PATENT SPECIFICATION

THE PATENT OFFICE LONDON

767,712

Date of Application and filing Complete Specification: Jan. 27, 1953.

No. 2316/53

Application made in Germany on Jan. 30, 1952.

Complete Specification Published Feb. 6, 1957

Index at acceptance:—Classes 1(1), A3B1; and 2(3), B1G, C3A10E(3A1 : 5H), C3A13A3(A1C : B1 : J2).

International Classification:—B01j. C07b, c.

COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German Company, of Oberhausen-Holten, Germany, and LURGI GESELLSCHAFT FUER WAERMETECHNIK M.B.H., a German Company, of Frankfurt a.M., Heddernheim, 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:—

The invention relates to a process for the catalytic hydrogenation of carbon monoxide.

The use of iron, cobalt and nickel catalysts for the hydrogenation of gas mixtures consisting of carbon monoxide and hydrogen or containing such gases in synthesis proportions, has been known for many years. Moreover, metals of the platinum group such, for example, as ruthenium, have also been suggested for this purpose. For the synthesis of methanol, the use of copper-containing catalysts and oxide catalysts such, for example, as zinc oxide and chromium oxide catalysts, has been described. Finally, the "iso-synthesis", in which carbon monoxide and hydrogen are converted predominantly into branched-chain hydrocarbons, can be effected with good results using oxide catalysts such as aluminium oxide and thorium oxide.

In the hydrogenation of carbon monoxide carried out with the use of metals of the iron group that is iron, cobalt and nickel, for the purpose of recovering liquid aliphatic hydrocarbons and oxygenated compounds, the use of promoters has been known for a long time. For this purpose almost all of the metals and non-metals of the periodic system have been used, particularly members of the groups I, II, III, IV, and V. Amongst the promoters which, according to the literature, are most frequently used, are the alkalis and the elements thorium, aluminium, silicon, calcium, magnesium and copper, depending on the type of catalyst. It is known that even relatively small amounts are effective to enhance the activity of the catalysts. However, calcium, for example, while being a good promoter for iron catalysts, has a detrimental effect on the activity of cobalt catalysts. Likewise, the use of copper as a promoter is advantageous only for iron catalysts, being disadvantageous for nickel and cobalt catalysts. Silver is claimed to have a similar effect on iron catalysts to that of copper. The quantity of promoter generally used lies between approximately 0.5% and 5% by weight, based on the metal of the iron group. For iron catalysts, as much as about 30% Cu based on Fe is known, and in certain cases even as much as 100%. This holds for the so-called "roasted catalysts" which give unfavourable results as regards yield and duration of life. These roasted catalysts were used only for the synthesis of hydrocarbons. In general, the quantity of copper actually employed in iron catalysts amounts to 5% by weight or less.

According to the invention, a process for the hydrogenation of carbon monoxide comprises contacting a synthesis gas containing carbon monoxide and hydrogen in synthesis proportions at a temperature within the range 150°—300°C, and at a pressure from atmospheric to 100 atmospheres gauge with a precipitated and reduced catalyst containing copper and a metal of the iron group in a proportion by weight of from 50: 50 to about 95: 5, together with an alkali-metal compound which, calculated as K_2O, is present to the extent of not more than 50% by weight of the metal of the iron group, the catalyst having been precipitated under such conditions that the pH value of the precipitation solution upon completion of the precipitation was in the range 6—11.

The synthesis is preferably effected at a temperature in the range 190°—250°C. and at a pressure within the range 10—50 atmospheres. The catalyst may also contain other promoters, for example, alkaline earths, oxides of zinc, chromium, aluminium and thorium. The catalyst may also contain a supporting material.

Synthesis products having a high content of oxygenated compounds, particularly alcohols, may be obtained by the process of the invention, as may products which consist mainly of low molecular weight hydrocarbons or of higher molecular weight hydrocarbons of a high olefin content.

It is of advantage to use bivalent copper salts such, for example, as copper nitrate, copper chloride or copper sulphate as starting compounds for the catalysts in accordance with the invention. Monovalent copper salts are less suitable. The use of alkaline earths as promoters is frequently of advantage. When other promoters are used, they are advantageously used in the form of their salts, such as in the form of nitrates, chlorides or sulphates.

