PATENT SPECIFICATION

Inventors: HERBERT KÖLBEL and ROBERT LANGHEIM

708,744

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COMPLETE SPECIFICATION

A process for the Catalytic Hydrogenation of Carbon Monoxide

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BUGBAU UND CHEMIE, of Homberg (Niederrhein), Germany, a German Joint Stock Company, 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:—

The invention relates to a process for the catalytic hydrogenation of carbon monoxide in the presence of an iron catalyst and particularly to a process whereby the yield of paraffin wax obtained at the beginning of the process is maintained or even increased during continuation of the process.

The term "paraffin wax" signifies high molecular paraffin hydrocarbons which are solid at normal temperature.

It is known that the formation of paraffin wax in the catalytic hydrogenation of carbon monoxide depends on the alkali-metal content of the iron catalyst, the paraffin wax yield increasing to a certain limit with increase in the amount of alkali-metal promoter in the catalyst. Unfortunately, however, the formation of paraffin wax diminishes as the synthesis process proceeds. This decrease is particularly evident where the process is operated under normal pressure.

In medium pressure operation, attempts have been made to cope with this inconvenience by treating the catalyst with oxygen as soon as decrease in the formation of paraffin wax occurs to an appreciable degree. Although this procedure is reported to have brought about some success it suffers from the disadvantage that the catalyst must, after each treatment with oxygen, be reactivated by reduction, which necessary measure involves loss of time and of gas. This method is not applicable to normal pressure operation as the catalyst, having been treated with oxygen, cannot be revivified by reduction.

It has now been found that the iron catalyst, both in normal and medium pressure operation, will lose none of its paraffin wax-forming capacity if it is periodically recharged with an alkali-metal compound by adding the alkali-metal compound to an agent used for the extraction of paraffin wax from the catalyst. The alkali-metal compound is preferably added to the extraction agent after the bulk of the paraffin wax has previously been extracted. In doing so, it is of particular importance that the alkali-metal compound, unless it is soluble in the extraction agent, should be ground as finely as possible, and that the suspension of extraction agent and alkali-metal compound should have a good degree of stability—for example, by using ultrasonics in preparing the suspension—as the efficiency of the process according to the invention depends greatly upon these factors. The finer the division of the alkali-metal compound and the more stable the suspension, the more intensive is the supplementary alkalization or re-alkalization of the catalyst. If the particles of the alkali-metal compound are too coarse and sedimentation of the alkali-metal compound occurs too rapidly, the greater part of the alkali-metal compound will be deposited upon the surface of the catalyst bed and but little of the alkali-metal compound will penetrate into the upper layers of the catalyst bed and none at all into the interior of the catalyst bed.

The hydrogenation of the carbon monoxide is preferably carried out at a temperature in the range of 160°—300° C. and at a pressure in the range of 1—30 atmospheres.

The alkali-metal compound used for the re-alkalization is preferably used in such a fine state of division that not more than 80%, preferably less than 50%, of the alkali-metal compound suspended in the extraction agent will precipitate within one hour.

Suitable alkali-metal compounds for use in the process of the invention are the oxides, hydroxides, carbonates, bicarbonates, phosphates, silicates and borates of sodium and

[*Price* 2/8]

potassium, also organic alkali-metal compounds, such as alkali-metal alcoholates, formates, acetates or the alkali-metal salts of higher organic acids, such as soaps.

The re-alkalization is not only a means for preventing any decrease in the formation of paraffin wax during the course of a period of operation, but the quantity of alkali-metal compound subsequently added will also induce an increase in the yield of paraffin wax from such iron catalysts which at first produce only small amounts of paraffin wax. The re-alkalization is preferably carried out at intervals of from 250 to 700 hours.

The process in accordance with the invention is further illustrated by the following examples:—

EXAMPLE 1.

