

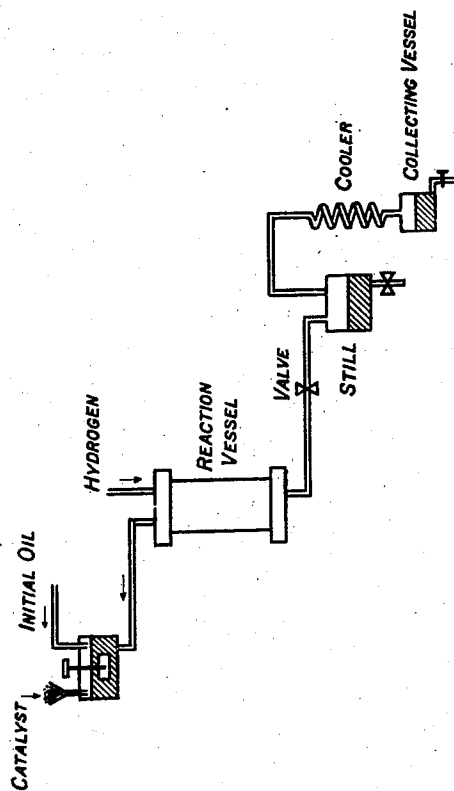
Aug. 31, 1937.

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2,091,831

WORKING UP OF HYDROCARBONS AND SIMILAR SUBSTANCES

Filed Aug. 17, 1931



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UNITED STATES PATENT OFFICE

2,091,831

WORKING UP OF HYDROCARBONS AND
SIMILAR SUBSTANCES

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Application August 17, 1931, Serial No. 557,720
In Germany August 20, 1930

2 Claims. (Cl. 196—53)

The present invention relates to improvements in the working up of hydrocarbons and similar substances.

We have found that in heat treatments of hydrocarbon products, such as tars, mineral oils, asphalts, resins, bitumens, distillation, conversion or refining products thereof, suspensions of coals in liquid hydrocarbon or residues of the oil and tar industries, in which a splitting of at least part of the said products to lower boiling substances takes place and which hereinafter are referred to as "destructive heat-treatments", such as cracking or the destructive hydrogenation, the latter also when carried out under such mild conditions that only a purification from compounds containing sulphur or oxygen or nitrogen by splitting thereof into hydrocarbons and hydrogen sulphide or water or ammonia occurs, valuable products are obtained, when the said treatments are carried out in the presence of oil-soluble salts of an acid organic compound selected from the group consisting of carboxylic acids and phenols with a metal of the 6th or 8th group of the periodic system, if desired in combination with a corresponding salt of a metal of group 2 of the periodic system, especially the oil-soluble salts with the said acid compounds of molybdenum, chromium, cobalt and zinc. For example the oil-soluble naphthenates or oleates of the said metals are especially suitable for employment as catalysts but salts of the said character of other organic acids, such as lanolates or resinsates may also be employed. As a rule the said acid compounds should contain at least 6 carbon atoms. It is frequently advantageous to employ mixtures of different oil-soluble salts of acid organic compounds of the metals hereinbefore specified.

The action of the said metal salts may be enhanced by the simultaneous presence of oil-soluble salts of alkaline earth metals with the said acid compounds. The oil-soluble salts with these compounds of iron or nickel are advantageously employed together with oil-soluble salts of metals of the 6th or 8th group, and, if desired, in addition thereto with other metals of the 2nd group of the periodic system.

The aforesaid oil-soluble salts are advantageously added in such amounts that between 4 and 20 per cent based on the weight of the carbonaceous materials are present in all.

As a rule temperatures of between 300° and 700° C. are employed in the process, and preferably those above 380° C. Good results are obtained at temperatures between 400° and 550° C.

Particularly in the destructive hydrogenation process pressures of 20, 50 or more atmospheres, for example of 100, 200, 500, 800 or 1000 atmospheres are employed with advantage.

The employment of these oil-soluble catalysts in the improvement of hydrocarbon oils has the advantage that the catalytically active substance may be readily dispersed homogeneously in the hydrocarbon product to be treated. When metals and metal compounds are formed from the oil-soluble salts by decomposition during the heat treatment, they are present in such a state of fine dispersion that the danger of the mixture separating into its components is very slight.

By the extremely fine dispersion of the catalyst resulting from the dissolution of the oil-soluble salt in the materials to be converted, a very marked and satisfactory catalytic action is obtained even with the employment of comparatively small amounts. Not only are high yields of hydrocarbons of low boiling point, such as benzines and middle oils obtained by in many cases, especially in destructive hydrogenations, there is the additional important advantage that an undesirable too far-reaching splitting with the formation of gas is substantially suppressed or wholly avoided.

The said oil-soluble salts may also be employed together with catalysts in suspension. When destructively hydrogenating coal in the form of suspensions in oils, tars and the like, the said catalysts may be advantageously dissolved in the oil or tar before the treatment.

