synthetic liquid hydrocarbons have a hydrogen content of 8-9%. Such oils poor in hydrogen are of course considerably cheaper than the oils rich in hydrogen which are manufactured by synthetic processes. A process for treating oils poor in hydrogen, which can be manufactured cheaply from coal, so as to enable them to be used in Diesel engines in place of ordinary Diesel oil, would therefore be very valuable. It has been found that the combustibility of hydrogenated oils poor in hydrogen is insufficient and that perfect combustion of these hydrogenated oils can only be obtained in Diesel engines at very high combustion temperatures. When starting and running idle, suitable auxiliary fuels must be employed in order to keep the engine running. A method of this nature is unsuitable for practical use.

The object of the present invention, therefore, is to improve the combustibility of Diesel oils which are poor in hydrogen and are manufactured synthetically by hydrogenation of mineral coal, brown coal and the like. Such oils can be obtained, for example, by a single-stage hydrogenation of coal to form oils poor in hydrogen or by a two-stage process in which, in the first stage, either a coal extract or a primary bitumen is obtained, which is then converted in a second stage into the oils poor in hydrogen.

The term "primary bitumen" means a substantially ash-free, fusible, bitumen-like hydrogenation product soluble in aromatic substances and naphthalene which is obtained by treatment of coal with insufficient hydrogen under pressure and at temperatures of about 380-420° C. in the presence of the aforesaid solvents. The term "coal extract" means an extraction product obtained from bituminous coal by means of solvents without the action of hydrogen.

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According to the invention the combustibility of synthetically manufactured oils poor in hydrogen and obtained by the hydrogenation of pit coal, brown coal and the like is improved by the addition of synthetically manufactured oils rich in hydrogen prepared by synthesis from carbon monoxide and hydrogen or by the hydrogenation of coal and the like.

Contrary to expectation, it has been found that the oils poor in hydrogen can be mixed with the oils rich in hydrogen generally without the occurrence of any precipitation. It has also been ascertained that the quantity of the additional oils can be kept relatively small so that the saving effected in the manufacture of an oil which is easily combustible by mixing large amounts of oil poor in hydrogen with small amounts of oil rich in hydrogen is very considerable as compared with other processes in which a Diesel oil of the normal richness in hydrogen is manufactured by direct hydrogenation of coal.

The oils rich in hydrogen which are employed in accordance with the present invention are made either by the hydrogenation of coal or by synthesis from carbon monoxide and hydrogen, for example by the known Fischer-Tropsch process. Experiments have been made with a middle oil poor in hydrogen obtained by hydrogenation of coal, which oil had a hydrogen content of 8.6%.

Increasing amount of a middle oil obtained by the Fischer process were added to the middle oil which was not easily combustible. This additional oil had a hydrogen content of 14%. An addition of 15—20% of the Fischer middle oil to the hydrogenation oil poor in hydrogen was sufficient to obtain faultless operation with a quickly-running Diesel engine having a pre-combustion chamber under all the road conditions which were met with. An addition of 30—40% of Fischer middle oil was sufficient to obtain faultless running under all operating conditions of a high speed engine with solid injection. Similar experiments were carried out with a coal hydrogenation oil distillate having a hydrogen content of 8.6% by adding a middle oil rich in paraffin which was made by further hydrogenation of the 300—330° O. fraction of a coal hydrogenation oil poor in hydrogen. These experiments with the addition of a middle oil rich in paraffin also proved that the combustibility of the oils poor in hydrogen could be considerably improved by relatively small additions of oils rich in hydrogen.

If it is desired to carry out the process with the addition of middle oils rich in paraffin obtained from the hydrogenation

of coal, one must determine in each case which fractions of the hydrogenation oil can be most easily converted into the oils rich in hydrogen. Fractions are preferably selected in which the content of hydrogen can be increased with only a small formation of gas and benzine. The selection of the fractions must be checked in each case and depends mainly on the starting material, that is to say on the coal to be hydrogenated.

The selection of the additional oil itself and the quantity of the additional oil rich in hydrogen which is added must also always be made so as to suit the kind of engine in which it is to be used. Thus for example, by varying the amount of the Fischer middle oil which is added to the hydrogenation oil poor in hydrogen various types of Diesel oils can be made which comprise grades of Diesel oil ranging from aeroplane Diesel oil down to normal motor car Diesel oil. In all cases, it is desirable when adding the oil rich in hydrogen to keep the proportion of high grade and expensive oil rich in hydrogen as small as possible.

A further possibility of cheapening this mixed fuel is by mixing with it coal extract or a primary bitumen itself. Instead of the bitumen, one can also admix high-boiling fractions obtained from primary bitumen or coal extract or high-boiling fractions from hydrogenation oil. Such high-boiling fractions are preferably obtained by vacuum distillation. The admixture of these substances, such as coal extract, primary bitumen, high-boiling hydrogenation oil fractions, not only reduces the cost of the fuel merely owing to the presence of the addition but it has been found that the solution or admixture of the solid extract, bitumen or high-boiling hydrogenation oil improves the combustibility of the hydrogenation oils poor in hydrogen. It has unexpectedly been found that these high-boiling materials, in spite of their rather low content of hydrogen, have a really good combustibility. The use of such high-boiling fractions or bitumen alone would not be satisfactory owing to their viscosity. In combination, however, with the middle oils poor in hydrogen obtained by hydrogenation they represent, however, an excellent means of keeping the fraction of high grade expensive middle oils rich in hydrogen within low limits.

