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COMPLETE SPECIFICATION

Improvements in the Manufacture and Production of High Quality Benzine and Diesel Motor Fuels

We, FRIEDRICH UHDE, of Deggingstrasse, 12, Dortmund, Germany, and THEODOR WILHELM PEIRRMANN, of Schuckertstrasse 32, Ludwigshafen-on-Rhine, Germany, both German Subjects, 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:—

The present invention relates to improvements in the production of high quality benzine and Diesel motor fuels.

By the new method of working according to this invention asphaltic tars and heavy hydrocarbons obtained by carbonisation can be worked up by a hydrogenation treatment together with a middle oil obtained by reduction of carbon monoxide with hydrogen (hereinafter referred to as cogasine middle oil) in such manner that the greatest possible yields of readily ignitable Diesel oil on the one hand and of non-knocking benzine on the other hand are obtained. The method of working is based on the new observation that cogasine middle oil not only precipitates asphalts and high molecular hydrocarbons of a non-paraffinic nature, but also selectively dissolves the hydrocarbons allied thereto from the tar, while the heavy hydrocarbons, which are poorer in hydrogen, separate as a second layer beneath the lighter cogasine middle oil solution. By this selective property of the cogasine middle oil, the hydrocarbon mixture of the tars is split up into two chemically different components so that it is possible to convert the two fractions thus obtained separately under the most favourable conditions for the purpose into benzine and Diesel motor oil by hydrogenation.

The following example describes the new method of working in greater detail:

Brown coal producer tar and cogasine middle oil are well mixed in the ratio by weight of 1:1. About 50 per cent of the tar separate as a heavy layer having a specific gravity of more than 1.0 together with any water present, while the other half forms the lighter upper layer dissolved in the cogasine middle oil. The

tar fraction dissolved in the cogasine middle oil consists for the most part of the non-aromatic hydrocarbons rich in hydrogen while the heavy tar oil layer mainly contains the aromatic and asphaltic substances poor in hydrogen. For example of about the 43 per cent of acid oils contained in the tar, 80.5 per cent are found in the heavy tar layer and only 19.5 per cent in the cogasine solution; a separation according to molecular weight is also effected because the cogasine solution mainly contains the low molecular weight phenols, while those of higher boiling point are found in the heavy layer.

The cogasine layer that is the solution in cogasine is fairly clear and of pale colour and may even be directly used as Diesel oil. By a light hydrogenation in the gas phase with rigidly arranged catalysts immune to poisoning by sulphur at from 420° to 440° Centigrade, the setting point stability in storage and colour are further improved and at the same time the phenols are hydrogenated to benzine hydrocarbons; the same are distilled off in the benzine up to 200° Centigrade, whereby on the one hand the ready ignitibility of the Diesel oil is improved and on the other hand a non-knocking benzine is obtained.

The heavy tar layer is hydrogenated in the liquid phase in the presence of finely divided molybdenum or tin catalysts at temperatures of from 450° to 500° Centigrade and if desired at higher pressures than in the gas phase, and thus converted into benzine and middle oil, while the heavy oil fraction is returned in known manner. The middle oil obtained is somewhat poorer in hydrogen than the middle oil occurring in the cogasine layer and yields by further hydrogenation in the gas phase also a non-knocking benzine; it may, however, equally well be incorporated as Diesel oil with the Diesel oil obtained in the first stage because it ignites more readily than the gas oils used at the present time and furthermore the point of ignition may be adjusted by varying the amount of cogasine middle oil.

[Price 1/-]

In the above example there is obtained by the hydrogenation in the gas phase from the cogasine-tar oil solution, about 8 to 12 per cent of benzine having an octane number of more than 70; the remainder is high quality Diesel motor oil; the gasification is very slight. The hydrogenation of the heavy tar residue in the liquid phase yields with a gasification of from 5 to 10 per cent, from 18 to 30 per cent of benzine depending on the temperature, the octane number of the benzine being up to 78; the residual distillate oil, from about 60 to 70 per cent of the heavy tar introduced, yields by conversion in the gas phase benzine with an octane number of between 66 and 70. Thus by mixing the benzines obtained from the tar there are obtained from 26 to 40 per cent of benzine with an octane number between 70 and 75, while the remainder, apart from gas, is converted into Diesel motor fuel having a cetene number lying above the average of gas oils. If the middle oil occurring in the liquid phase also be converted into benzine, the amount of Diesel oil is reduced in favour of benzine, the octane number of which then lies at about 70.

