

UNITED STATES PATENT OFFICE.

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PRODUCING COMPOUNDS CONTAINING CARBON AND HYDROGEN.

1,201,850.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that we, ALWIN MITTASCH and CHRISTIAN SCHNEIDER, citizens of the German Empire, residing at Ludwigshafen-on-the-Rhine, Germany, have invented new and useful Improvements in Producing Compounds Containing Carbon and Hydrogen, of which the following is a specification.

It is known that methane can be obtained from carbon monoxid and carbon dioxid and hydrogen at a raised temperature by means of catalytic agents, in particular nickel, and it has also been stated that by altering the conditions of the experiment small quantities of formaldehyde and ethylene are also sometimes produced.

We have found that a new result can be obtained and that we can build up a number of organic compounds when working under pressure under suitable conditions as herein-after set forth.

We have found that the compounds containing carbon and hydrogen, including hydrocarbons, (in particular such as are liquid or which can be easily liquefied,) and also oxygen compounds of hydrocarbons can be obtained by passing an oxid of carbon and hydrogen either alone or in admixture with other gases over a heated catalytic agent under a pressure exceeding that of five atmospheres. According to the nature of the catalytic agent employed and the conditions of working, different compounds or mixtures are obtained, for instance, liquid hydrocarbons either saturated or unsaturated, and alcohols, aldehydes, ketones and acids. In order to obtain larger quantities of liquid compounds, it is often advantageous to employ gas mixtures in which the percentage of hydrogen contained is comparatively small. As instances of catalytic agents which can be employed according to this invention, we mention cerium, chro-

mium, cobalt, manganese, molybdenum, osmium, palladium, titanium, zinc and oxids or other compounds of these metals and if desired, mixtures of two or more of these catalytic agents can be employed, and it is often advantageous to add a basic compound, such for instance, as alkali metal hydroxid, but this invention is not limited to the use of the foregoing specific catalytic agents.

Although the advantages of our invention can be obtained by working at a pressure above about 5 atmospheres, we prefer to employ higher pressures ranging say from 20 atmospheres upward.

The temperature of the reaction may, generally, be kept between about 200 to 500° C.

The following examples will serve to illustrate further the nature of our invention, which, however, is not confined to these examples.

Example 1: Impregnate pure asbestos with pure cobalt oxid, or osmium oxid, together with a little caustic soda, and then, while employing a coppered iron vessel with steel jacket and working at a pressure of 100 atmospheres and a temperature of from 300-400° C. pass over the catalyst thus prepared a mixture containing one part of pure hydrogen, and two or more parts of pure carbon monoxid. During the reaction some carbon is deposited and some water and carbon dioxid are produced, while in addition to methane higher hydrocarbons, as well as oxygen derivatives of the hydrocarbons, are formed and can be at once condensed or absorbed in a cold receiver. Generally, an aqueous solution of aldehydes and the like is obtained in addition to a light, oily liquid consisting chiefly of saturated and unsaturated hydrocarbons which boil up to 250° C. or even higher. It is preferred to maintain the receiver under the same pressure as the reaction space and to effect the condensation by cooling. If desired, a frac-

tionated cooling can be effected either with or without releasing the pressure. A similar procedure can be followed when using carbon dioxid instead of, or in addition to carbon monoxid, more oxygen-containing compounds and less hydrocarbons being then obtained.

Example 2: Impregnate a suitable carrier, for instance, calcined magnesia, pumice, or diatomite with potassium carbonate solution and then dry the mass and introduce it into a concentrated solution of zinc nitrate, pour off the liquid and dry and heat the contact mass which is then placed in a suitable apparatus; while employing a pressure of 120 atmospheres and a temperature of from 360-420° C. pass through the apparatus a gas mixture containing 62% of carbon monoxid, 28% of hydrogen, 4% of carbon dioxid, 2% of methane and 4% of nitrogen. The products consist chiefly of higher hydrocarbons and derivatives thereof. In this case carbon is generally not deposited or at the most only to a slight extent. The greater part of the products capable of liquefaction or absorption can be separated at ordinary temperature and the remaining gas generally contains olefins, such as ethylene and propylene, and further, paraffins such as methane and ethane. Analysis of the products obtained shows that the oily layer consists chiefly of hydrocarbons of boiling points from 20° to well above 200° C. For instance, about two-thirds are saturated and the rest olefinic, but this proportion can vary considerably. In addition to these hydrocarbons, organic oxygen compounds of various kinds are contained dissolved in the hydrocarbons. The oily layer, either before or after special purification possesses the character of the natural ethereal oils. Analysis of the aqueous layer shows a varying content of saturated and unsaturated organic compounds consisting, for instance, of alcohols, ketones, (such as acetone), aldehydes, (such as formaldehyde), acids, (such as acetic acid and higher homologues thereof,) and also other condensation products.