An iron catalyst obtained by precipitation with sodium carbonate in known manner, contained, apart from 3 parts of an alkali-metal compound (calculated as the monoxide) and 10 parts of copper, 10 parts of magnesium as activator and 50 parts of kieselguhr as carrier or support, all parts being by weight and relative to 100 parts by weight of iron in the catalyst. The catalyst was used in synthesis with water gas under normal pressure at 230° C., the space velocity being 70 normal cubic metres of water gas per hour per cubic metre of reactor space. At the end of 345 hours of operation the paraffin wax was extracted from the catalyst for the first time, a heavy naphtha fraction boiling in the range 180°—220° C. being used as the extraction agent or solvent. Operation was then immediately resumed and continued under the same conditions. Up to the 345th hour of operation, the yield of paraffin wax amounted to 35.7% of the total synthesis products. Extraction of the catalyst was repeated at the end of the 605th hour of operation. Between the 346th and 605th and between the 606th and 896th hours of operation the yields of paraffin wax amounted to 27.5% and 24.2% resepectively. On the other hand, the production of paraffin wax is almost constant when the catalyst is treated according to the invention, which fact will be seen from Table 1 and from the following description.

TABLE 1.

Formation of paraffin wax without and with treatment of the iron catalyst according to the process of the invention in normal pressure operation.

FORMATION OF PARAFFIN WAX

Without supplementary alkalization		With supplementarly alkalization	
Hours of operation	Total % yield of paraffin wax	Hours of operation	Total % yield of paraffin wax
1—345	35.7	1—374	34.9
346—605	27.5	375—624	36.2
606—896	24.2	625—915	34.1

The same catalyst was employed in the process according to the invention under the synthesis conditions particularly described. At the end of the 374th hour of operation the catalyst was extracted with a heavy naphtha (boiling range 180°—220° C.). After the bulk of the paraffin wax had thus been removed, the final step in the extraction was carried out with a further quantity of the heavy naphtha which contained 50 grams of finely ground potassium carbonate per litre in suspension. Operation was then continued under the same synthesis conditions. The yield of paraffin wax in the first operating period amounted to 34.9% of the total synthesis products. At the end of the 624th hour of operation, the catalyst was again extracted by the same method as that employed in the first extraction at the end of 374 hours of operation. The synthesis was then continued until the 915th hour. The yields of paraffin wax in the 2nd and the 3rd operating periods amounted to 36.2% and 31.1% respectively. It is thus possible to maintain, by means of the supplementary alkalization, in accordance with the invention the yield of paraffin wax at the value obtained during the first period of operation.

EXAMPLE 2.

A precipitated iron catalyst, containing dolomite as carrier, was employed under an absolute pressure of 11 atmospheres and at a temperature of 214° C. with a synthesis gas in which the H_2/CO ratio was 1.7, the space velocity being 600 normal cubic metres of synthesis gas per hour per cubic metre of reactor space. At the end of the 1037th and 1875th hours of operation, the catalyst was extracted in known manner with a hydrocarbon fraction boiling in the range 200°—250° C. and obtained by the catalytic hydrogenation of carbon monoxide. In the three operating periods up to the 2558th hour of operation, the yields of paraffin wax are shown in Table 2.

TABLE 2.

Formation of paraffin wax without and with treatment of the iron catalyst according to the process of the invention in medium pressure operation.

FORMATION OF PARAFFIN WAX

Without supplementary alkalization		With supplementary alkalization	
Hours of operation	Total % yield of paraffin wax	Hours of operation	Total % yield of paraffin wax
1—1037	28.7	1— 275	30.5
1038—1875	24.2	276— 995	38.5
1876—2558	21.8	996—1668	41.2
		1669—2124	39.4
		2125—2678	38.9

A precipitated iron catalyst of precisely the same composition was used, in the process, according to the invention, under the same operating conditions and with a synthesis gas of the same composition. The paraffin wax was removed from the catalyst by extraction with the hydrocarbon fraction of 200°—250° C. boiling range at the end of 275, 995, 1668 and 2124 hours of operation, the hydrocarbon fraction having 53 grams of potassium phosphate (K_3PO_4) per litre in suspension.

