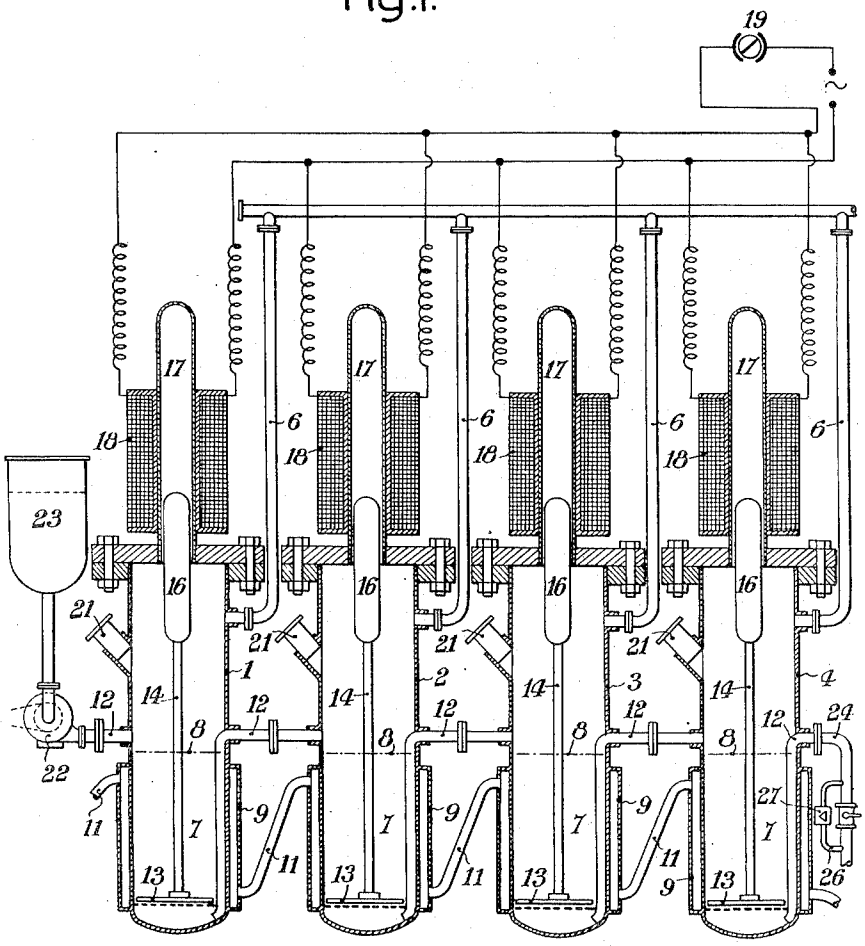
Sept. 18, 1956 P. MASTAGLI 2,763,666

METHOD FOR THE CATALYTIC HYDROGENATION OF FURFURAL

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Fig.1.