If the tar be previously distilled as far as possible or up to 360° Centigrade and the distillate worked up together with cogasine middle oil in the gas phase into benzine, benzines having poorer non-knocking properties and an octane number of between about 40 and 48 are obtained; the benzine obtained by hydrogenation of the distillation residue also has an octane number of only from 58 to 66 as compared with from 70 to 78 by the hydrogenation of the heavy tar fraction separated by precipitation. It is true that the middle oil obtained can also be used as Diesel oil, but its readiness to ignite is also about 5 to 10 points below the cetene number of the Diesel oils prepared according to this invention because by the known methods of working a separate working up of aromatics and paraffins is impossible.

The process according to this invention is especially suitable for working up producer tar and low temperature carbonisation tar of mineral and brown coals, but may also be used for high temperature tar and suction tar. The yields of benzine and Diesel oil of best quality obviously fluctuate according to the composition of the tars used: thus high temperature tars rich in aromatics always yield less Diesel oil than for example brown coal producer tars rich in paraffin; in the working up of high temperature tar, however, the yield of Diesel oil is

also always higher than when, for example, the tar is first distilled in known manner and the resulting fractions are mixed with cogasine middle oil; the stability in storage of the cogasine solution obtained in the said manner and hydrogenated is also considerably better. A further advantage of the said method of working consists in the better separation of the water from the tars; many tars can only be separated from water by a pressure treatment, whereas by the separation with cogasine middle oil the water is usually separated between the cogasine middle oil and the heavier layer and can then readily be removed.

The separation of the cogasine middle oil and heavy oil layers may be effected by sedimentation or by separating centrifuging. A certain influence on the amount and nature of the final product to be prepared may be obtained by varying the amount of cogasine middle oil to tar. By using less cogasine middle oil, the fraction of tar oil dissolved is usually less and the heavy layer is increased in size accordingly. Increase in temperature favours the separation and often displaces the equilibrium in favour of the cogasine layer. The separation of the dust constituents present in most tars can be effected before the precipitation; with some tars it has proved advantageous not to separate the dust, which exists exclusively in the heavy layer, until subsequently, for example by filtration, because the amount to be filtered is then usually only half as great.

In order to render the precipitation complete, a certain amount of cogasine middle oil is always necessary; this may vary between 50 and 150 per cent of the amount of tar used. If it is desired to save cogasine middle oil, it is possible, after precipitation has been effected, to remove a part of the cogasine middle oil used by distillation and to use it again for precipitation; for this purpose cogasine middle oil having a low boiling point of from about 180° to 220° Centigrade is used because the tar usually contains such constituents usually only in small amounts. Such a recovery of a cogasine fraction by distillation is also possible in the case of mineral coal low temperature carbonisation tar, which tends to decompose during distillation, because the readily decomposable substances are found exclusively in the heavy tar layer.

It is known that hydrocarbons containing bitumen can be converted into benzine together with cogasine; in this case, however, it is impossible to use solid catalysts. It has also been pro-

posed to hydrogenate tars of the above-mentioned kind by themselves; the hydrogenation products of such tars have also been subsequently mixed with cogasine. Neither of these methods leads to high quality final products because a separation of the tars into their chemical constituents and the conversion of the separate products in a manner appropriate to their nature is lacking. The hydrogenation process in the presence of cogasine middle oil always proceeds more smoothly and better than without the same, and even high boiling oil fractions, when they have been separated from the heavier constituents poor in hydrogen according to this invention, may be hydrogenated without trouble with solid catalysts; this is impossible in the absence of cogasine middle oil.

It has been proposed to split up hydrocarbon mixtures of the abovementioned kind by means of selective solvents before their further working up. Such a separation is usually attended by high costs however, because special apparatus are necessary for the separation and the solvents, usually of a different chemical nature, have to be completely recovered and this is often very expensive. In the present case, however, the solvent is at least partly itself further worked up in the process and is not only a precipitant but also an initial material for the products to be prepared. Moreover it was not hitherto known that hydrocarbon mixtures of the abovementioned origin

could be split up by cogasine middle oil in such manner that benzine on the one hand and Diesel oil on the other hand could be prepared therefrom in a specially high quality by hydrogenation.

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:—

1. A process for the manufacture and production of high quality benzine and Diesel motor fuels by hydrogenation from tars which have been prepared by carbonisation which consists in separating the tar constituents by mixing with middle oils obtained by the reduction of carbon monoxide with hydrogen into two components of different specific gravity, the lighter component being subjected to hydrogenation in the gas phase, together with at least a part of the said middle oils, and the heavier component subjected to hydrogenation in the liquid phase.

2. The process for the manufacture and production of benzine and Diesel motor fuels substantially as herein described.

3. Benzine and Diesel motor fuels when obtained by the process particularly described and ascertained.

Dated this 29th day of August, 1938.

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