The precipitation of the catalysts used in accordance with the invention is advantageously effected at temperatures of about 80° to 110° C. with the addition of boiling alkali solutions such, for example, as sodium carbonate, potassium hydroxide, and ammonia. Precipitation temperatures below 80° C. are less suitable. Although active catalysts may be obtained at such temperatures, filtration of the precipitated mass becomes more difficult as the temperature decreases. It is of advantage to add the copper and iron group metal solution to the alkali solution. The precipitation time should be as short as possible. The concentration of the salts in the solutions may be varied. The preferred concentration is about 20—60 grams of copper per litre. The alkali concentration should be about 50—120 grams per litre in the form of hydroxide or carbonate. Higher and lower concentrations may, however, also be used. The precipitation itself may be effected batchwise; a continuous precipitation, however, is particularly advantageous because a more homogenous catalyst structure is obtained. Moreover, the activity of the catalyst is in general increased to a certain extent. Continuously precipitated catalysts may be readily reproduced.

The pH value upon completion of the precipitation is preferably between 7 and 9. In certain cases, the use of supporting materials such, for example, as aluminium oxide, kieselguhr, and activated earths or clays, such as those marketed in Germany under the name "Tonsil", is advantageous for the catalysts employed in the process according to the invention.

Upon termination of the precipitation the catalyst slurry is advantageously freed as quickly as possible from the excess alkali used in the precipitation. For this purpose, the slurry is washed as quickly as possible with hot water, the use of both condensate water and tap water being possible. If it is desired to effect the synthesis so as to obtain a high yield of oxygenated compounds, the catalyst is to be adjusted to an alkali-metal content calculated as K_2O, of 1—50% by weight based on the metal of the iron group present in the catalyst. This alkali-metal content may be obtained either by a partial washing of the precipitated catalyst mass and/or by a subsequent impregnation with alkali, particularly advantageous results being obtained by the use of potassium compounds.

If, on the other hand, the synthesis is to be carried out so as to yield synthesis products rich in hydrocarbons, the alkali-metal content (calculated as K_2O) should be less than 5% by weight of the metal of the iron group when the weight ratio of copper: metal of iron group is 90: 10. When the weight ratio of copper: metal of iron group is 50: 50, the alkali-metal content should be less than 1% by weight of the metal of the iron group. This alkali-metal content is advantageously maintained by extensively washing out the excess precipitation alkali. For the hydrocarbon synthesis, the impregnation of the catalyst mass with alkali-metal salts of phosphoric, silicic or boric acids has been found to be particularly advantageous. When using alkali-metal salts of phosphoric acid, a ratio of alkali-metal oxide (calculated as K_2O) to P_2O_5 of about 1: 1 by weight in these catalysts is particularly advantageous. The same holds for the impregnation with alkali-metal salts, preferably potassium salts, of boric acid, the preferred $K_2O: B_2O_3$ ratio being correspondingly 1: 1 by weight. When alkali-metal salts, preferably potassium salts, of silicic acid are used, it is preferred to maintain a $K_2O: SiO_2$ ratio of between 1: 3 and 1: 6 by weight with the use, if necessary or desired, of an after-neutralization with nitric acid.

By combining the measures for obtaining a primary product with as high as possible a content of oxygenated compounds with those for obtaining a primary product with as high as possible a yield of low molecular weight or high molecular weight hydrocarbons, it is possible to produce at will primary products which contain from about 3% to 70% of oxygenated compounds, particularly alcohols, referred to the total product.

After the impregnation it is of advantage to mould the catalyst mass, the moulding being preceded, if necessary or desired, by an intermediate drying. Extruding presses or the like have been found to be particularly suitable for this purpose. For small outputs, mechanical crushing of the precipitated and dried catalyst mass without previous moulding may be sufficient under certain circumstances. In this way, a so-called lump catalyst is obtained. Thereafter, the catalyst mass is dried to a low water content. This water content may be as high as 15% but is preferably in the range 3%—8% by weight. The drying temperature should be between 50° C and 150° C., preferably between 70° and 110° C.

