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PATENT SPECIFICATION

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2452

PROVISIONAL SPECIFICATION.

Improvements in the Catalytic Synthesis of Hydrocarbon Oils.

We, ROBINSON BINDLEY PROCESSES LIMITED, a British Company, of 31, East Street, Epsom, in the County of Surrey, and WILLIAM WHALLEY MYDDLETON, a British Subject of 3, Woodland Avenue, New Malden, in the County of Surrey, do hereby declare the nature of this invention to be as follows:—

This invention relates to processes for the production of hydrocarbon oils by the reaction in the presence of a catalyst of gases containing hydrogen and carbon monoxide. In carrying out such processes the catalytic bed may be formed by a mass of granular material contained in a vertical tube of circular cross section and the reaction materials passing continuously through this tube in a downward direction. The reaction is highly exothermic and it is necessary to provide cooling means, for maintaining the required temperature, which is in the neighbourhood of 200° C. Any considerable increase of temperature above the optimum value causes very large reduction in the yield of the required products.

Satisfactory results have been obtained by the use of catalyst tubes some 16 millimetres in diameter containing a catalytic bed some two feet in depth, but the volume of gas which can be treated by a catalytic bed of this size in a given time is necessarily small and it would be far more economical to employ a bed of larger dimensions if this were possible. It is found, however, that if either the diameter of the tube or the depth of the bed is increased substantially and the rate of flow of gas correspondingly increased, overheating of the catalyst takes place. It has been considered hitherto that if the velocity of the gases entering the reaction chamber is increased substantially above that required for a catalytic bed two feet in depth, satisfactory cooling can only be obtained by the use of tubes which do not exceed seven millimetres in diameter. The reduction in the diameter of the tubes must be offset against the advantage gained by increasing the depth of catalyst employed.

We have found that, at least initially, the overheating which takes place when the velocity of the reaction gases is increased is confined to a very shallow layer at the upper surface of the catalytic bed. It appears to be caused by small irregularities or projections on the topmost granules becoming inflamed and gradually communicating their excessive temperature to the neighbouring portions of the catalytic mass. We have also found that this overheating can be prevented by at first limiting the velocity of the entering gases to a low value and only gradually increasing it to the normal working rate. It appears that the small projections or irregularities referred to above are removed in some way (possibly by mechanical action or possibly by slow sintering) during the initial period when the gas velocity is low and there is no danger of overheating, so that by the time the full velocity is attained the surfaces of the topmost granules on which the gases impinge are smooth and free from projections. It will be understood that the correctness or otherwise of this theory is immaterial to our invention which consists in the practical application of our discovery that the overheating of the catalyst which occurs when the velocity of the gases is made greater than is usual can be prevented by starting the process with a low gas velocity and only later increasing it to the normal working rate.

We have found that by the application of our invention it is possible to use a catalytic bed six feet in depth without causing overheating and without reducing the diameter of the tubes; indeed we have found that it is possible to increase the diameter of the tubes to one inch. The yield from a single treating unit is thus very much in excess of what has hitherto been possible. By way of example of the method of carrying out our invention we may mention that with a catalytic bed of the dimensions given (one inch in diameter by six feet in length) the rate of flow of gases during normal working is 800 litres per hour; we find that overheating is prevented if at the start of the process the rate of flow is limited to six litres per hour, then after an interval increased to 20 litres per hour, after another inter-

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val to 60 litres, after another to 100 litres and so on by stages until some two and a half hours after the start of the process the full rate of 900 litres has been attained. It will, however, be understood that our invention is in no way confined to the particular dimensions, rates and times mentioned, which are given solely by way of example.

It will also be understood that our invention is not confined to apparatus in which the catalytic bed is contained in vertical tubes of circular cross section as described above. The invention is equally applicable to apparatus in which the catalyst vessel is of any other form. In particular the catalyst may be contained in the annular space between two concentric tubes, through and around which a temperature regulating fluid is circulated.

Dated this 21st day of May, 1937.

A. A. THORNTON,
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7, Essex Street, Strand, London, W.C.2,
For the Applicants.

COMPLETE SPECIFICATION.

