Patented Oct. 24, 1933 1,932,369

UNITED STATES PATENT OFFICE

1,932,369

REMOVAL OF SULPHUR COMPOUNDS FROM CRUDE HYDROCARBONS

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No Drawing. Application April 9, 1931, Serial No. 528,965, and in Germany June 24, 1927

2 Claims. (Cl. 196—24)

The present invention relates to the removal of sulphur compounds from crude hydrocarbons containing the same.

I have found that not only the crude aromatic hydrocarbons specifically referred to in my aforesaid copending application can be freed from sulphur bearing impurities but that saturated and/or unsaturated hydrocarbons of the aliphatic series including cycloaliphatic hydrocarbons can be purified in a similar manner by treating them in the vaporous or in the liquid state with hydrogen, or gases containing the same, while heating, and, if desired, at superatmospheric pressure, in the presence of catalysts containing metal sulphides, which are stable under the conditions of working, the conditions of working at the temperature employed precluding the cracking of the materials under treatment. Thus, the temperature employed must be lower in case cracking occurs or when working in a continuous manner the rate of flow must be increased. The pressure too must be sufficiently low so as to prevent any hydrogenation of the said hydrocarbons from taking place. Metal sulphides coming into consideration are the sulphides of the metals from the 6th to the 8th group of the periodic system, such as the sulphides of molybdenum, tungsten, nickel, cobalt and the like. The metal sulphides may be used singly or in mixture with one another and/or with activators, such as different compounds, and preferably the oxides, of the aforesaid metals or of alkaline earth metals and of earth metals or zinc sulphide; the aforesaid catalytic substances may be deposited on carriers, such as pumice, active carbon, silica gel, fuller's earth and the like. The quantity of hydrogen employed may correspond to that required for the conversion of the sulphur bearing impurities, or a higher quantity may be employed. By working in the manner described the removal of sulphur bearing impurities may be carried to such an extent that the purified substances can be easily employed as initial materials in sensitive catalytic processes, such as catalytic hydrogenation, a poisoning of the catalysts in these processes being avoided. During the treatment according to the present invention the sulphur is converted into sulphuretted hydrogen or other readily separable sulphur compounds. The temperatures to be employed depend, generally speaking, on the state of combination of the sulphur, i. e., the more firmly the sulphur is bound in the impurities, the higher temperatures are to be used. In the case of a benzine containing a small quantity of sulphur bearing compounds a temperature of about 250° C. is usually sufficient, gas oils generally requiring a temperature of from about 300° to 330° C. and residues and crude oils a temperature of about 350° to 400° C. Thus temperatures ranging from about 200° to 420° C. are suitably employed in most cases, but when working with a particular initial material higher or lower temperatures may be employed. As stated above, the conditions must be so regulated that no cracking of the aliphatic hydrocarbons occurs which undesirable side reaction can be easily ascertained and avoided as soon as an undue increase of the volume of gases occurs.

The process according to the present invention is particularly suitable for the purification of the mixtures of aliphatic open chain hydrocarbons or of mixtures thereof with cycloaliphatic hydrocarbons, such as the mineral oils of different origin or fractions of such oils. In most cases not only sulphur bearing impurities are removed but also acids, other compounds which contain oxygen and nitrogenous compounds.

I have, moreover, found that the refining of crude hydrocarbons and in particular of crude benzines can be carried out in a particularly advantageous manner by treating the said hydrocarbons at atmospheric pressure or at an only slightly elevated pressure, in no case exceeding 48 atmospheres, and usually of up to 20 atmospheres and preferably not exceeding 10 atmospheres with hydrogen in the presence of metal sulphides, which are stable under the said conditions of working and by maintaining a temperature of more than 300° C. and not exceeding the temperature at which the said oils crack. As a rule temperatures of between 300° and 450° C. have proved very suitable, and preferably temperatures of the order of about 350° C.

In the said process the impurities containing sulphur, oxygen, ntirogen and halogen and those impurities consisting of highly unsaturated hydrocarbons are converted into hydrocarbons rich in hydrogen, whereas the hydrocarbon to be refined itself remains substantially unchanged.

The process according to the present invention is of great economic importance, since it allows of carrying the degree of refinery, for example the degree of the removal of sulphur compounds only to the extent desired for any particular purpose. Thus, the degree of refining required for petrol, motor benzene, solvent benzine, benzene for dyestuffs, pure benzene is different in each case. The desired degree of purity is attained according to the present invention by the removal of the impurities of a strongly unsaturated nature and of those containing oxygen, nitrogen and halogen, simultaneously with the removal of the sulphur. The treatment is preferably carried out by passing the hydrocarbons to be purified in a gaseous or liquid state together with hydrogen or gases containing hydrogen over the catalyst.