The catalyst is reduced prior to use. The use of low reduction temperatures lying between 150° C. and 300° C. and preferably between

150° and 250° C. is possible due to the high copper content. The reduction temperature is determined by the particular use to be made of the catalyst. In general, the synthesis of hydrocarbons requires low reduction values of preferably below 40% and consequently low reduction temperatures and short reduction periods. Reduction value as herein used denotes the proportion of the metal of the iron group which is in elementary form. Catalysts for the formation of oxygenated compounds should have reduction values of above 40% and preferably of above 60%. They require higher reduction temperatures and extended reduction periods. In all cases, the use of high gas flow rates in the reduction is of advantage. The gas flow rates lie between 30 and 200 cm./second and preferably between 100 and 150 cm./second, referred to standard conditions. This measure has in addition the advantage that the thickness of the layer of catalyst to be reduced may be increased very considerably. For example, layers of a thickness of from 50 cm. to 20 metres, preferably of 5—12 metres, may be used without encountering any substantial difficulty in obtaining a thorough and uniform reduction of the whole mass. After the reduction the whole catalyst mass has a substantially uniform reduction value. According to the prior art, the reduction of catalysts of this type has hitherto been effected in layers of a thickness of 1—35 cm. It is the advantage of the new reduction method with thick layers that, due to the low reduction temperature required by the catalysts to be used in accordance with the invention, the reduction may be carried out without difficulty in the synthesis reactor itself, thereby eliminating the provision of a special reduction apparatus.

The reducing gas is conveniently used under atmospheric pressure. It is possible, however, to operate with a sub-atmospheric pressure or slight excess pressure. Recycling of the reducing gas, which should be as free as possible from water and should advantageously contain less than 1 gram of water/cu.m., is practicable.

The catalysts according to the invention will give good results in the synthesis even at atmospheric pressure. The composition of the gas may be varied from about 2 CO: 1 H_2 to above 1 CO: 2 H_2. The best results are obtained when using pressures of more than 5 atmospheres and preferably of more than 10 atmospheres gauge. Owing to the excellent activity of the catalysts, it is readily possible to increase the gas load beyond the level so far used in large-scale operation. For example, 500 litres and more of the synthesis gas per litre of catalyst per hour may be passed through the reactor.

The particular advantage of the catalysts described above is their surprisingly favourable thermal conductivity. As a result of this, they are less sensitive to temperature fluctuations with regard to carbon desposits than catalysts in which the main constituent is iron, nickel or cobalt.

As with almost all catalysts, the use of gas recycling, i.e. the return of a part of the tail gas to the synthesis reactor, is of advantage. It is also possible to operate with a single pass of the gas. The synthesis reactor may be cooled with water, thus providing uniform temperatures within the reactor. It is also possible, however, to use other cooling media which consist, for example, of several components, thereby providing the possibility of operating the synthesis with temperature gradients. While high conversion rates may be obtained even with single-stage operation, multi-stage operation with the removal of a part of the carbon dioxide formed in the synthesis is frequently of advantage. Catalyst layers of, for example, 10 metres and more may be used in the synthesis.

The invention is illustrated by the following examples.

EXAMPLE 1

A solution consisting of copper nitrate and iron nitrate, the concentration of copper in which was approximately 40 grams per litre and the copper/iron weight ratio of which was 75: 25, was continuously added in the hot state (90° C. to 100° C.) to a hot solution of sodium carbonate, which was likewise at a temperature of approximately 100° C., so that the pH value during the precipitation was constantly at about 9 to 9.2. The concentration of the sodium carbonate solution was approximately 100 grams of anhydrous Na_2CO_3 per litre.

The precipitated catalyst mass was washed immediately with hot condensed steam so as to be largely free from alkalis (0.4% of residual alkali, calculated as K_2O, relatively to the total catalyst mass) and was then impregnated with potassium carbonate in such manner that, based on iron and calculated as K_2O, 32% by weight was present, corresponding to 8% by weight based on the total catalyst. This mass was then dried in a drying chamber at 110° C. for 24 hours, disintegrated and sieved to a grain size of between 2 mm. and 4 mm.

Reduction of the catalyst was carried out for two hours at 300° C. with the use of a mixture consisting of 75% H_2 and 25% N_2, an almost complete conversion of the copper as well as of the iron into the metallic state being obtained. In a so-called double-tube reactor (24 mm. x 44 mm.), 4.8 litres of this catalyst were used with water gas in single pass operation at a synthesis pressure of 30 atmospheres gauge, and a gas load of 100 litres per litre of catalyst per hour. A conversion of 61% to 62% was obtained at a temperature of 200° C., the methane formation, based on converted CO + H_2, being approximately 6% (that is, of every 100 volumes of CO+H_2 converted, 6 volumes were converted into methane).

