

UNITED STATES PATENT OFFICE

2,188,015

PROCESS FOR THE REFINING OF LIGNITE
TAR, SHALE TAR, PEAT TAR, AND THE
LIKEFriedrich Schick, Berlin-Schoneberg, Germany,
assignor to the firm Deutsche Erdol-Aktien-
gesellschaft, Berlin-Schoneberg, GermanyNo Drawing. Application August 4, 1936, Serial
No. 94,291. In Germany August 8, 1935

7 Claims. (Cl. 196—13)

The present process relates to the treatment of tars, such as lignite tar, shale tar and peat tar, with selective solvents. According to this invention that fraction of the tar which contains the phenols is to be removed first, suitably by topping it until about 260° C., whereupon the remaining tar residue is decomposed or separated into a raffinate portion and an extract portion by means of the thus obtained phenols of low boiling point, or if desired, by means of other selective solvents, in such a manner that both these portions can be processed to yield marketable products such as paraffin, lubricating oil, asphalt, in spite of a considerable limitation of the refining with sulphuric acid and soda lye. Under certain circumstances the tar may, however, be treated or decomposed together with the portions thereof boiling below about 260° C., i. e., after only partly removing them previously by topping or without removing them at all.

It has already been proposed, it is true, to dissolve by means of phenol, preferably in a diluted state, from tars and mineral oils and from the distillates thereof, associated substances, such as asphalts, resins and bad smelling materials. Also the recrystallization of lignite tar paraffin has been made in the presence of creosote from lignite tar. For these processes, however, the use of phenols or other selective solvents, such as liquid sulphurous acid, for the refining of lignite tar or of lignite tar products has been provided for only in a very slight measure, and all these proposals are but unimportant details in the general refining of lignite tar. These refining determinations are executed generally by distillation in combination with treatment with sulphuric acid, and a removal of the creosote by means of alkali or by washing with alcohol. It has frequently been tried, it is true, to avoid the use of sulphuric acid because it involves many difficulties, as the acid oils and unsaturated compounds contained in the lignite tar on the one hand cause the formation of emulsions when treated with soda lye after said treatment with sulphuric acid, and on the other hand, heavy losses of substance result from said acid treatment. It, however, had not been previously possible to find a procedure satisfactory in every respect. A further disadvantage connected with the employment of sulphuric acid consists in its being available only from other plants, and the same is true when alcohol or soda lye are used for the removal of creosote.

The present invention, on the contrary, relates to a means for the treating of lignite tars, shale

tars and the like preferably and essentially with substances produced from the tars themselves, i. e., with the phenols; and for producing an intermediate petroleum-like product wherefrom finished products like lubricating oils, paraffins, cracked distillates and the like, may be produced by means known per se, which finished products are superior to the products hitherto obtainable and are obtained in higher yield. For this purpose the tar, according to the present invention, is topped until about 260° C., and the tar residue then is treated at temperatures exceeding 50° C. with phenols of low boiling points, which if desired, may be diluted with water, or it may be treated therewith at about 30° C. after having been thinned with benzine or the like. Instead of phenols other selective solvents may be used for the treatment of the tar, such as liquid sulphurous acid, nitrobenzene, furfural, chlorex (di-chlor ethyl ether), aniline, pyridine and the like, though the use of the phenols is to be preferred because they are easily obtained from low temperature tar of lignite, and because they possess good stability even after long use, have very high selective capability, may be diluted to any desired extent with water or the like, so that their dissolving capacity may be regulated thereby, and are not too volatile, thus making unnecessary the use of vessels which are tightly sealed. In diluting the phenols, in addition to water, lower alcohols, esters ketones and saturated hydrocarbons may be used.

Preferably the procedure may be executed as follows:

The raw tar is topped, conveniently after centrifuging off the mechanical impurities, and advantageously two fractions are taken off, the fraction boiling between about 200–220° C., and the fraction boiling at about 260° C. The detached separation of the fraction boiling below about 200 to 220° C. is advantageous in that after freeing it from the creosote, the phenols needed for the further treatment of the tar distillation residues are obtained and a light oil is left which, owing to its aromatic nature forms a motor fuel of high anti-knock rating. The second fraction, i. e. that boiling up to about 260° C. is utilizable as a Diesel oil. It may be improved considerably for this employment by a treatment with selective solvents, e. g. by means of liquid sulphurous acid.

The further treatment of the topped tar aims at the manufacture of an intermediate product free from all those special tar components such as phenols, other acid oils, unsaturated and sulphur compounds of unknown nature, which in-

terfere with the refining and the production of finished materials from lignite tars, shale tars and peat tars and the like, in contradistinction to that of petroleum or naphtha. For this purpose the topped tar (about 85% of the crude tar) is treated at a temperature of 50-60° C. or higher with phenol, preferably that obtained by topping of the tar, the phenol being employed in a quantity of 100% or more, calculated on the topped tar. Instead of phenol, cresol, or a mixture of phenols, as obtained when the tops (i. e., fraction removed by primary distillation) of the tar may be used. If the tar is readily soluble and therefore no substantial formation of layers takes place, the phenols are first diluted with water or the like. Under some circumstances it may also be convenient to execute the extraction after an addition of thinning oils up to 100% calculated on the distillation residue used. In the case of such a dilution the temperature of treatment may be reduced, for instance down to about 30° C. The treatment with the phenols may also be made in several steps whereby the extraction is improved.

