# PATENT SPECIFICATION

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COMPLETE SPECIFICATION

## Process for producing Solid Paraffins

We, STUDIEN- UND VERWERTUNGS-GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, of 2, Kaiser-Wilhelm Platz, Mülheim-Ruhr, Germany, Manufacturers, a body corporate organised and existing under the Laws of the German State, do hereby declare the nature of this invention 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 consists in a process for the preferential recovery of paraffin that is solid at room temperature from gases containing carbon monoxide and hydrogen; the process is carried out by passing the gases that contain carbon monoxide and hydrogen over immovable cobalt catalysts at temperatures below 250° C. and under pressures that are a multiple of the pressure of the atmosphere, the cobalt catalysts having first been impregnated with paraffin that is solid at room temperature, without the paraffin filling the spaces between the particles of contact material, the catalyst being further so disposed that the paraffin produced can continuously drip from it.

It is well known that when benzine synthesis is being effected under atmospheric pressure in accordance with the process of the prior British Patent No. 255,818 from gases containing carbon monoxide and hydrogen in the presence of highly active catalysts that contain metals of the eighth group of the periodic system, aliphatic hydrocarbons having quite different boiling points are formed, included among them being solid paraffin. The amount of paraffin varies, according to the condition under which synthesis is carried out, between 4 and 10%, and is thus in quantity far below the other reaction products. Thus, by far the greater part of the reaction products passes out of the reaction chamber in the form of vapour or gas. The relatively small quantities of paraffin remaining on the catalyst are removed from the catalyst by extraction or other known means at the end of a suitable period, that is to say after several weeks or months.

Furthermore, catalytic reactions of carbon monoxide and hydrogen under pressure in the presence of iron catalysts are known. These reactions are carried out either in vertically or horizontally disposed reaction tubes. A preferential production of paraffin as a reaction product has not been observed. The iron catalysts employed in the known method are unsuitable for the continuous production of any considerable quantities of paraffin.

Furthermore, carbon monoxide and hydrogen have been caused to react under a high pressure, such as 5 or 80 atmospheres, in the presence of cobalt catalysts. When carrying out these reactions the possibility of producing paraffin was thought of but paraffin would not have been preferentially produced under the reaction conditions employed, in fact the reaction products obtained were normally liquid and gaseous hydrocarbons. As already stated, it is necessary, for the purpose of initiating the desired formation of paraffin, that the catalyst be so impregnated with paraffin that the spaces between the particles of the contact substance shall not be filled with paraffin—that is to say, it is possible either to commence with a well impregnated catalyst or to allow the catalyst to become thus thoroughly impregnated during synthesis. In the latter case the starting period amounts to several days, that is to say the catalyst is converted during the starting period into a condition in which the formation of solid paraffin is very much facilitated. In the already proposed conversion under pressure of gases containing hydrogen and carbon monoxide, in the presence of cobalt catalysts, the reactions were however, always interrupted after a few hours, at most after one night, and then the catalysts were exposed to oxidation in air. This alternate use of a mixture of hydrogen and carbon monoxide on the one hand, and air on the other, rendered impossible a thorough impregnation of the catalyst with paraffin and therefore made the recovery of paraffin impossible. Moreover, the apparatus employed in the method referred to did

not appear to be altogether suitable for carrying out the process according to the invention because the reaction products could only pass out of the horizontally disposed reaction tube laterally, for it is important to the method claimed that the paraffin produced in the reaction shall be capable of running off from the catalyst in order that it may not be necessary for the latter to be withdrawn from the reacting gases in the paraffin pool that forms during the process.

The process of the invention may be carried out by passing over cobalt catalysts a mixture of carbon monoxide and hydrogen in the proportion of 1:2 at temperatures below 250° C. and under pressures of more than 2 atmospheres, for example 4 to 10 or 20 atmospheres or over. At the same time care has to be taken that by known means the reaction heat is carried off and the temperature maintained constant. It is important that the paraffin forming on the catalyst shall be permitted to flow off, so that it is not exposed to further change. If the paraffin that is formed during the reaction were not drawn off there would soon be formed a paraffin pool in which the catalyst would be immersed and the reaction gases would be screened from the catalyst. Further, to secure the solid paraffin desired the catalyst must, as already indicated, be thoroughly impregnated at the outset with paraffin, or it must be well impregnated during a starting period amounting to several days, the particles of the catalysts not undergoing change either in condition or position. At pressures of over 100 atmospheres the cobalt is slightly volatilised into carbonyl. Formation of paraffin is however also possible at these pressures.