The liquid product obtained contained 33%

of components having a boiling point above 320° C. and containing considerable amounts (more than 45%) of esters. A high proportion of esters (above 40%), in addition to 8% of alcohols, was also present in the fraction boiling in the range 180°—320° C. The esters in the fraction boiling in the range 100°—180° C. amounted to 15%, while the proportion of alcohols rose to 35%. In this case the amounts of aldehydes and ketones were approximately 8%. The reaction water contained large amounts of water-soluble oxygen-containing organic compounds, more particularly alcohols.

When the gas load was doubled, the $CO-H_2$ conversion amounted to 62% at 218° C. and the methane formation, based on converted $CO+H_2$, was approximately 7%. The liquid product contained 29% of components boiling above 320° C. In all fractions, the content of esters was somewhat reduced, whilst, inversely, the content of alcohols increased accordingly in all fractions.

With a gas load of 300 litres per litre of catalyst per hour there was obtained at a temperature of 226° C. a $CO\ H_2$ conversion of 62%. The methane formation, based on converted $CO+H_2$, was approximately 8%. The liquid product contained 26% of components having a boiling point of above 320° C. As compared with the previous runs, the amount of esters and alcohols remained practically unchanged.

When the gas load was increased to 400 volumes per volume of catalyst per hour, a $CO-H_2$ conversion of 62.5% was obtained at a temperature of 235° C., the methane formation, based on converted $CO+H_2$, being approximately 8.7%. The yield in esters and alcohols was slightly reduced.

Finally, when the gas load was increased to 500 volumes per volume of catalyst per hour, a $CO+H_2$ conversion of 60% was obtained at 242° C. In this case, the methane formation amounted to 9.0% based on converted $CO-H_2$. The yield in esters as well as of alcohols was further slightly reduced, but, for example in the fraction boiling above 320° C., the yield of esters still amounted to 34%, in the 180°—320° C. fraction to 32%, and in the 100°—180° C. fraction to 10%. The corresponding amounts of alcohols were approximately 3%, 10% and 43% respectively. The reaction water again contained larger amounts of oxygen-containing organic compounds of low molecular weight. In the liquid product, the proportion of compounds having a boiling point of above 320° C. was approximately 26%.

EXAMPLE 2

In the same manner as in Example 1, a catalyst was produced which contained 10 parts by weight of iron per 100 parts by weight of copper, and was impregnated with potassium carbonate in such manner that, based on the copper present, 8% by weight, calculated as K_2O, was present. The reduction of the catalyst was effected under the conditions described in Example 1.

A $CO+H_2$ conversion of 65% was obtained in a test reactor similar to the synthesis reactor used in Example 1, at a synthesis pressure of 30 atmospheres gauge, using water gas at a temperature of 236° C., and a gas load of 100 volumes per volume of catalyst per hour. The methane formation, based on converted $CO+H_2$, was approximately 8%. The liquid product contained 28% of components having a boiling point of above 320° C. The ester content of this fraction amounted to 36%, the alcohol content to 17%. 32% of esters in addition to 12% of alcohols were present in the 180°—320° C. fraction. 17% of esters and 22% of alcohols were present in the 100°—180° C. fraction. The reaction water also contained large amount of oxygen-containing organic compounds of low molecular weight.

EXAMPLE 3

From a solution which contained iron and copper in the ratio 1:1 by weight and the metals in the form of their nitrates, the concentration being 45 grams per litre, a catalyst was precipitated by adding this hot solution to a gently boiling potassium carbonate solution. After the precipitation, the pH value was approximately 7.1. After washing the precipitate in known manner, impregnation with potassium carbonate, calculated as K_2O, was effected in such manner that 8 parts by weight of K_2O were present for every 100 parts by weight of iron. After drying at 110° C. for 24 hours, the catalyst mass was disintegrated and sieved to a grain size of between approximately 1.5 mm. and 3.5 mm. The reduction was effected within 90 minutes at 300° C., a linear gas velocity of 1.5 metres per second being used with hydrogen as the reducing gas. The reduction value was approximately 62%.