In most cases the metals may be recovered in the form of the salts from the residues remaining after the hydrogenation or cracking in a simple manner, for example by burning the said residues for heating purposes and treating the resulting ashes with hydrogen chloride.

The oil-soluble salts employed according to the present invention may be prepared by heating inorganic salts of the metals in question with the said organic acid compounds.

Oil-soluble organic salts of molybdenum may be obtained for example from the chlorides thereof as hereinafter described, in particular the compound obtained by treating oxides of molybdenum, whether molybdenum trioxide or lower oxides of molybdenum, with hydrogen halides at elevated temperatures, for example between 200° and 300° C. The said compounds of molybdenum are treated with the said organic acid compounds, if desired while warming. The formation of the oil-soluble salts may also be effected by treating the said molybdenum compounds

with oils in which the acid components are contained in a sufficiently high amount. The preparation of the oil-soluble molybdenum salts may be illustrated by the following examples. The preparation of oil-soluble salts of the other metals suitable as catalyst is brought about quite analogously.

(1) By passing dry hydrogen chloride over molybdenum trioxide at about 280° C. a chlorine compound is obtained as a sublimate. 48 parts of this compound are introduced in a finely pulverized state in 100 parts of naphthenic acid while heating to about 120° C. and while stirring. The chlorine escapes in the form of hydrogen chloride. A compound of molybdenum and naphthenic acid containing 14.3 per cent by weight of molybdenum is thus obtained. This compound is of a blue color, from viscous to gelatinous, and soluble, in particular in the warm, in mineral oils and tar oils. In addition to this compound a small amount of a solid residue is obtained, which after carefully ashing and heating in a current of hydrogen chloride may be converted into a chlorine compound of molybdenum.

(2) 58 parts of a finely pulverized dry chlorine-compound of molybdenum obtained as described in the foregoing example are introduced by portions into 100 parts of phenol while heating to from 110° to 150° C. and while stirring. The resulting compound of phenol and molybdenum containing 13 per cent of molybdenum has similar properties, as regards appearance and behaviour to oils, as the above mentioned molybdenum compound of naphthenic acid. A negligible residue, if formed, may be worked up as in the foregoing case.

(3) 50 grams of a finely pulverized chlorine-compound of molybdenum obtained as described in the first example are added in portions to 100 grams of stearic acid heated to about 170° C., the whole being stirred for about half an hour. A compound solid at ordinary temperature and of blue color is obtained, which contains 13.66 per cent by weight of molybdenum and which may be dissolved in mineral oils and tar oils even in the cold.

(4) A finely pulverized chlorine-compound of molybdenum obtained as described in Example 2 is introduced, while stirring, into a warm 6 per cent solution of thymol in benzene. The said compound is instantly dissolved imparting to the liquid a deep blue coloration.

In the accompanying drawing an apparatus suitable for carrying out our process is illustrated. The manner in which the process is carried out in the apparatus shown is made clear by appropriate legends on said drawing.

The following examples will further illustrate the nature of this invention but the invention is

not restricted to these examples. The parts are by weight.

Example 1

Cobalt naphthenate 3 per cent of cobalt based on the weight of the oil) is dissolved by stirring and slightly warming in a middle oil boiling between 180° and 325° C. and which is distilled from brown coal tar. The solution is treated in the liquid phase at 440° C. with flowing preheated hydrogen under a pressure of 200 atmospheres. A considerable part of the middle oil is converted into low-boiling products which are condensed in a stripper and relieved of pressure. About 30 to 40 per cent of the initial hydrocarbon is converted into benzine, which is separated from the said product by distillation. Without employing the said catalyst the yield of benzine under otherwise identical conditions is only about half.

A mixture of 0.20 per cent of molybdenum and 0.27 per cent of zinc in the form of their naphthenates or a mixture of 0.36 per cent of molybdenum and 0.25 per cent of zinc in the form of their oleates may be employed for example instead of cobalt naphthenate.

Example 2

American gas oil, having the boiling range of from 200° to 350° C., in which 0.5 part of molybdenum and 0.25 part of zinc in the form of their naphthenates have been dissolved, is split at atmospheric pressure and at 480° C. in a column filled with Raschig rings of glass. About 30 to 40 per cent of the gas oil is thus converted into hydrocarbons boiling below 180° C. Under the same conditions but without any catalyst less than half the amount of products boiling below 180° C. is obtained.

What we claim is:—

1. In the destructive hydrogenation of a hydrocarbon product at a temperature between 300° and 700° C. and under an elevated pressure of at least 20 atmospheres the step which comprises employing as a catalyst a hydrocarbon oil soluble molybdenum salt of a naphthenic acid and which salt is not entirely decomposable in the hydrocarbon oil under the conditions of reaction.

2. In the destructive hydrogenation of a hydrocarbon product at a temperature between 300° and 700° C., the step which comprises employing as a catalyst a hydrocarbon oil soluble salt of a naphthenic acid and of a heavy metal in the group comprising the metals in the sixth group and the iron group in the periodic system, and which salt is not entirely decomposable in the hydrocarbon oil under the conditions of reaction.

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