Instead of a gas mixture containing carbon monoxide and hydrogen in the proportion of 1:2, gas mixtures having some other ratio of carbon monoxide to hydrogen, as well as gases diluted with other constituents, may be used.

It is possible to employ as catalysts, inter alia all those that contain cobalt or cobalt together with other catalytic agents, such as can be used for benzine synthesis. To facilitate the draining off of the paraffin, the catalyst is advantageously provided in vertical reaction chambers, the reaction products being drawn off at the bottom of the vessel; vertical reaction chambers are not however essential. Thus, conversion can be effected for example in obliquely disposed chambers, or the catalyst may be laid on horizontal perforated sheets of metal, sieves or the like.

If a pressure of about 5 to 20 atmospheres is employed, the catalyst maintains almost unlimited efficiency in comparison with former syntheses with carbon monoxide and hydrogen.

EXAMPLE 1.

4 litres of gas per hour calculated at atmospheric pressure and containing 30% of carbon monoxide and 60% of hydrogen, is passed over a granulated and reduced catalyst of cobalt thorium and kieselguhr produced by precipitation and containing 4 grammes of cobalt, which, lying on wire gauze, is contained in a vertical pressure tube open at the bottom, the gas being at a temperature of 190° C. and a pressure of 4 atmospheres. The contraction of the gases resulting from conversion amounts to 75%. The remainder consists for the greater part of unconverted carbon monoxide and hydrogen, also of nitrogen and gaseous hydrocarbons. The yield of paraffin leaving the catalyst and solid at room temperature amounts, counting from the second day, to from 90 to 100 grammes per cubic metre of gas mixture admitted. About 1% of this paraffin is insoluble in boiling ether, and it has a melting point of from 110 to 114° C. The part of the tube which extends beyond the reaction zone must lead to a storage vessel at a temperature higher than the melting point of paraffin in order to avoid an accumulation of paraffin in the catalyst mass. The waste gas from the reaction contains about 20 grammes of benzine. The activity of the catalyst remains uniform for many months.

EXAMPLE 2.

The process is carried out at 10 atmospheres pressure with the catalyst referred to in Example 1 and in the same apparatus, at the same temperature, and with the same quantity of carbon monoxide and hydrogen gas. With a contraction of approximately 76% per cubic metre of gas, 100 to 110 grammes of paraffin solid at room temperature are obtained commencing on the third day; 13% of this product is insoluble in boiling ether, and it has a melting point of from 110 to 114° C. The waste gas from the reaction contains about 20 grammes of benzine. The activity of the catalyst does not change for months.

EXAMPLE 3.

In the same apparatus at the same temperature and with the same mixture of carbon monoxide and hydrogen, the process is carried out at 20 atmospheres pressure with the catalyst referred to in Example 1. Approximately 120 grammes of paraffin solid at room temperature are obtained with a contraction of from 75 to 80% per cubic metre of gas. The total

quantity of crude paraffin (approximately 120 grammes) obtained per cubic metre from the fourth day does not melt completely until it is over 100° C.; it is pure white and is almost odourless. 22% of the paraffin is insoluble in boiling ether, and its melting point lies between 110 and 114° C. The waste gas from the reaction also contains about 20 grammes of benzine. The activity of the catalyst remains for months. If after a lengthy period the catalyst be extracted it will be found to contain paraffins having a melting point which is higher than that just described (and heretofore generally known) namely, 130° C. or over.

We disclaim the step of trickling liquid media, such as liquid hydrocarbons, over the catalyst during the conversion reaction. We further disclaim such conditions of low pressure as will permit the paraffin impregnating the catalyst to be carried away by the flowing gases or vapours, after the conversion reaction has commenced, in the manner contemplated in Specification No. 471,595. It will be appreciated that, at the temperatures employed in the reaction, the use of pressures that are a multiple of the atmospheric pressure does not permit the object of the prior invention to be attained.

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

1. A process for the production of paraffin that is solid at room temperature by catalytic synthesis from gases containing carbon monoxide and hydrogen, in which the initial gases containing carbon monoxide and hydrogen are passed at pressures that are a multiple of the atmospheric pressure and at temperatures lying below 250° C. over immovable solid cobalt catalysts that have been impregnated with paraffin which is solid at room temperature, without the paraffin filling the spaces between the particles of catalyst, the catalyst being so provided that the paraffin formed during the reaction can drip continuously from it.

2. A process for producing paraffin according to claim 1, characterised in that the paraffins that accumulate in the catalysts and that have a particularly high melting point are separated off and recovered by extraction or other known means.

3. A process for the preferential production of paraffin substantially as hereinbefore described.

Dated this 17th day of July, 1937.

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