By the process described above a refined product or raffinate is obtained which after removal of the phenols and of the thinning agent, if such are employed, considerably differs as to its chemical composition from the tar used as starting material, and which shows a petroleum-like character. It is processed further as follows:

First the high melting paraffin, contained in the raffinate is filtered off at a temperature of about 20° C. The thus obtained crude paraffin wax is sweated immediately, omitting the usual treatment with alkali, and the thus obtained sweated material is decolorized by decolorizing agents, preferably by lignite semi-coke, which coke is freed totally or partially from ash. By this method the customary after refining of the sweated material obtained from lignite tar with sulphuric acid may be omitted. In some cases, particularly if a carefully produced tar, for instance one prepared by treatment of the coal with scavenging or inert gases are used as a starting material, it is suitable for the recovery of the paraffin to distill the raffinate or even the crude paraffin wax before sweating.

The oil running off from the sweating treatment is a most suitable starting material for cracking processes, as will be discussed below. There are several ways to utilize the de-waxed raffinate. First according to the present invention, lubricating oils, for instance for bearings, with low solidifying point may be produced therefrom by further removal of paraffin through pressing in the cold. Under certain circumstances it is preferable to treat the cold pressed oils for further refining once more with selective solvents, for instance with phenols or with liquid sulphurous acid, nitrobenzene, furfural and the like, or they may also be improved by treatment with condensing agents, such as metal chlorides.

On the other hand, the de-waxed raffinate may advantageously be utilized also, if desired in mixture with the run off oil from the sweating treatment, as a starting material for the liquid phase or the vapor phase cracking processes. In every case the raffinate can be cracked with the formation of a small amount of coke, resulting in an increase of the capacity of the plant. That the deposition of coke is avoided, is specially of benefit with such cracking processes which operate in the presence of catalysts. The regeneration of such catalysts when using said raffinates of

the present procedure becomes necessary only after very long use. For instance it has been found, that when using untreated lignite tar-oil the same quantity of contact substance (activated coal) was required for the recovery of 13.5 kilos of light oil, as was sufficient for the recovery of 30 kilos of oil from the raffinate obtained by the present process. In addition thereto the per cent yield in the former case was only 17%, and in the latter case, it was 28% of the starting oil. Depending upon the market conditions, it may be expedient to crack the starting oil to produce gas oils, which it has been shown, have a better ignition point than the oils produced by cracking crude lignite tar oil, and therefore are of special value as Diesel oils.

The pretreating of lignite tars and the like with phenols is of profitable influence, too, when transforming the tars in lighter hydrocarbons, insofar as the walls of the apparatus used are not at all or merely slightly attacked, whereas the corresponding action of the unrefined tar is very detrimental.

The described process thus affords a method of processing liquid and solid hydrocarbons rich in hydrogen and contained in tars like lignite tars, shale tars and so on, apart and separated from the oxygen-, sulphur- and unsaturated compounds. If desired, one may proceed by first distilling the tar after the fraction containing the phenols has been eliminated by topping, and then treating the distillate with the phenols of low boiling points according to the above described method. Or one may remove the paraffin from the tar before the latter is treated with said phenols. In this case the treatment with the phenols may be made at a temperature below 20° C. practically excluding the solution of the remaining paraffin. Any after-treatment of the extract for the removal of such remaining paraffin in order to render it applicable for road-making purposes and the like, may thus be dispensed with.

The extracts obtained in the described method may be utilized in different ways after removing the phenols used as solvents by distilling or blowing off with steam. Among other purposes they are suited for the manufacture of motor oils free from knocking, by cracking or still better by hydrogenation under pressure. Especially, however, it is intended to render applicable the tarry components contained in the extract for road making purposes. A rather inconvenient fact in such employment is to be found in that the extract still contains paraffin. But it has been found that it is possible to separate this paraffin by diluting the extract with benzine or the like while adding selective solvents, for instance again phenols. It is, however, still more expedient to dilute the extract layer obtained by treating the topped tar with phenols, while cooling, with benzine or other thinning agents dissolving paraffin only slightly, such as different light and middle oils, petroleum, gas oil, furthermore decalene and others, an extract practically free from paraffin and a so-called separated raffinate being obtained thereby. This separated raffinate may be added afresh to the starting material in treating paraffin containing mineral oils and tars with selective solvents.

From the dewaxed extract by distillation a fuel oil is obtained, whereas the residue, if desired after additional further treatment, as for instance by oxidation, forms the desired pavement asphalt.

