Oct. 11, 1938. J. FRANÇON 2,132,613

HYDROGENATION CATALYST

Filed Sept. 28, 1935

Fig. 1.

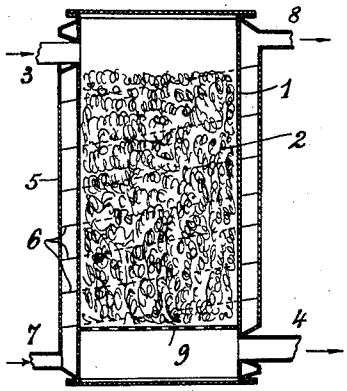
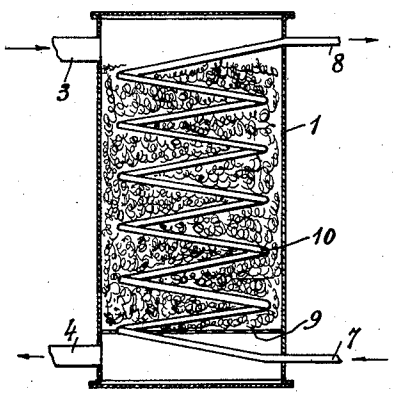


Fig. 2.



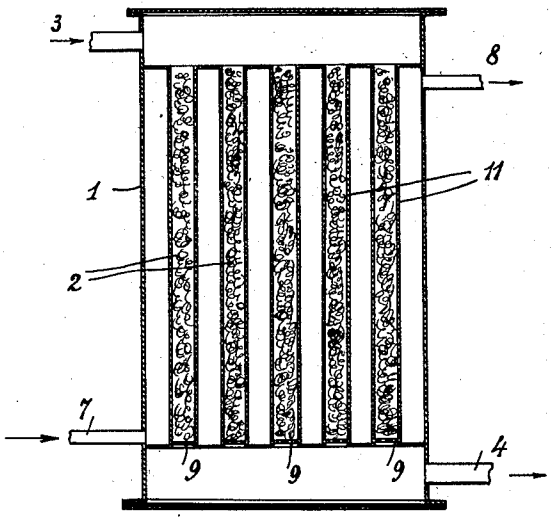


Fig. 3.

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HYDROGENATION CATALYST

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In France October 5, 1934

2 Claims. (Cl. 23—236)

The process forming the object of the present invention relates to a plant which can be used for effecting the catalytic hydrogenation, with or without pressure, of gases and vapours resulting from the carbonization of solid fuels or from the pyrolysis of liquid fuels and their derivatives such as: petroleums, tars, creosotes, coal oils and for the vaporization of some hydrocarbons such as benzols, naphthalene, anthracene and the like, for the purpose of obtaining, for example, formaldehyde, light hydrocarbons, naphthalene and anthracene hydrides and the like.

The catalytic plant consists essentially of a metallic tube, of a suitable thickness, having an effective length of about 6 meters and maintained at the required temperature (which can vary according to circumstances between 150 and 220° C.) by a circulation of superheated oil, either internally by means of coils, or externally by means of a double wall or in any other suitable manner. The said apparatus is filled with simple, double or treble concentric metallic coils or windings, from 50 to 60 m/m. long, or with metallic gauzes rolled on themselves, formed of gauze strips or ribbons, from 20 to 35 m/m. wide and from 50 to 100 m/m. long; said gauzes are woven with meshes of suitable sizes; the wires or threads which constitute the coils or the gauzes are composed of wires of nickel, iron, chromium, or an alloy of two or three of said metals. The said gauzes or the said coils or windings constitute the metallic support of the catalytic metals. It is necessary to cover the said support either with a similar metal or with any other metal, in a porous state, in order to obtain a catalytic action.

In the accompanying drawing, Fig. 1 is a vertical section of an embodiment of a catalyzing device adapted for carrying out the method described herein;

Figs. 2 and 3 are similar views respectively of modified forms of the device.

In all the figures, 1 is the metallic tube filled with metallic coils or gauzes 2. The gases or vapours to be hydrogenized enter at 3 and after having passed through the chamber filled with the coils or gauzes the said gases or vapours leave at 4.

The tube 1 is heated by a stream of hot oil. In Fig. 1, the tube 1 is surrounded by a casing or jacket 5 separated from the tube 1 by an annular space in which is placed a helical guide 6. The hot oil enters at 7, streams around the tube 1 along a helical path and leaves at 8. A grid 9 mounted in the tube 1 supports the metallic coils or gauzes 2.

In Fig. 2, the heating oil flows through a helical tube 10 mounted in the tube 1. In Fig. 3, the tube 1 contains a nest of vertical tubes 11 filled with the coils or gauzes 2, while the hot oil flows around the said tubes 11.