Improvements in the Catalytic Synthesis of Hydrocarbon Oils.

We, SYNTHETIC OILS LIMITED (formerly Robinson Bindley Processes Limited), a British Company, of 81, East Street, Epsom, in the County of Surrey, and WILLIAM WHALLEY MYDDLETON, a British Subject, of 3, Woodlands Avenue, New Malden, in the County of Surrey, 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:—

This invention relates to processes for the production of hydrocarbon oils by synthesis reactions, in the presence of a catalyst, of mixtures of gases containing hydrogen and oxides of carbon, such as carbon-monoxide.

In carrying out such processes the catalyst may be a solid or porous mass or may be of granular material. It may be contained in a vertical tube of either circular or other cross section or it may be disposed in layers of suitable thickness on trays or plates in a container of cylindrical or other shape. Such tubes or trays may be advantageously provided with heat conducting diaphragms attached to the supporting surface. It has been found in many cases desirable to use a catalytic bed formed by a mass of granular material contained in a vertical tube of circular cross-section. The reaction constituents are normally passed downward continuously over the catalyst but the direction of flow is not inherent to the mechanism of such processes. Synthesis reactions of this type are exothermic and moreover require close temperature control, and it is necessary usually to provide cooling means for maintaining the required temperature, which in the case of the hydrocarbon syntheses, employing certain now known catalysts, is in the neighbourhood of 392° F. Any considerable increase of temperature above the optimum value for such reactions causes an appreciable reduction in the yield of the required products. Satisfactory results have been obtained by the use of catalyst tubes some 16 millimetres in diameter containing a catalytic bed some two feet in depth, but the volume of gas which can be treated by a catalytic bed of this size in a given time is necessarily small and it would be far more economical to employ a bed of larger dimensions if this were possible. It is found, however, that if either the diameter of the tube or the depth of the bed is increased substantially and the rate of flow of gas correspondingly increased, overheating of the catalyst takes place. It has been considered hitherto that if the velocity of the gases entering the chamber is increased substantially above that required for a catalytic bed two feet in depth, that satisfactory cooling can be obtained only by the use of containers so dimensioned that the maximum distance from any point in the catalyst mass to the inner surface of the container is not over 8.5 millimetres when measured in a plane normal to the major axis of the catalyst mass; i.e. in the case of catalyst contained in a tube the maximum tube diameter would be 7 millimeters. The advantages gained by the increased velocity of the gases and the increased depth of catalyst must be offset against the reduction in diameter of the tube.

We have found that, at least initially, the overheating which takes place when the velocity of the reaction gases is increased is confined to a very shallow layer at the upper surface of the catalytic bed. It appears to be initiated on small areas of irregularities or projections on the topmost catalyst granules which become inflamed and soon communicate their excessive temperature to the neighbouring portions of the catalytic mass. This observed effect may merely be the overall result of an intensely active

chemical reaction between the synthesis gases on particularly active centres; the exact mechanism is difficult, and at present, impossible to determine. On the basis of experiments it was found desirable to prevent a temperature rise of more than about 30° F. in the hottest layer of the catalyst. We have found that this over-heating can be prevented by at first limiting the velocity of the entering gases to a sufficiently low value so that the temperature rise of a specified point or points in the catalyst bed does not increase above a predetermined value, as determined by a thermocouple or other adequate thermometric device suitably placed, and thereafter either continuously or in stepwise fashion increasing the velocity of the gas flow to a desired rate, in such a way as not to exceed the predetermined temperature of the catalyst mass. The desired incremental increase in the gas flow rate may be made by hand control or may be effected by suitable automatic devices for regulating gas flow actuated by the thermometric device installed in the catalyst bed.

It will be understood from the foregoing that our invention consists essentially in the practical application of our discovery that the overheating of the catalyst which occurs when the synthesis gases are passed over a new or freshly reactivated catalyst at the substantially full operating flow rate can be prevented by starting the operation of a catalyst bed with a low gas velocity and only later increasing it to the desired normal working rate either gradually or stepwise. Our invention can therefore be broadly stated as a method of conditioning a catalyst for hydrocarbon synthesis reactions which comprises initially passing the gases or vapours over the catalyst at a flow rate substantially below the desired full flow rate and subsequently gradually or stepwise increasing the rate of flow to the desired full rate.