The degree of refining of the desired product varies with variation of the rate of flow, of the amount of hydrogen and of the temperature employed. The longer the material under treatment is in contact with the catalyst, or the higher is the temperature employed within the limits given, and the greater is the amount of hydrogen employed, the greater will be the degree of refining of the resulting products. Thus, from a crude benzene containing from 0.6 to 0.8 per cent of sulphur according to the conditions of working employed, a motor benzene containing from 0.1 to 0.02 per cent of sulphur, a benzene for dyestuffs containing 0.02 to 0.01 per cent of sulphur, or a pure benzene containing from 0.005 to 0.0002 per cent of sulphur is obtained, the resulting products conforming in respect of the sulphuric acid reaction, bromide number and all other tests to the prescribed specifications. In the refining of crude benzol between 1 and 2 molecules of hydrogen for each molecule of benzol are preferably employed, although larger or smaller amounts also give good results. In order to illustrate the influence of the rate of flow the following figures are given by way of example, though it should be understood that the invention is not limited thereto. Thus, if 1.5 volumes of hydrocarbon be treated daily under atmospheric pressure with 1 volume of the catalyst 65 per cent of impurities are removed from the material, whereas if 1.0 volume of hydrocarbon be treated under the same conditions about 82 per cent of impurities are removed, and if only 0.5 volume of hydrocarbn be subjected to the treatment about 90 to 93 per cent of the impurities are eliminated.

The process according to the present invention has the further advantage that in case of the treatment of hydrocarbons containing large amounts of unsaturated compounds, the refining may be so regulated that anti-knocking compounds are contained in the products to be employed as motor fuels in a sufficiently high degree. On the other hand all those impurities which are injurious when present in motor fuels can be removed.

The range of temperature employed according to the present invention is particularly efficacious in allowing the exact degree of regulating the reaction.

In order to remove the hydrogen sulphide and ammonia and the like, formed in the refined products, these are preferably washed out with acid, alkali solution and water.

The following examples will further illustrate how the invention is carried out in practice, but the invention is not restricted to these examples.

Example 1

An American gas oil having a boiling range between 180° and 320° C., a content of sulphur of 0.56 per cent and a specific gravity (at 20° C.) of 0.852 is passed in the liquid state at a temperature of about 340° C. and, while maintaining a pressure of 20 atmospheres, together with hydrogen over a catalytic substance consisting of nickel sulphide and molybdenum sulphide deposited on fuller's earth. The process is preferably conducted in a cycle, the hydrogen being continuously freed from the main quantities of hydrogen sulphide by passing it at a high pressure through water. A colourless water-white oil of a boiling range from 170° to 315° C. having a content of sulphur below 0.01 per cent and a specific gravity of 0.843 is obtained. The product is practically free from sulphur compounds without having taken up any considerable quantity of hydrogen or having been cracked. The efficiency of the catalysts does not slacken even on a very extended use thereof.

The purified product can be further worked without any difficulty, for example by cracking or by hydrogenating even with the aid of catalysts which are very sensitive to sulphur.

Example 2

A benzine of Russian origin (Baku benzine) consisting mainly of naphthenes and paraffins and having a boiling range of 79° to 180° C., a sulphur content of 0.017 per cent and a specific gravity of 0.760 is passed in the vapour phase at 280° C. and at 40 atmospheres together with hydrogen over a catalyst consisting of cobalt and tungsten sulphides deposited on active coal. The product obtained possesses practically the same physical properties as the initial material but its content of sulphur is below 0.001 per cent.

Example 3

A blackish brown crude Panhandle oil, 70 per cent of which distil over between 95° and 370° C. and which has a specific gravity of 0.890 and a content of sulphur of 0.13 per cent is passed together with hydrogen at 20 atmospheres through a reaction vessel heated to 380° C. after the oil has been mixed with a catalyst consisting of nickel and tungsten sulphides deposited on active silica. A purified brown product is obtained which has a specific gravity of 0.865, a content of sulphur below 0.01 per cent, 85 per cent of the product being distillable within the range from 95° to 370° C. More than 92 per cent of the sulphur originally present have been removed and the content of unsaturated compounds has been reduced.

Example 4

A crude benzine from the neighbourhood of Baku, boiling between about 79° and 180° C., which contains 0.06 per cent of sulphur and which, when refined with concentrated sulphuric acid, suffers a loss in weight of about 4 per cent, if passed under atmospheric pressure together with hydrogen at a temperature of about 450° C. over a catalyst consisting of molybdenum sulphide and cobalt sulphide. A colourless product containing less than 0.02 per cent of sulphur is thus obtained which shows only a slightly yellow colouration, when shaken with concentrated sulphuric acid, in a yield of 99 per cent.

I claim:

1. The process of purifying a crude saturated

aliphatic hydrocarbon boiling up to 180° C. from sulphur bearing impurities which comprises treating said crude aliphatic hydrocarbon at a pressure between atmospheric pressure and 10 atmospheres with hydrogen in the presence of a catalyst comprising an added sulphide of a metal from groups 6 to 8 of the periodic system at a temperature between about 200 and 300° C. under conditions precluding the cracking, polymerization and hydrogenation of said hydrocarbon at the temperature employed.

2. The process as defined in claim 1 wherein the temperature is one of about 250° C. and the catalyst comprises a sulphide of a metal of the sixth group of the periodic system.

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