

## UNITED STATES PATENT OFFICE

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PROCESS FOR THE TREATMENT OF COAL  
TAR OIL

Herbert Koelbel, Moers, Neiderheim, Germany

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The present known processes for the treatment of coal tar oil or of tar oils of similar composition, such as fractional distillation or acid treatment, yield products which are suitable for a great variety of purposes. But the degree of purity of the tar oils obtained in this manner is not sufficient to permit their use as motor fuels, particularly for Diesel engines. The object of the present invention is to purify coal tar oils or similar tar oils to such an extent that they may be used as a motor fuel for Diesel engines.

It is already known that primary tars may be purified by heating them with 78% sulphuric acid monohydrate to 180° C. to enable the oils to be used as solvents or for the manufacture of lubricants. Attempts have been made in the same way to improve the odour of heavy tar oils by treating them at 80–90° C. with 50–60% sulphuric acid monohydrate. Primary coal tar oils free from bases and phenols, with a boiling range of 100–200° C. have also been purified by treatment with concentrated sulphuric acid diluted with paraffin oil, followed immediately by distillation. For the manufacture of lubricating oils, products of hydrogenation under pressure, more particularly products obtained by hydrogenation of coal, have also been treated by solution in organic media and by treatment with diluted mineral acids.

It is true that with these processes—partly intended for oils of a composition different from that of the coal tar oil—it is possible to attain a degree of purity that is requisite for some desired purpose, but such processes are not practical for producing therefrom Diesel motor fuel. A special process of purification is necessary for removing from the tar oils the undesirable asphalt, resin and pitch ingredients and more particularly the phenolic substances, which when present in Diesel fuel cause formation of resin and coke.

These disadvantages are eliminated by the process of treatment according to my invention in which the coal tar oils to be treated are mixed with mixtures of paraffin hydrocarbons, the boiling range of which is between 180°–350° C., and this mixture is treated at room temperature for a short time with diluted acid until a complete reaction has been effected. After settling or centrifuging, the following three layers are produced, i. e.,

(1) A mixture of tar oil and paraffinic hydrocarbons,

(2) Acid, and

(3) Sediment, which three layers can be easily separated from each other in any known manner.

The mixture under (1) can be completely deacidified by repeated washing, dried, and if desired bleached.

It has been found particularly advantageous in the manufacture according to my invention of Diesel fuel, to mix the coal tar oils with paraffinic hydrocarbons of the boiling range of 180°–350° C. obtained from benzine synthesis by the Fischer-Tropsch process. This hydrocarbon fraction which differs from the natural products of the same boiling range by its purely paraffinic structure (recognizable by the extraordinarily low specific gravity of 0.77 (15° C.)), offers considerable "motor advantages" by reason of its readiness to ignite and its clean combustion.

The chemical advantages derived from the use of this synthetic product in the process are that the tar oil is dissolved in such a manner that its desirable constituents pass into solution while the undesirable constituents are eliminated by the action of the sulphuric acid.

The use heretofore of fuel mixtures containing tar oils proved a failure owing to the relatively high proportion of resin, pitch and asphalt therein, and thus their use as motor fuels was impracticable and their keeping properties were impaired.

The proportion of phenol or phenolic oils present therein would cause the formation of coke in the combustion chamber of the Diesel engine, or the injection nozzles would become clogged by resinification. With the acid treatment according to the present invention it is possible to remove the greater part of these phenols or phenolic oils so that the above mentioned drawbacks are mostly eliminated.

The acids which are readily separated after the treatment, may be utilized again for treating a fresh quantity of the mixture. If the process is effected in several stages, the acid which has already been used may be returned to the first stage of purification.

As the sediment easily separates on the one hand from the tar oil—hydrocarbon mixture, and on the other hand from the acids, it is readily available for further treatment. Such treatment can be effected either by a mechanical method, for instance, by solution, extraction or distillation, or by a chemical method, for instance by acid treatment, treatment with lye, or by cracking.

As compared with the usual treatment of tar oils with concentrated acids, the diluted acids used in my process according to the invention are readily recoverable and can be returned into the process without any special treatment. Moreover the refining losses are substantially smaller than when using concentrated acids.

The use of the process according to the present invention offers the advantages of small consumption of acid, small refining losses, ready separation of the desired constituents, ready

separation of the undesirable constituents, more particularly elimination of the phenolic constituents, and recovery of the acids.

The following example serves to illustrate how the invention can be carried into effect.

35 kgs. of a coal tar oil having a boiling point between 180°-350° C., and 17 kgs. of a paraffin oil having a boiling point within the same range, such as obtained for instance by the Fischer and Tropsch process, are mixed together, and this mixture, without being heated, is shaken for a short time with about 15 litres of 20% sulphuric acid.

The mixture separates immediately into three layers. The upper one contains the considerably lighter-coloured refined oil, the central layer contains the light yellow-coloured sulphuric acid, and the bottom layer contains the separated dark impurities constituting the sediment.

The three layers are separated from each other. About 47 kgs. of the refined oil from the upper layer and 5 kgs. of the separated impurities are obtained, which can be treated to provide phenols or heating oil. The acid which has been employed is used for the purification of further mixtures. The refined oil is washed in the usual manner; if desired it may be further purified, in which case treatment with bleaching earth is particularly advantageous.

