# PATENT SPECIFICATION

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COMPLETE SPECIFICATION

# Improvements in the production of Solid Paraffin Hydrocarbons by the Hydrogenation of Carbon Monoxide

We, BADISCHE ANILIN- & SODA-FABRIK (IG. Farbenindustrie Aktiengesellschaft "In Auflosung") a Company recognised under law, of Ludwigschafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

We have found that in the reaction of carbon monoxide with hydrogen in the presence of catalyst which contain iron and copper in precipitated form and alkali metal, unexpectedly high yields of solid paraffin hydrocarbons are obtained by using the catalysts in the presence of such amounts of calcined substances containing silica, as for example silica gel or kieselguhr, that the molar ratio of alkali metal oxide to silicon dioxide lies between 0.05 and 0.25 and in particular between 0.08 and 0.2. If this ratio is exceeded, the products still contain relatively large amounts of solid paraffin hydrocarbons, but an appreciable increase in acid formation takes place; as a by-product there are formed undesirable amounts of carbon dioxide. Moreover the otherwise white solid product is discoloured dirty green to brown and the distillation residue is dark brown to black. If on the other hand a catalyst is used in which the ratio of alkali metal oxide to silicon dioxide is less than stated above, the formation of paraffin wax decreases considerably and the ratio of hard paraffin wax to soft paraffin wax becomes lower.

Potassium and sodium are the preferred alkali metals. It is advantageous, however, to take care that potassium predominates. In this case the molar ratio of alkali metal oxide to silicon dioxide is advantageously between 0.1 and 0.16.

The relative proportions of siliceous substance to the iron of the catalyst may vary within wide limits. It is preferable, however, to use 15 to 100, advantageously 25 to 60, parts by weight of silicon dioxide to each 100 parts of iron. Such catalysts exhibit a specially uniform action and have a long life.

The catalysts are prepared in the usual way by precipitation, for example from solutions of the salts of the said metals. It is preferable to take care that sodium originating from the precipitant is washed out as thoroughly as possible from the moist precipitated mass because its activating action is less than that of the potassium to be added. This washing out of the sodium is possible almost completely if the precipitation is carried out at a constant *p*H value. The maintenance of a constant *p*H value may readily be achieved by allowing the hot concentrated solutions of the metal salts and the alkali solution to flow uniformly through flow meters into a vessel in which the calcined, finely ground silica gel or kieselguhr is suspended in water.

The catalyst is preferably employed in highly porous form, i.e. without pressing, for example in the form in which it is obtained on a heated grooved roller. In order to adjust its activity in such a way as is preferable for the production of the highest possible yields of solid paraffin hydrocarbons, there is first of all allowed to flow over it at about 170° C. about 1000 litres of synthesis gas per litre of catalyst per hour (measured without pressure), the charge then being slowly reduced to 500 litres per litre of catalyst per hour. The catalyst may however also be pretreated at about 180° C. with hydrogen or synthesis gas before use, a charge of 200 litres per litre of catalyst per hour then being sufficient. In such a treatment only a partial reduction takes place. There is practically no metallic iron present in the catalyst,

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The reaction of carbon monoxide with hydrogen proceeds under the usual conditions, in particular at temperatures of about 210° to 230° C. and at pressures of about 5 to 30 atmospheres. A special advantage of the said catalyst is that good yields of solid paraffin hydrocarbons are obtained even from synthesis gases which contain less carbon monoxide than the mixtures usually employed for the production of hydrocarbons for instance from initial gases in which the ratio by volume of hydrogen to carbon monoxide is greater than 2:1. Thus for example the waste gases from the synthesis of methyl or isobutyl alcohol from carbon monoxide and hydrogen can be worked up into solid paraffin hydrocarbons with good yields.

The following example will further illustrate this invention but the invention is not restricted to this example. The parts are by weight.

### EXAMPLE

A hot concentrated solution of iron and copper nitrates, in which the ratio of iron to copper is about 100:25, and an equivalent amount of concentrated soda solution are passed in uniform streams through flow meters in the course of an hour into a vessel in which extremely finely ground calcined silica gel is suspended in water. The *pH* value in the vessel is kept at 8.2. After precipitation it is heated to 90° C. and the precipitate is washed almost completely free from alkali metal with hot water in a filter press. The resulting moist mass is then thoroughly kneaded and analysed. By the addition of potassium carbonate in the calculated amount, the molar ratio of alkali metal oxide to silicon dioxide is adjusted so that in the finished catalyst it amounts to 0.135. The moist mass is predried on a grooved roller heated with steam and shaped into small rods. The after-drying is effected in an electrical drying chamber at 110° C. The finished catalyst has a bulk density of 420 grams per litre and contains 25 parts of copper, 30 parts of silicon dioxide, 5.6 parts of potassium oxide and 0.5 part of sodium oxide to each 100 parts of iron.

Over the catalyst thus prepared there is led at 220° C. waste gas free from sulphur from the isobutyl alcohol synthesis, in which the ratio by volume of carbon monoxide to hydrogen is 1:2.7. The loading of the catalyst amounts to about 514 cubic meter of gas per litre of catalyst per hour. The carbon monoxide reacts to the extent of 64% and from each cubic metre of initial gas there are obtained 48 grams of solid and liquid products of which 79% boil above 320° C. The ratio of hard paraffin wax to soft paraffin wax in the pure white product is 1.9:1. The distillation residue is only slightly yellowish in colour.

What we claim is:—

1. A process for the production of solid paraffin hydrocarbons by hydrogenation of carbon monoxide in the presence of catalysts which consists in carrying out the process in the presence of catalysts containing iron and copper in precipitated form, alkali metal and such an amount of a calcined substance containing silica that the molar ratio of alkali metal oxide to silicon dioxide lies between 0.05 and 0.25, in particular between 0.08 and 0.2.

2. A process as claimed in claim 1 wherein, when employing catalysts containing predominantly potassium as the alkali metal component, the molar ratio of alkali metal oxide to silicon dioxide lies between 0.1 and 0.16.

3. A process as claimed in claim 1 or 2, wherein a catalyst is employed which contains 15 to 100, in particular 25 to 60, parts by weight of silicon dioxide to each 100 parts by weight of iron.

4. A process as claimed in any of claims 1 to 3, wherein the catalyst is pretreated with the initial gas or with hydrogen under such conditions that practically no metallic iron is thereby formed.

5. A process as claimed in any of claims 1 to 4, wherein an initial gas is employed in which the ratio by volume of hydrogen to carbon monoxide is greater than 2:1.

6. A process as claimed in any of claims 1 to 5, wherein the waste gases from the synthesis of methyl or isobutyl alcohol from carbon monoxide and hydrogen are used as the initial gas.

7. The process for the production of solid paraffin hydrocarbons substantially as described in the foregoing example.

8. Solid paraffin hydrocarbons when obtained by the process claimed in any of claims 1 to 7.

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