The aforesaid substances, such as coal extract, primary bitumen and the like are in general not soluble in oils of a paraffin base which are rich in hydrogen. If the said extract or bitumen or other substance mentioned is dissolved in the

hydrogenation oils poor in hydrogen and middle oils of a paraffin base are then added, flocculation occurs which, however, can be eliminated, after mixture 5 has been effected, by filtering or centrifuging. The solution obtained can be made quite stable, so that after long standing in contact with the air and even if variations in temperature occur, there 10 is no further separation or flocculation. For this purpose a somewhat larger proportion of the middle oil of a paraffin base which is rich in hydrogen and has a precipitating effect is added. By this 15 means somewhat more bitumen is precipitated than with a normal mixture. By heating the solution the precipitated bitumen is caused to ball together and can easily be separated by filtering or 20 centrifuging. The excess of oil rich in hydrogen which has been added can again be distilled off and there is obtained in this manner a normal mixture of middle oil poor in hydrogen with bitumen which 25 has the desired content of middle oil rich in hydrogen and is stable at a low temperature and does not exhibit any tendency to form a precipitate.

EXAMPLE.

30 A hydrogenation oil produced by further hydrogenation of primary bitumen, having a hydrogen content of 8.5% and of which 40% boils up to 300° C. and 85% up to 380° C. is treated 35 with 25% of bitumen while being heated. To 100 parts of the heated solution are added 25 parts of a middle oil rich in hydrogen boiling at from 200—300° C. The middle oil rich in hydrogen can be 40 obtained either by destructive hydrogenation of distillable carbon-containing materials or by synthesis from carbon monoxide and hydrogen. After the mixture has been made, about 8% of a 45 pasty asphalt-like substance is precipitated and this is removed by centrifuging and can be added to the primary bitumen being hydrogenated. The remaining solution is distilled up to a temperature 50 of 220° C. whereby 12% of the oil rich in hydrogen which has been added is recovered. This fraction rich in hydrogen which is separated is always used over again. The cooled solution is relatively 55 fluid and exhibits no precipitation with variations in temperature and has a good combustion power in the Diesel engine.

Instead of the aforesaid addition of 25 parts of primary bitumen, a corresponding 60 proportion of a primary bitumen fraction boiling up to 400° C. which is obtained by vacuum distillation, can be employed. This fraction which boils below 400° C. is dissolved in the hydrogenation oil poor in hydrogen and

improves its combustibility so that the proportion of additional oil rich in hydrogen can be reduced to 8—12%.

The products obtained by means of the above process are equivalent to normal 70 Diesel oils as regards their combustibility. If a Diesel oil having an equally good combustibility is to be obtained by hydrogenation of coal, then, owing to the 75 higher hydrogen content then necessary, a considerable formation of benzine and gases rich in hydrogen cannot be avoided. Therefore, in the hydrogenation of coal in this manner to form Diesel oil, the 80 total consumption of hydrogen becomes very nearly as great as in the hydrogenation of coal to form motor spirit. It is, therefore, not only cheaper but also considerably simpler to carry out the hydro- 85 genation of the distillable carbon-containing materials only so far as to obtain a middle oil poor in hydrogen and to improve the combustibility by the addition of middle oil rich in hydrogen. If it is desired to manufacture the additional 90 oil by hydrogenation under pressure, those fractions which can be hydrogenated to a further extent most simply and with the smallest formation of benzine and gas, are preferably selected. 95

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:— 100

1. A process for the manufacture of Diesel fuels according to which an oil poor in hydrogen is manufactured synthetically by hydrogenation of a distillable carbon-containing material 105 such as mineral coal, brown coal, coal extract, primary bitumen and the like, and is mixed with an oil rich in hydrogen, which is manufactured by synthesis from carbon monoxide and hydrogen or 110 by the hydrogenation of coal and the like.

2. A process according to Claim 1 wherein a high-boiling hydrocarbon obtained by distillation of coal extract or 115 primary bitumen is added to the oil poor in hydrogen before or after its admixture with the oil rich in hydrogen.

3. A process according to Claim 1, wherein a solid bituminous hydrocarbon, 120 for example coal extract or primary bitumen, obtained from coal is added to the oil poor in hydrogen before or after its mixture with the oil rich in hydrogen.

4. A process according to Claim 2 or Claim 3, wherein a proportion of low boiling oil rich in hydrogen in excess of that necessary is added and the excess of this oil rich in hydrogen is again removed 130 after separation of the precipitated sub-

stances of high molecular weight, stabilisation of the mixture being thereby effected.

5. A process for the manufacture of Diesel oils substantially as described in accordance with the foregoing example.

6. Diesel oils when obtained by a process claimed in any of the preceding claims.

Dated this 25th day of March, 1937.

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Reference has been directed, in pursuance of Section 8, sub-section (2), of the Patents and Designs Acts, 1907 to 1938, to Specification No. 491,221.