

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Process for the Regenerating Catalysts for the Hydrogenation of Carbon Monoxide

I, HAROLD EDWIN POTTS, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention which has been communicated to me by N. V. INTERNATIONALE KOOLWATERS-TOFFEN SYNTHES MAATSCHAPPIJ (INTERNATIONAL HYDROCARBON SYNTHESIS COMPANY), of 20, Wasenaarscheweg, The Hague, Holland, a Dutch Company, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the regeneration of catalysts which have been used in the conversion of mixtures of carbon monoxide and hydrogen for the synthesis of hydrocarbons with more than one carbon atom in the molecule.

Hitherto the regeneration has been carried out by dissolving the active constituents (for example, metals and metal oxides), filtering the solution for separating insoluble substances, such as carriers and reprecipitation, drying and reduction of the catalytic constituents.

For this method of regenerating used catalysts it has already been proposed to previously treat the catalytic material with streaming hydrogen or gases containing hydrogen at temperatures of 300° Centigrade and thereabove, preferably at temperatures between 350° and 400° Centigrade. According to this prior proposal the treatment with hydrogen is finished as soon as the high molecular products, such as paraffin wax, which have been segregated on the catalyst during the synthesis, are removed. The treatment with streaming hydrogen may be preceded by an extraction with a suitable solvent or purifying agent as a result of which the treatment with hydrogen becomes more economical.

It has now been found that when continuing the treatment with hydrogen or gases containing hydrogen beyond the period of time required for removing the high molecular products and at higher temperatures, the full original activity of the catalyst can again be obtained. When

working in this manner the very important technical advantage is obtained that the measures necessary for the regeneration of the used catalyst in the wet way are no longer required.

The process is of particular importance for catalysts containing cobalt, but is also applicable to catalysts containing iron or nickel or catalysts containing mixtures of these metals. The catalysts may contain activating substances such as thorium oxide, manganese oxide, uranium oxide, cerium oxide, and magnesium oxide. They are advantageously brought on to carriers such as diatomaceous earth, pumice stone, diatomite, and magnesia.

In the process according to the present invention the used catalysts may also first be freed from paraffin wax in the usual manner, for example, by a treatment with hydrogen at 350° Centigrade for two hours, if desired, after a previous treatment with solvents. For restoring the full activity of the catalyst the treatment with hydrogen is continued, preferably at temperatures between 400° and 450° Centigrade or thereabove, for such a period of time until the catalyst has again attained the activity of a freshly prepared catalyst. The time required can be determined by experiments and in general amounts to 2 to 4 hours, so that the total treatment with hydrogen takes 4 to 6 hours.

In the treatment with hydrogen it is advantageous to let the temperature increase gradually to avoid a formation of decomposition products which may lead to the deposition of carbon and other difficultly removable high molecular products on the catalyst.

It has further proved to be advantageous to pass the gas, after the removal of the paraffin wax, at very high velocities over the catalyst to be regenerated. A velocity of more than 500 cubic metres, for example, of 1000 cubic metres of hydrogen per hour and square metre of cross-section of the passageway, is particularly advantageous.

In view of the large amounts of hydrogen which are required, it is necessary in practice to lead the hydrogen in a

circular course. Prior to being reintroduced into the catalyst mass to be regenerated, the hydrogen is preferably freed as far as possible from gases containing oxygen, such as, for example, carbonic acid, carbon monoxide and water vapour.

The water vapour can be removed by absorption agents, such as silica gel, or by low cooling or any other suitable measure. For the removal of the carbonic acid the usual absorption agents, such as alkali lye or the like, may be employed. The carbon monoxide can be catalytically converted into methane which in its turn can easily be removed.

It is advantageous to carry out the removal of the water vapour and the oxides of carbon to such an extent that the gas returned contains less than 2.5 grams of oxides of carbon and less than 1 gram of water vapour per cubic metre.

The activity of the catalyst regenerated in the described manner equals in every respect that of catalysts freshly prepared by precipitation. This result cannot be obtained, even not approximately, by the hitherto known treatment of the catalyst with hydrogen.

It has also proved to be advantageous to subject the catalysts prior to the proper activation with hydrogen to an oxidising treatment. This can be carried out with oxygen or gases containing or giving off oxygen, such as, for example, water vapour or carbonic acid, or with mixtures of these gases at elevated temperatures. Thereby a superficial oxidation of the catalytic metal is obtained. In this manner also those places of the used catalyst are reached which are only difficultly accessible to the action of hydrogen alone. The subsequent reduction with hydrogen can then be carried out more simply and easily and with greater certainty.

The following Example will further illustrate how the invention can be carried out in practice but it should be understood that the invention is not limited to the said Example.

#### EXAMPLE.

A catalyst obtained in the usual manner by precipitation, which contains 100 parts of cobalt, 5 parts of thorium oxide ( $\text{ThO}_2$ ) and 8 parts of magnesium oxide ( $\text{MgO}$ ) on 200 parts of kieselguhr and which has been used for 3500 hours at temperatures between  $185^\circ$  and  $192^\circ$  Centigrade in the synthesis of benzine, was treated with a mixture of nitrogen and hydrogen containing 75 parts by volume of hydrogen for each 25 parts by volume of nitrogen

during 150 minutes at  $200^\circ$  Centigrade. Thereafter the temperature was raised within 30 minutes to  $350^\circ$  Centigrade. The subsequent treatment with hydrogen was carried out in such a manner that the catalyst mass was first heated during 30 minutes at  $350^\circ$  Centigrade, then during a further 30 minutes at  $400^\circ$  Centigrade and finally during 120 minutes at  $450^\circ$  Centigrade. Thereupon the catalyst was again taken into operation at  $185^\circ$  Centigrade. It thereby showed the same activity which it originally possessed.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

1. Process for the regeneration of catalysts which have been used in the catalytic conversion of mixtures of carbon monoxide and hydrogen for the production of hydrocarbons with more than one carbon atom in the molecule with the aid of hydrogen or gases containing hydrogen, characterised in that the treatment with hydrogen is continued beyond the period of time required for removing the high molecular products and at higher temperatures.

2. Process according to claim 1, characterised in that the regeneration of the catalysts is carried out after the removal of high molecular products at temperatures between  $350^\circ$  and  $450^\circ$  Centigrade.

3. Process according to claims 1 and 2, characterised in that gas velocities are used of at least 500 cubic metres, preferably 1000 cubic metres per hour and square metre of cross-section of the passageway.

4. Process according to claims 1 to 3, characterised in that the hydrogen is led in a circular course.

5. Process according to claims 1 to 4, characterised in that the hydrogen to be used again is previously freed from water vapour and oxides of carbon, whereby these substances are preferably removed to such an extent that the hydrogen returned contains less than 2.5 grams of oxides of carbon and less than 1 gram of water vapour per cubic metre.

6. Process according to claims 1 to 5, characterised in that prior to the activation with hydrogen the catalyst to be regenerated is subjected to an oxidising treatment.

Dated this 6th day of November, 1939.

W. P. THOMPSON & CO.,  
12, Church Street, Liverpool, 1.  
Chartered Patent Agents.