The processes which bring about this result and which also form the subject-matter of the invention are characterized as follows:

1st—By the fact that the vapours of an organometallic compound are conveyed through the materials which are to be coated and kept under such conditions that the said vapours disintegrate and that the metal of which they are composed is deposited upon the metallic or other supports.

Nickel in a pulverulent state can thus be deposited upon coils or grates of nickel or upon grates of iron, chromium or any other metal by proceeding as follows:

A stream of carbon monoxide is caused to react at a suitable temperature—about 50° C.—over reduced nickel; there being thus formed tetracarbonyl of nickel $Ni(CO)_4$ which is removed in the form of vapour by the excess of the gaseous stream. The mixture is led over the metal grates which are intended to be coated or covered, enclosed in a closed space and heated at a temperature higher than 100° C. Under these conditions, the tetracarbonyl of nickel is destroyed: $Ni(CO)_4=4CO+Ni$ and the metal is deposited upon the grates or upon the coils or windings.

Proceeding by the same way, it is possible to obtain deposits of iron or cobalt, by starting from cobalt and iron carbonyl; deposits of lead, by starting from tetraethyl lead; deposits of tin, zinc, silicon and of all metals by starting from their organic compounds.

2nd—By the fact that the support is lined with or embedded in a paste of nickel hydrate by complying with the following procedure. In order to obtain 1 kilog. of paste of hydrate of nickel which must contain from about 12% of nickel oxides (that is to say 9.5% of pure nickel), 95 grams of pure nickel are treated, the same being in the form of powder, threads or wires, or in lumps; the same are attacked by 250 cubic centimeters of pure nitric acid at 40° which are diluted in 250 cubic centimeters of water; said action being effected by heat treatment or preferably by the cold method. When the operation is completed, the product is filtered if required.

The solution of nitrate of nickel thus obtained is diluted in a receptacle with from 40 to 50 liters of water; the same is dissolved by means of a solution of caustic soda at 10% while stirring

frequently and until a slightly alkaline reaction with litmus paper is obtained. Then the product is allowed to rest and the liquid which floats and which contains the nitrate of sodium is decanted by syphonage. The receptacle is again filled with water, the whole is stirred and decanted and the operation is repeated from 5 to 6 times in order to give a well washed hydrate. For the purpose of ascertaining whether the paste of hydrate of nickel has been sufficiently washed, there is introduced into a test tube a few cubic centimeters of a solution of a ferrous salt, then very slowly and with care, a few cubic centimeters of the washing water to be examined are supplied, the two liquids being of a different density are clearly separated. Through a graduated cylinder, a few drops of sulphuric acid are caused to arrive at the point of contact between the two liquids; when the hydrate is sufficiently washed, no colouration will occur; but if not sufficiently washed, a brownish colouration will appear.

The paste having been sufficiently washed, the same is thrown upon a wire gauze and left to drip until it is sufficiently dry. It is also possible to operate with a filter undergoing the action of vacuum or a filter-press. Every one of the following metals are added to the nickel in the ratio of 1 to 2% of its weight: silver, vanadium, cobalt, cadmium or their alloy which has previously been dissolved in nitric acid and precipitated by soda under the same conditions.

Said paste is thoroughly mixed with the supports or carriers, coils or gauzes, previously oxidized by heat treatment, either under the action of air or under the action of steam, or by a mixture of both and the catalyzer is filled with the said mixture.

The best mixture is obtained when the weight of the supports or carriers and the weight of the metals are in the proportions of 90 to 10.

The foregoing procedure effects the deposit upon any metallic or other support of pulverulent and porous metals, capable of catalytic action.

The catalyzer is reduced at a temperature ranging between 240 and 280° C., by causing dry hydrogen to pass during a period of 40 to 60 hours.

I claim:

1. A process for depositing catalytic metals on metallic supports, comprising heating the said metallic supports at a temperature above 100° C. and leading a gaseous organo-metallic compound over the heated metallic supports, so as to cause decomposition of the said gaseous organo-metallic compound at the surface of the heated metallic supports and precipitation of the metal contained in the gaseous compound upon the said metallic supports.

2. A process for depositing catalytic metals in a porous state on metallic supports of a metal selected from a group comprising nickel, iron, chromium and alloys of these metals, comprising heating the said metallic supports at a temperature above 100° C. and leading over the same a gaseous organic compound of a metal selected from a group comprising nickel, iron, chromium, cobalt, lead, tin, zinc and silicon so as to cause decomposition of the said gaseous compound at the surface of the heated metallic supports and precipitation of the metal contained in said gaseous compound upon the said metallic supports.

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