

UNITED STATES PATENT OFFICE

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TREATMENT BY PRESSURE AND HEAT OF HEAVY MINERAL OILS AND CARBON
MATERIAL

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This invention relates to the treatment of heavy mineral oils, and carbon products, such as, for instance, distillation products from carbonaceous materials, liquids in
5 which carbon exists in a dispersed state, such as suspensions of carbon, and similar material, and more particularly the invention relates to an improved method of effecting the hydrogenation of these substances in the
10 presence of a suitable hydrogen-transferring metallic agent.

In the manufacture of light distillation products, such as benzine and illuminating oils from heavy mineral oils, distillation
15 products from carbonaceous materials and the like, as heretofore practised, these raw materials are generally split or decomposed by heating them under pressure, that is to say, by a combination of pressure and heat
20 treatment. The raw products directly resulting from such treatment must then be submitted to a rather complicated and expensive refining process, in order to reduce their sulphur contents to the degrees which are per-
25 missible in commercial products.

If the refining operation is carried out by means of sulphuric acid, concentrated sulphuric acid, oleum and the like, the consumption of chemicals and the loss in hydrocarbons is considerable. If the refining is done
30 with the aid of metal oxides or metals, such as lead, sodium, and similar metals, the organic sulphur-compounds of the oils are converted into hydrocarbons containing unsaturated groups, thereby considerably impairing
35 the quality of the products, and particularly impairing their keeping qualities.

From the prior art it has become known to make use of heat in the presence of hydrogen
40 under high pressure, the so-called hydrogenation by heat and pressure, either without or in the presence of a catalyzer for the purpose of effecting the splitting of heavy mineral oils and carbon distillation products, and for
45 the liquefaction of carbon dispersed or distributed in liquids as a kind of carbon suspension or the like. As most suitable catalyzers the following have been suggested, example, platinum, palladium, nickel, nickel
50 oxide, and electrolytically obtained iron.

But the crude products heretofore obtained in this manner require subsequent refining.

In accordance with the present invention the treatment of heavy mineral oils, distillates from carbonaceous materials, carbon
55 suspensions or dispersions and the crude products obtained therefrom is effected at high temperature and in the presence of sodium or of other agents of similar activity. It has been ascertained by me that in the pres-
60 ence of sodium in the process of hydrogenation under pressure and heat it is not only possible to effect a perfect or almost complete desulfurization in a comparatively short time, but at the same time the bromine mem-
65 ber of the products is greatly reduced and products of a higher degree of hydrogenation are produced.

The possibility of effecting desulfurization and hydrogenation simultaneously by the
70 use of sodium as a catalyzer may be due to the fact that sodium sulfide as distinguished from the sulfides of the metals heretofore used as catalyzers is unstable in an atmosphere of hydrogen at the temperature em-
75 ployed.

Example 1

100 kilograms of Mexican Panuco-oil are heated in a closed vessel under a pressure of
80 50 atmospheres of hydrogen to a temperature of about 420 degrees centigrade with the addition of five per cent of sodium. The strongly viscid, crude oil, containing about
85 3.5 per cent of sulphur is thereby converted into a freely fluent oil the benzine and kerosene fractions of which contain only traces of sulphur and are of a nearly saturated chemical composition.

Example 2.

100 kilograms of anthracene of 65 per cent are heated in an autoclave with the addition
90 of 3% of metallic sodium and 4% of fuller's earth under an initial pressure of 100 atmospheres of hydrogen to a temperature of about
95 300 degrees centigrade. A rather vigorous desulphurizing and hydrogenating reaction soon commences, the hydrogenation being indicated by the large fall in pressure, and
100

the rise in temperature. After forcing in several new charges of hydrogen, so as to bring the pressure to the former value the reaction is finally completed. The principal product obtained by the fractional distillation of the contents of the autoclave is the chemically pure deca-hydride of anthracene.

Example 3

50 kilograms of coarsely granular and well dried upper-Silesian coal are heated in a closed vessel with 50 kilograms of tar oil and 3 kilograms of metallic sodium to a temperature of 430 degrees C. under a pressure of 100 atmospheres of hydrogen. After repeatedly forcing in new charges of hydrogen the carbon is decomposed or broken up to such an extent, that is to say, converted into liquid and soluble compounds, that only about eight per cent of elemental carbon (about 3 and 6 tenths kilograms) remain. By distillation the decomposed or dissolved portions may be separated into fractions suitable for use as fuel for motor engines, and into oil of superior quality for use for heating purposes.

The reaction may be accelerated by vigorous agitation or by the simultaneous addition of fuller's earth, powdered wood charcoal, coke ashes, and similar adsorbing agents or the like.