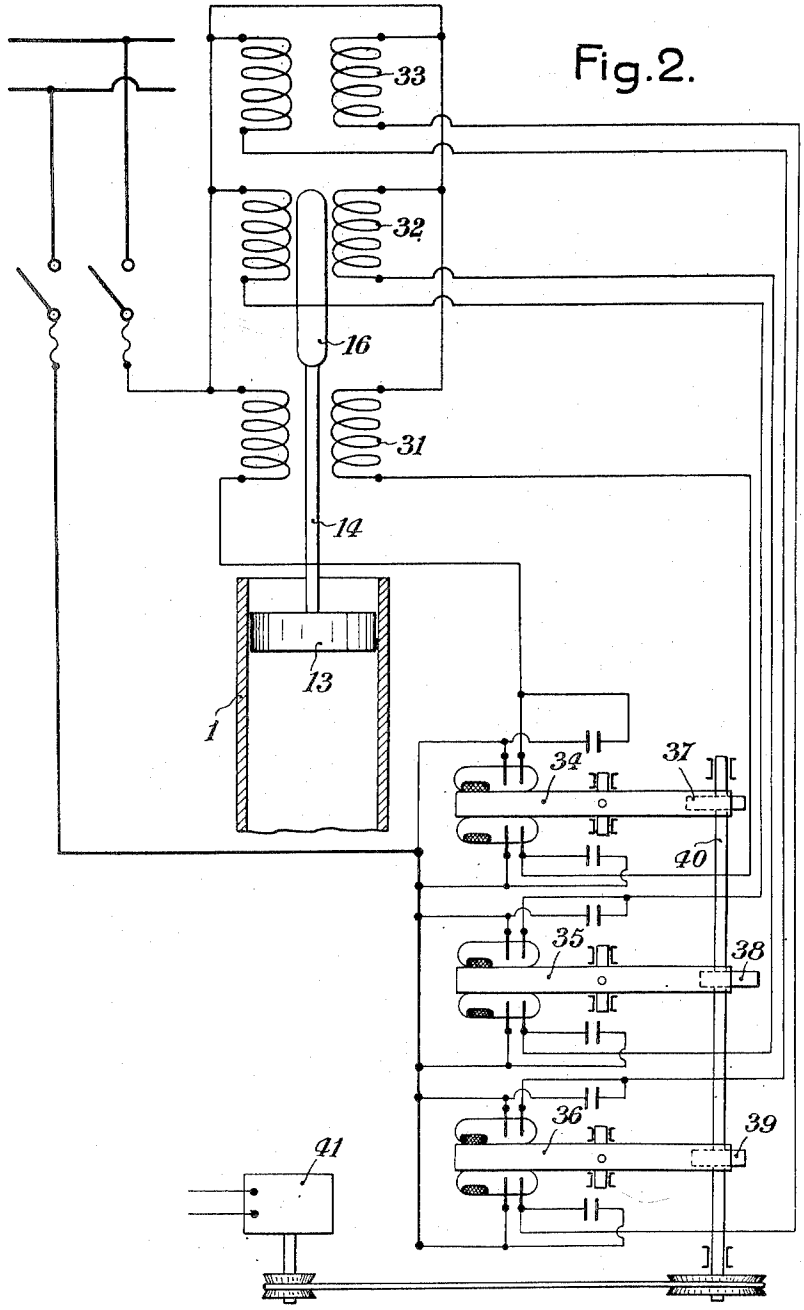
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Fig.2.



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METHOD FOR THE CATALYTIC HYDROGENATION OF FURFURAL

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Claims priority, application France March 20, 1951

6 Claims. (Cl. 260—347.8)

Up to the present, furfuraldehyde has been hydrogenated to furfuryl alcohol in the presence of copper chromite, at a temperature of about 170° C. and under a pressure of about 70 kg./sq. cm.

According to my invention, it has been found that such a hydrogenation process can be carried out under more easily attainable temperature and pressure conditions in the presence of a more easily preparable catalyst.

A first object of my invention is to provide a method for hydrogenating furfuraldehyde to furfuryl alcohol clear of tetrahydrofurfurylic alcohol, said method comprising subjecting furfuraldehyde at a temperature ranging from 80 to 130° C. and under a pressure ranging from 2 to 20 kg./sq. cm. to the action of hydrogen in the presence of pre-inhibited nickel powder, which is prepared from a powder of the so-called Raney's nickel-aluminum alloy by treating the same with an alkali.

Another object of my invention is to prepare a pre-inhibited nickel powder capable of effecting the hydrogenation of furfuraldehyde to furfuryl alcohol clear of tetrahydrofurfurylic alcohol.

A further object of my invention is to provide an apparatus suitable for the performance of the continuous hydrogenation of furfuraldehyde to furfuryl alcohol in the presence of pre-inhibited nickel powder.

A still further object of my invention is to provide a method for regenerating the nickel powder spent in the hydrogenation process.

Further purposes and features of my invention will be set forth in the following description given for the purpose of exemplification and by no means of limitation, of a few ways of carrying the method into effect and of a plant for use in the hydrogenation process. In the said description reference is made to the drawing appended hereto in which:

Figure 1 is a diagrammatical complete view of said plant.

Figure 2 is a diagrammatical view of a preferred embodiment of means to actuate the stirrers.

The plant comprises one, two, three, four or more similar vertical units 1, 2, 3, 4, and so on, to which hydrogen is supplied through pipes 6. Each unit contains a hydrogenation chamber 7 which, in normal operating conditions, is only filled up to the line 8, that is approximately at the same level as the pipe 12. In these conditions, the capacity of the chamber is 20 litres. Said chamber is surrounded with a jacket 9 to which steam is supplied through a pipe 11. The bottom of each chamber is connected through a pipe 12 to the middle portion of the next unit. The chamber 7 is swept periodically by one or several disc stirrers 13 which are actuated by means of a rod 14 which carries a magnetic core 16. The latter is freely movable within the cylindrical chamber 17 by the action of an electromagnet 18 which is energized periodically through a make-and-break switch 19.