When this catalyst was used in one of the reactors above referred to at a synthesis pressure of 30 atmospheres gauge and with water gas in single pass operation, a $CO-H_2$ conversion of 72% was obtained at a temperature of 200° C. The methane formation based on $CO+H_2$ was approximately 7.7%.

When the same catalyst was used under the same conditions with a gas consisting of approximately 50 parts of carbon monoxide, 40 parts of hydrogen, residual carbon dioxide, nitrogen and methane, a $CO+H_2$ conversion of 67% could be obtained at a temperature of 198°C. The methane formation was approximately 4%, based on converted $CO+H_2$.

When the same catalyst was used under the same conditions as hereinbefore described and with a synthesis gas which contained approximately 31% of CO, 61% of H_2, residual carbon dioxide, nitrogen and methane, a $CO+H_2$ conversion of 55% was observed at a temperature of 195° C. In this case the methane formation was approximately 7% based on converted $CO+H_2$.

The liquid product of all the runs contained considerable amounts of oxygen-containing organic compounds. Thus in the case first referred to, 45% of esters and 5% of alcohols were present in the fraction boiling above 320° C., 3% of esters and 17% of alcohols in the 180°—320° C. fraction, and 14% esters and 32% of alcohols in the 100°—180° C. fraction. In addition, approximately 7% of carbonyl compounds were found in this fraction. The proportion of products boiling above 320° C. was approximately 31% based on the liquid product.

In the case of the gas rich in carbon monoxide, the proportion of products boiling above 320° C. amounted to 52% based on the liquid product. Here the ester portion was approximately 50% in addition to 3% of alcohols. In the 180°—320° C. fraction the ester content amounted to 30% in addition to 10% of alcohols; the 100°—180° C. fraction contained 13% of esters in addition to 31% of alcohols. The content of carbonyl compounds was approximately 9% in the 100°—180° C. fraction, and 3% in the 180°—320° C. fraction.

Finally, when the hydrogen-rich gas was used, the liquid product contained 35% of components having a boiling point above 320° C. The ester content had then dropped to 29%, and there were also present 7% of alcohols. The ester content in the 180°—320° C. fraction amounted to approximately 23%, in addition to 30% of alcohols, and in the 100°—180° C. fraction to 7% in addition to 41% of alcohols. 6% of carbonyl compounds were found in 100°—180° C. fraction, and approximately 3% in the 180°—320° C. fraction.

EXAMPLE 4

In the same manner as that described in Example 3, a catalyst was precipitated which consisted of 75 parts by weight of copper and 25 parts by weight of iron. After washing in known manner, impregnation of the precipitated mass was effected with secondary potassium phosphate in such manner that, based on the amount of iron, the same amount of potassium phosphate, calculated as K_2O, was present in the catalyst. After drying and disintegration, likewise in known manner, reduction with hydrogen was effected for 2 hours at a temperature of 300° C., and at a gas velocity of 1.5 metres per second.

In a synthesis reactor as employed in the preceding Examples, water gas being used at a temperature of 210° C., the $CO+H_2$ conversion obtained was 65%, the methane formation being approximately 5% based on $CO+H_2$ converted. The synthesis pressure was 30 atmospheres gauge.

The liquid product obtained contained 36% of components having a boiling point of above 320° C. The ester content thereof amounted to 35%, and the alcohol content to 3%. In the 180°—320° C. fraction, the ester content amounted to 35%, and the alcohol content to 10%, and in the 100°—180° C. fraction the ester content amounted to 17% and the alcohol content to 45%.

What we claim is:—

1. A process for the hydrogenation of carbon monoxide, which comprises contacting a synthesis gas containing carbon monoxide and hydrogen in synthesis proportions at a temperature within the range 150°—300°C, and at a pressure from atmospheric to 100 atmospheres gauge with a precipitated and reduced catalyst containing copper and a metal of the iron group in a proportion by weight of from 50: 50 to about 95: 5, together with an alkali-metal compound which, calculated as K_2O, is present to the extent of not more than 50% by weight of the metal of the iron group, the catalyst having been precipitated under such conditions that the pH value of the precipitation solution upon completion of the precipitation was in the range 6—11.