It will be seen from Table 2 that under the same operating conditions, the same catalyst will produce a considerably higher yield of paraffin wax if it is more frequently extracted and at the same time subjected to supplementary alkalization in accordance with the invention.

What we claim is:—

1. A process for the production of paraffin wax by the hydrogenation of carbon monoxide in the presence of an iron catalyst, which comprises periodically recharging the iron catalyst with an alkali-metal compound by adding the alkali-metal compound to an agent used for the extraction of paraffin wax from the catalyst.

2. A process according to claim 1, in which the alkali-metal compound is in suspension in the extraction agent, the state of division and distribution of the alkali-metal compound being such that not more than 80% preferably less than 50%, of the compound will precipitate within one hour.

3. A process according to claim 1 or claim 2, in which the extraction agent is a heavy naphtha.

4. A process according to any of the preceding claims, in which the iron catalyst is recharged with the alkali-metal compound at intervals from 250 to 700 hours.

5. A process for obtaining a high yield of paraffin wax by the hydrogenation of carbon monoxide in the presence of an iron catalyst containing an alkali-metal compound as promoter, which comprises periodically treating the catalyst with an extraction agent for the removal of paraffin wax, the bulk of the paraffin wax being first removed from the catalyst at each treatment by one or more washes with the extraction agent, the catalyst being then given a final wash with the extraction agent charged with an alkali-metal compound, and where the alkali-metal compound is not soluble in the extraction agent, the suspension of the alkali-metal compound in the extraction agent being such that not more than 80% of the alkali-metal compound will be precipitated when the suspension is allowed to stand for one hour.

6. A process according to any of the preceding claims, in which the alkali-metal compound is an oxide, hydroxide, carbonate, bicarbonate, phosphate, silicate, borate, or an organic compound such as an alcoholate, formate, acetate or a salt of a higher organic acid.

7. A process according to any of the preceding claims, in which the alkali-metal compound is a compound of sodium or potassium.

8. A process according to any of the preceding claims, in which the hydrogenation is carried out at a temperature within the range 160°—300° C. and at a pressure within the range 1—50 atmospheres.

9. A process for maintaining and/or increasing the content of paraffin wax in the products obtained from the catalytic hydrogenation of carbon monoxide over iron catalysts, substantially as hereinbefore described with reference to the Examples.

10. A process for the production of paraffin wax, substantially as hereinbefore described.

11. Products containing paraffin wax whenever obtained by the process claimed in any one of the preceding claims.

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ERRATA

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Page 1, In Heading *for* "July 25, 1950" *read* "July 25, 1951,".
Page 1, line 2, *for* "Bugbau" *read* "Bergbau".
Page 2, line 53, *for* "supplementarly" *read* "supplementary".
Page 2, line 86, *for* "31.1%" *read* "34.1%".
Page 3, line 47, *after* "80%" *insert* ",".
Page 3, line 56, *after* "intervals" *insert* "of".

THE PATENT OFFICE,
22nd October, 1954

DB 68862/1(13)/3468 150 10/54 R

ERRATA

SPECIFICATION NO. 708,744

Page 2, line 58, *for* "supplementarly" *read* "supplementary".
Page 2, line 86, *for* "31.1%" *read* "34.1%".
Page 3, line 47, *after* "80%" *insert* ",".
Page 3, line 56, *after* "intervals" *insert* "of".

THE PATENT OFFICE,
18th October, 1954

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venience by treating the catalyst with oxygen as soon as decrease in the formation of paraffin wax occurs to an appreciable degree. Although this procedure is reported to have brought about some success it suffers from the disadvantage that the catalyst must, after each treatment with oxygen, be reactivated by reduction, which necessary measure involves loss of time and of gas. This method is not applicable to normal pressure operation as the catalyst, having been treated with oxygen, cannot be revivified by reduction.

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