Crude lubricating oil distillates are not only desulfurized and hydrogenated by the process of this invention, but they are also most favorably influenced with regard to their characteristic and valuable properties. For a good lubricating oil it is required that its viscosity be as independent as possible of its temperature, that is, the temperature viscosity curve should be flattened. Furthermore, the point of solidification should be as low as possible. These two requirements may be collectively stated in the single requirement that a good lubricating oil should show an extended range of fluidity, and this result is accomplished by the hydrogenating refining operation above described.

By heating, for example, a crude California lubricating oil distillate in an autoclave previously charged with hydrogen under 100 atmospheres pressure, and with the addition of 5 per cent of sodium for half an hour to a temperature of about 350 degrees C. its viscosity is reduced from 53.5 to 24.8 degrees Engler at 20 degrees C. The viscosity at higher temperature is only slightly changed, that is to say, the viscosity temperature curve of the raw material is considerably flattened. Besides, the point of solidification of the product is lowered to minus 18 degrees C.

As regards color, odor and other qualities, the refined product satisfies all requirements of a good lubricating oil.

As a further example of the utilization of

the hydrogenating refining process I may refer to its application for the purpose of manufacturing hydro-naphthalene from commercial naphthalene in a single operation with simultaneous desulfurization.

Heretofore naphthalene has been hydrogenated with hydrogen by the use of catalyzers, such as platinum, palladium and nickel. In order to prevent poisoning and inoperativeness of the catalyzers in these processes it is necessary to first purify the material to be treated, and in particular to free it from sulphur, thus for instance by treatment with metallic sodium.

According to the new process of the present invention desulfurizing and hydrogenation are carried on simultaneously by heating commercial impure naphthalene in an autoclave with metallic sodium or with equivalent metals under high pressure of hydrogen and at high temperature.

Thus for instance I may proceed by heating 1 kilogram of crude naphthalene (with 0.3% of sulfur) with the addition of 8 grams of sodium in an autoclave to a temperature of about 300 degrees C., under a pressure of hydrogen of 100 atmospheres. Even during the rise of temperature a relative reduction of pressure is noticed which is due to hydrogenation. At 300 degrees C. the progress of the reaction becomes rather violent with the generation of considerable heat. The pressure remains constant after a few minutes. The product obtained in this manner after filtration shows a specific gravity of 0.975 at 15 degrees C., and upon distillation is found to consist of pure tetrahydro-naphthalene.

Also in this case, as already mentioned above, distributing agents may be added, such as fuller's earth, powdered diatomaceous earth or the like or other additions may be made, such as metals, for instance iron powder, or metal compounds, such as for instance oxide of magnesium.

One may either begin the process with naphthalene, or with solutions thereof, or with intermediate products of low hydrogen content. It is not necessary to particularly purify the hydrogen as must be done in the hydrogenation processes heretofore known.

The process may also be carried out in an uninterrupted operation, and it is capable of various modifications and alterations to suit existing conditions without deviating from the principles of the invention.

What I claim is:

1. Process for simultaneously hydrogenating and purifying mineral oils which comprises submitting the same to the combined action of hydrogen and metallic sodium under superatmospheric pressure and at a temperature of at least about 300° C.

2. Process for the treatment of mineral oils which comprises subjecting the same to

the combined action of hydrogen and metallic sodium under superatmospheric pressure and at a temperature of at least about 300° C. in the presence of a solid adsorbing agent.

5 3. Process for the treatment of mineral oils as defined in claim 2 in which the solid adsorbing agent contains fuller's earth.

4. Process for simultaneously hydrogenating and purifying oils derived from coal
10 which comprises subjecting the same to the combined action of hydrogen and metallic sodium under superatmospheric pressure at a temperature of at least about 300° C.

5. Process for simultaneously hydrogenating and purifying oils derived from coal
15 which comprises subjecting the same to the combined action of hydrogen and metallic sodium under superatmospheric pressure at a temperature of at least about 300° C. in the presence of a solid adsorbing agent.

6. Process for simultaneously hydrogenating and purifying oils derived from coal which comprises subjecting the same to the combined action of hydrogen and metallic
20 sodium under superatmospheric pressure at a temperature of at least about 300° C. in the presence of fuller's earth.

7. Process for simultaneously hydrogenating and purifying crude naphthalene derived
30 from coal which comprises subjecting the same to the combined action of hydrogen and metallic sodium under superatmospheric pressure at a temperature of at least about 300° C.

8. Process for simultaneously hydrogenating and purifying crude naphthalene derived
35 from coal which comprises subjecting the same to the combined action of hydrogen and metallic sodium under superatmospheric pressure at a temperature of at least about 300° C. in the presence of a solid adsorbing agent.

9. Process for simultaneously hydrogenating and purifying crude naphthalene derived
45 from coal which comprises subjecting the same to the combined action of hydrogen and metallic sodium under superatmospheric pressure at a temperature of at least about 300° C. in the presence of fuller's earth.

50 In testimony whereof, I affix my signature.

MAX HOFSSÄSS. [L. s.]