The application of bleaching earth on the mixture before the action of the acid, has no visible effect. The refined oil can be utilised at once as Diesel fuel. A comparison of the chemical and physical properties of the mixture before and after the use of the process shows the advantages obtained.

Chemical-physical data of tar oil—paraffin hydrocarbon mixtures.

	Before treatment	After treatment
Density at 20°	0.950	0.933
Viscosity	1.33 E°, 20° C.	1.32 E°, 20° C.
Spec. Parachor	24.14	23.48
Separation at	—	—
Hard asphalt content	0.24	0.06
Coking residue	0.40	0.09
Phenol content—volume percent	5.6	1.2

The refined oil may be effectively used as motor fuel, since the purification as shown by the above analysis results in the reduction of the density from 0.950 to 0.933 and the consequent lowering of the specific parachor, obtained by the elimination of impurities having specific gravities of over 1.0, thereby providing a Diesel fuel having a greater readiness to ignite and having better combustion properties. The reduction of viscosity gives better spraying qualities. The reduction of the hard asphalt content from 0.24 to 0.06% for the first time enables this mixture to be used as motor fuel, since the risk of carbonization in the combustion chamber and of the clogging the nozzles as well as of scoring of the pistons, is eliminated by the treatment according to my invention. The same advantage is expressed by the reduction of the coking residue from 0.40 to 0.09%. A very important advantage is the considerable reduction of the phenol content, as phenols in Diesel fuels easily lead to resinification and nozzle clogging, as well as to corrosion and piston scoring.

What I claim is:

1. A process for treating tar oils to render them suitable for use as motor fuels particularly for Diesel engines, which comprises the steps of ad-

mixing with the tar oils, paraffinic hydrocarbons having a boiling range between 180° C. and 380° C., treating the mixture with diluted sulphuric acid substantially 20% of concentration at ordinary temperature, and separating the upper stratum of refined oil from the intermediate sulphuric acid stratum and the bottom sediment stratum.

2. A process for treating coal tar oils to render them suitable for use as motor fuels particularly for Diesel engines which comprises the steps of admixing with the coal tar oils, paraffinic hydrocarbons having a boiling range between 180° C. and 380° C., treating the mixture with diluted sulphuric acid of substantially 20% concentration at ordinary temperature, and separating the upper stratum of refined oil from the intermediate sulphuric acid stratum and the bottom sediment stratum.

3. A process for treating tar oils to render them suitable for use as motor fuels particularly for Diesel engines which comprises the steps of admixing with the tar oils, paraffinic hydrocarbon mixtures obtained in the benzene synthesis according to Fischer and Tropsch, treating the mixture with diluted sulphuric acid of substantially 20% concentration at ordinary temperature, and separating the upper stratum of refined oil from the intermediate sulphuric acid layer and the bottom sediment stratum.

4. A process for treating coal tar oils to render them suitable for use as motor fuels particularly for Diesel engines which comprises the steps of admixing with the coal tar oils, paraffinic hydrocarbon mixtures obtained in the benzene synthesis according to Fischer and Tropsch, treating the mixture with diluted sulphuric acid of substantially 20% concentration at ordinary temperature, and separating the upper stratum of refined oil from the intermediate sulphuric acid stratum and the bottom sediment stratum.

5. A process for treating tar oils to render them suitable for use as motor fuels particularly for Diesel engines, which comprises the steps of admixing with the tar oils, paraffinic hydrocarbons having a boiling range between 180° C. and 380° C., treating the mixture with diluted sulphuric acid of substantially 20% concentration at ordinary temperature, separating the upper stratum of refined oil from the intermediate sulphuric acid stratum and the bottom sediment stratum, washing and drying the refined oil and treating it with bleaching earth.

6. A process for treating coal tar oils to render them suitable for use as motor fuels particularly for Diesel engines, which comprises the steps of admixing with the coal tar oils, paraffinic hydrocarbons having a boiling range between 180° C. and 380° C., treating the mixture with diluted sulphuric acid of substantially 20% concentration at ordinary temperature, separating the upper stratum of refined oil from the intermediate sulphuric acid stratum and the bottom sediment stratum, washing and drying the refined oil and treating it with bleaching earth.

7. A process for treating tar oils to render them suitable for use as motor fuels particularly for Diesel engines, which comprises the steps of admixing with the tar oils, paraffinic hydrocarbon mixtures obtained in the benzene synthesis according to Fischer and Tropsch, treating the mixture with diluted sulphuric acid of substantially 20% concentration at ordinary temperature, separating the upper stratum of refined oil from the intermediate sulphuric acid stratum and the

bottom sediment stratum, washing and drying the refined oil and treating it with bleaching earth.

5 8. A process for treating coal tar oils to render them suitable for use as motor fuels particularly for Diesel engines which comprises the steps of admixing with the coal tar oils, paraffinic hydrocarbon mixtures obtained in the benzine synthesis according to Fischer and Tropsch, treating

the mixture with diluted sulphuric acid of substantially 20% concentration at ordinary temperature, separating the upper stratum of refined oil from the intermediate sulphur acid stratum and the bottom sediment stratum, washing and 5 drying the refined oil and treating it with bleaching earth.

HERBERT KOELBEL.