In those cases in which the gas mixture employed is not sufficiently pure, but contains traces of substances deleterious to the reaction, it is preferred to purify the gases specially, for instance, by passing them beforehand at a raised temperature through a purifier containing material similar to that employed as the catalytic agent. The gases leaving the receiver can be used over again after correcting their contents, for instance, by removing carbon dioxid and adding hydrogen, and the process can be carried out under continuous pressure.

Now what we claim is:—

1. The process of producing compounds

containing carbon and hydrogen by passing an oxid of carbon and hydrogen over a heated catalytic agent under a pressure exceeding that of 5 atmospheres. 65

2. The process of producing compounds containing carbon and hydrogen by passing an oxid of carbon and hydrogen over a heated catalytic agent under a pressure exceeding that of 20 atmospheres. 70

3. The process of producing compounds containing carbon and hydrogen by passing carbon monoxid and hydrogen over a heated catalytic agent under a pressure exceeding that of 20 atmospheres. 75

4. The process of producing compounds containing carbon and hydrogen by passing hydrogen with an excess of carbon monoxid over a heated catalytic agent under a pressure exceeding that of 20 atmospheres. 80

5. The process of producing compounds containing carbon and hydrogen by passing hydrogen with an excess of carbon monoxid over a heated metallic catalytic agent under a pressure exceeding that of 20 atmospheres. 85

6. The process of producing compounds containing carbon and hydrogen by passing hydrogen with an excess of carbon monoxid over a heated catalytic agent containing a compound of a heavy metal and some alkali under a pressure exceeding that of 20 atmospheres. 90

7. The process of producing compounds containing carbon and hydrogen by passing hydrogen with an excess of carbon monoxid over a heated catalytic agent containing a compound of a heavy metal and some alkali under a pressure exceeding that of 20 atmospheres and at a temperature between 200 and 500° C. 95

8. The process of producing compounds containing carbon and hydrogen by passing an oxid of carbon and hydrogen over a heated catalytic agent containing cobalt under a pressure exceeding that of 20 atmospheres. 100

9. The process of producing compounds containing carbon and hydrogen by passing an oxid of carbon over a heated catalytic agent containing zinc oxid under a pressure exceeding that of 20 atmospheres. 110

10. The process of producing compounds containing carbon and hydrogen by passing a gas mixture containing an oxid of carbon and hydrogen and free from substances deleterious to the reaction over a heated catalytic agent under a pressure exceeding that of 20 atmospheres. 115

11. The process of producing compounds containing carbon and hydrogen by passing gases containing an oxid of carbon and hydrogen over a heated catalytic agent under a pressure exceeding that of 20 atmospheres, and then separating by means of cooling the 120 125

liquid compounds which have been formed, while maintaining a pressure exceeding that of 20 atmospheres.

12. The continuous process of producing 5 compounds containing carbon and hydrogen by passing gases containing an oxid of carbon and hydrogen over a heated catalytic agent, then separating by means of cooling the liquid compounds which have been 10 formed, then correcting the composition of the remaining gas mixture, and passing it

anew over the catalytic agent, the whole process being carried out at a pressure exceeding that of 20 atmospheres.

In testimony whereof we have hereunto 15 set our hands in the presence of two subscribing witnesses.

ALWIN MITTASCH.
CHRISTIAN SCHNEIDER.

Witnesses:

J. ALEC. LLOYD,
S. S. BERGER.