2. A process according to claim 1, in which the catalyst contains other compounds known to be effective as promoters in the catalytic hydrogenation of carbon monoxide, such as alkaline earths, oxides of zinc, chromium, aluminium and thorium.

3. A process according to claim 1 or claim 2, in which the catalyst is supported.

4. A process according to any one of the preceding claims, in which the temperature is within the range 190°—250° C.

5. A process according to any one of the preceding claims, in which the pressure is within the range 10—50 atmospheres.

6. A process according to any one of the preceding claims, in which the precipitation of the catalyst has been effected in continuous operation.

7. A process according to any one of the preceding claims, in which the pH value upon completion of the precipitation of the catalyst was in the range 7—9.

8. A process according to any one of the preceding claims for obtaining a product rich in oxygen-containing organic compounds, in which the alkali-metal compound is introduced by impregnation of the precipitated catalyst mass and/or by partial washing of the precipitated mass.

9. A process according to any one of claims 1 to 7 for obtaining a product which consists chiefly of hydrocarbons, in which the amount of alkali-metal compound, calculated as K_2O, varies from less than 5% by weight of the metal of the iron group when the weight ratio of copper: metal of iron group is 90: 10 to less than 1% by weight when the weight ratio of copper: metal of iron group is 50: 50.

10. A process according to claim 9, in which the alkali-metal content of the catalyst is adjusted by washing the mass obtained upon precipitation of the catalyst by an alkali.

11. A process according to any one of claims

1 to 7, 9 and 10, in which the catalyst contains an alkali-metal salt of phosphoric acid, silicic acid or boric acid introduced by impregnation.

12. A process according to claim 11, in which the catalyst mass has been impregnated with an alkali-metal salt of phosphoric acid to give a $K_2O:P_2O_5$ ratio in the catalyst of about 1:1 by weight.

13. A process according to claim 11, in which the catalyst mass has been impregnated with an alkali-metal salt of boric acid to give a $K_2O:B_2O_3$ ratio in the catalyst of about 1:1 by weight.

14. A process according to claim 11, in which the catalyst mass has been impregnated with an alkali-metal salt of silicic acid to give a $K_2O:SiO_2$ ratio in the catalyst of from 1:3 to 1:6 by weight.

15. A process according to claim 14, in which, after impregnating the catalyst mass with the alkali-metal salt of silicic acid, the $K_2O:SiO_2$ ratio is brought within the given range by neutralisation.

16. A process according to any one of the preceding claims, in which the alkali-metal in the alkali-metal compound is potassium.

17. A process according to any one of the preceding claims, in which the reduction of the precipitated catalyst mass was effected with hydrogen and/or carbon monoxide-containing gases at temperatures in the range 150°—300°C.

18. A process according to claim 17, in which the reduction of the catalyst was effected at a temperature in the range 150°—250° C.

19. A process according to any one of the preceding claims, in which the reduction value of the metal of the iron group in the reduced catalyst is below 40% when the catalyst is to be used for a hydrocarbon synthesis.

20. A process according to any one of the preceding claims, in which the reduction value of the metal of the iron group in the reduced catalyst is more than 40%, preferably more than 60%, when the catalyst is to be used for the production of products rich in oxygen-containing organic compounds.

21. A process according to claim 17 or claim 18, in which the flow rate of the reducing gas is in the range 30—200 centimetres per second.

22. A process according to claim 21, in which the flow rate is in the range 100—150 centimetres per second.

23. A process according to any one of the preceding claims, in which the catalyst mass has been reduced in a layer of a thickness of from 50 centimetres to 20 metres, preferably of from 5 metres to 12 metres.

24. A process according to any one of the preceding claims, in which the metal of the iron group present in the catalyst is cobalt or iron.

25. A process for hydrogenation of carbon monoxide carried out in the presence of a precipitated catalyst containing copper and a metal of the iron group in a proportion by weight of from 50:50 to about 95:5, substantially as hereinbefore described.

26. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to any one of Examples 1 to 4.

27. Hydrocarbons and oxygen-containing organic compounds, whenever produced by the process of any preceding claim.

EDWARD EVANS & CO.,
14-18 High Holborn, London, W.C.1,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by J. Looker Ltd., Poole, Dorset. 1957.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.