We have found, for example, that in hydrocarbon synthesis processes operating in accordance with our invention it is possible to use a catalytic bed at least six feet in depth without causing overheating and without reducing the cross-section of the container; indeed we have found that where the catalyst mass is contained in tubes, it is possible to increase the diameter of the tubes to at least one inch or in the case of containers of rectilinear cross-section to an equivalent area.

The yield obtainable from a single treating unit is thus very much in excess of what has hitherto been possible. By way of example of the method of carrying out our invention we may mention that with a catalytic bed of the dimensions given (one inch in diameter by six feet in length) the rate of flow of gases during normal working is 900 litres per hour: we find that overheating is prevented if when putting a catalyst mass into service the rate of flow is limited at starting to six litres per hour then after an interval of 10 minutes increased to 20 litres per hour, after another interval of 10 minutes to 60 litres, after another interval of 10 minutes to 100 litres after 20 minutes to 200 litres, after 20 minutes to 300 litres, after 30 minutes to 500 litres, after 30 minutes to 700 litres and then after 20 minutes the velocity can be increased to the desired normal velocity. Thus after some two and a half hours after the start of the process the full rate of 900 litres has been attained. It will, however, be understood that our invention is in no way confined to the particular dimensions, rates and times mentioned, which are given solely by way of example. Neither is the working of this invention limited by conditions of temperature or pressure.

It will also be understood that our invention is not confined to apparatus in which the catalytic bed is contained in vertical tubes of circular cross-section as described above. The invention is equally applicable to apparatus in which the catalyst vessel is of any other form suitable for the required reaction.

In particular the catalyst may be contained in the annular space between two concentric tubes, or even between the parallel walls of two or more containers of other than circular cross-section, around and through which retaining tubes or walls a temperature regulating fluid is circulated. It will also be understood that, whereas we have stated that in a preferred embodiment of this invention the synthesis gas contains carbon-monoxide and hydrogen, suitable gas mixtures for carrying on hydro-carbon syntheses to which this invention is applicable may properly contain also carbon-dioxide, water vapour, nitrogen and low molecular weight hydrocarbons such as members of methane series and our invention is equally applicable to these also.

Our invention is not to be limited by any theory of the mechanism of the reactions nor to any specific example which is given merely for purpose of illustration.

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. The method of conditioning a catalyst for hydrocarbon synthesis reactions

which comprises initially passing the gases or vapours over the catalyst at a flow rate substantially below the desired full flow rate and subsequently gradually or stepwise increasing the rate of flow to the desired full rate.

2. The method of conditioning a catalyst for reactions between gases or vapours for the production by synthesis of hydrocarbon oils, which comprises initially passing the gases or vapours over the catalyst at a flow rate substantially below the desired full flow rate and gradually or stepwise increasing the flow rate to the desired full rate in such increments that an excessive rise in the catalyst temperature is prevented.

3. In a catalytic process for synthesizing hydrocarbons from gaseous mixtures containing carbon-monoxide and hydrogen, the method of conditioning the catalyst which comprises initially passing the gaseous mixture over the catalyst at a flow rate substantially below the desired full flow rate and gradually or stepwise increasing the flow rate to the desired full rate in such increments that an excessive rise in the catalyst temperature is prevented.

4. The process according to claim 2 or 3 in which the initial flow rate and its increments of increase are so chosen that the hottest layer of the catalyst will not rise more than 30° F. above the pre-determined reaction temperature.

5. The process according to claim 3 in which the order of magnitude of the initial rate of flow is below 1% of the desired full flow rate.

6. The process according to any of the preceding claims in which the catalyst is a granular porous or solid mass arranged in a highly elongated form.

7. The process according to claim 6 in which the catalyst is arranged between two concentric cylindrical surfaces.

8. The improved method of working catalytic processes for the synthetic production of hydrocarbon oils substantially as described.

Dated this 21st day of June, 1938.

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