Example

Lignite low temperature tar (specific gravity=0.94 at 20° C.) is topped or distilled up to 250° C., a residue of 85% being formed, having a specific gravity 0.95 at 20° C., the solidifying point +45° C. and a content of creosote=8.0%. After eliminating mechanical impurities by centrifuging, this residue is mixed, by means of a gear-wheel pump at +50° C., during continuous operation, with 120% of aqueous phenol having a phenol content of 90%, whereupon the obtained mixture is immediately separated by means of centrifuges at +50° C. into extract and raffinate. The raffinate is also continuously freed from phenol in an evacuated column, 51% of hotly produced raffinate, free of creosote and having the specific gravity 0.895 thus being obtained.

The hotly produced extract which contains the phenol is mixed by means of a gear-wheel pump with 50% of test benzine, the obtained mixture is cooled to +20° C. and separated at this temperature into a coldly obtained or separated raffinate and a coldly obtained extract by treatment in a centrifuge.

The phenol and the benzine are recovered from the coldly produced raffinate and the coldly produced extract by evaporation of the phenol and benzine, 53% of coldly produced raffinate with a specific gravity of 0.960 at 20° C. and 47% of coldly produced extract with a specific gravity of 1.09 at 20° C. and a paraffin content of 1% thus being obtained.

The phenol recovered from the raffinates and from the extract together with the remaining content in neutral oil is returned to the continuous procedure.

After the selective treatment of the tar as described above, the products obtained thereby are processed in the following manner:

From the hotly and the coldly produced raffinate there may be obtained by cracking under pressure 25% of benzine (gasoline) and 55% of gas-oil which without further refining will have a cetene number of 60.

The coldly produced extract obtained is concentrated to form asphalt. This asphalt among others has the following favourable properties: Softening point according to the method of Kraemer-Sarnow=38° C., dropping point according to the method of Ubbelohde=58° C., penetration=37°, ductility=150 cms., paraffin content=1%, evaporating loss=2%.

The first runnings obtained in topping the tar up to 250° is processed by fractionation and treatment of the obtained fractions with alkali lye, about 10.3% of motor oils, 1% of pure phenol, 1% of cresol and xylene, and 1.5% of higher phenols, calculated on the crude tar, thus being obtained.

Having now particularly described and ascertained the nature of my said invention, I declare that what I claim is:

1. Process for obtaining valuable products from paraffin containing tar from solid carbonaceous material which comprises topping said tar to remove constituents boiling below about 260° C., subjecting the residue from said topping to treatment with a selective solvent which forms an extract portion containing in solution tarry components of the said residue and a raffinate portion which contains paraffin, the said treatment being

conducted at a temperature above 50° C., but below the temperature at which the selective solvent becomes completely miscible with the said residue, and separating the extract portion and the raffinate portion produced by said treatment.

2. A process for obtaining valuable products from paraffin containing tar from solid carbonaceous material which comprises topping the tar to remove constituents boiling below about 260° C., subjecting the residue at a temperature of about 50° to 60° C., to a treatment with phenols of low boiling point to form two liquid phases, one of which is a raffinate and the other an extract phase.

3. Process for obtaining valuable products from paraffin containing tar from solid carbonaceous material which comprises topping the said tar to remove constituents boiling below about 260° C., subjecting the residue from said topping treatment to treatment with a phenol of low boiling point at a temperature of about 50° C. to form an extract portion containing in solution tarry components of the said residue and a raffinate portion containing paraffin, and cooling said raffinate portion to produce the separation of paraffin therefrom.

4. In the process of treating paraffin containing tar from solid carbonaceous material, the steps of topping the tar to remove constituents boiling below about 260° C., adding a diluent of the kind represented by benzine to the residue and treating the diluted residue at about 30° C., with phenols of low boiling point to produce a raffinate phase and an extract phase.

5. A process of treating paraffin containing tar from solid carbonaceous material, comprising topping the tar to remove constituents boiling below about 260° C., de-waxing the residue and thereafter subjecting the residue at a temperature not higher than about 20° C. to a treatment with phenols of low boiling point to form a raffinate portion and an extract portion, whereupon the raffinate portion thus obtained is separated from the formed extract portion.

6. A process for the production of valuable products from paraffin containing tar from solid carbonaceous material which comprises topping the tar to remove constituents boiling below about 260° C., separating the phenols from the distillate obtained by said topping, subjecting the topped tar at a temperature above 50° C., but below the temperature at which the said phenols become completely miscible with the said topped tar, to a selective treatment with said phenols separated before from said distillate, and separating the thus formed raffinate phase from the extract phase formed at the same time.

7. Process for obtaining valuable products from paraffin containing tar from solid carbonaceous material which comprises topping said tar to remove constituents boiling below about 260° C., subjecting the said residue from said topping to treatment with a phenol of low boiling point to form an extract portion containing in solution tarry components of the said residue and a raffinate portion which contains paraffin, the said treatment being conducted at a temperature above 50° C., but below the temperature at which the phenol becomes completely miscible with the said residue, and separating the extract portion and the raffinate portion produced by said treatment.

FRIEDRICH SCHICK.