Preferably, the electromagnet 18 is comprised of three pile-up coils 31, 32, 33; which are equal in height and

which are capable of attracting a soft iron core 16 the height of which is twice that of any one of them.

The current fed into the lowermost (so-called first) coil 31, will attract the core 16, whereby the rod 14, and the stirrer 13 is moved upwards. The current is immediately flowed through the intermediate (so-called second) coil 32 and almost immediately interrupted in the "first" coil. The core goes on moving upwards owing to the attraction exerted thereon by the "second" one 32. The current is then fed to the top coil 33, i. e. the "third" one and almost immediately interrupted in the second one. The core is attracted by the said "third" one 33 through which the electric flow is maintained until the upward movement of the core 16 is stopped. Since current is flowed through the second coil and immediately cut off from the third one, the core is attracted downwards all the more powerfully as gravity now acts in the same direction. As soon as the core is positioned opposite the second coil 32, the current is switched into the first coil 31 which at first will accelerate its downward movement and thereafter retard it as soon as the core 16 tends to move beyond it. Once the movement is stopped, current is cut off from the first coil 31 and the stirrer 13 drops onto the bottom of the chamber 7 until it will be urged upwards by the next series of impulses.

The current supplied to each coil is switched in or out by means of mercury switches 34, 35, 36 actuated by suitably profiled cams 37, 38, 39 keyed on a rotatable shaft 40 driven through a reduction gear 41.

Moreover, each unit is equipped with a loading tail pipe 21 closed in fluid-tight manner by a cover. The furfuraldehyde contained in the tank 23 is forced into the unit 1 through a volumetric feed pump 22. The outlet tail pipe 12 leads from the last unit to a pipe line 24 the output of which is arranged to control the input at 22 as a result of the determination of the refraction index of the outflowing liquid by means of an optical device 27 interposed in a duct 26 shunting said pipe line.

In carrying the hydrogenation process into effect, first of all, a measured amount of nickel powder is introduced through each of the tail pipes 21 of the vertical units, which powder is prepared from nickel aluminium alloy containing 25 to 50% of nickel. In addition to the nickel and the aluminum the starting alloy may contain a small percentage of chromium, or a small percentage of copper, or small percentages of both of them. The percentage of either last-mentioned metals should not exceed about 5%.

The thus prepared nickel Raney powder catalyst should not be used in its normal state, since in this state it would be too much effective and would reduce the double bonds in the furfuryl alcohol resulting from the hydrogenation of the aldehyde. It is necessary to inhibit it as will be explained later on.

Nickel-aluminium alloy powder should first of all be treated with an aqueous solution containing about 20% of aqueous alkali hydroxide by stirring the former in the latter at a temperature of about 100 to 120° C. It is preferable, at first, to take care that the powder is poured in progressively while the alkali hydroxide solution is kept preferably at a temperature below 50° C. For instance, sodium or potassium hydroxide may be used, whereby only the aluminum in the alloy will be attacked whereas the nickel will remain unaffected in the state of a very finely divided powder.

After at least one, or preferably two or more hours, the finely divided Raney nickel is allowed to settle in the bottom of the vessel and the liquid solution separated by decantation. The residue is washed thereafter, preferably twice, with lukewarm water and then with a slightly acid water, e. g. with water admixed with 1% of acetic acid, with a view to eliminate the alkali.

The Raney nickel powder thus obtained would be too much effective as a catalyst. Its effectiveness should be reduced by heating it for at least half an hour at a temperature of 100° C. with furfuraldehyde. The process may be carried out e. g. in the vessel **23** of the plant, or in a vessel from which the furfuraldehyde is supplied to said vessel **23**; an advantage of said process is that the furfuraldehyde is purified thereby. However, the effectiveness of the powder can also be reduced in other hydrogenation processes. For instance, the Raney nickel powder may be used previously in the hydrogenation of preferably vegetable oils or animal fats. A catalyst which is thus fatigued or partly spent consequent to such a hydrogenation process will be quite suitable for the furfuraldehyde hydrogenation process.

It is to be noted that after the catalyst has been used for the purification of the crude furfural it may require being regenerated. The regeneration is carried out by heating it for at least half an hour with an about 20% aqueous alkali solution, the aforesaid treatment being followed with repeated rinsings with pure water and finally with a slightly acid water.

For the hydrogenation of furfuraldehyde a Raney nickel powder may also be utilized which has already been used in a previous process and which has been subjected to a regeneration process by keeping it for several hours at boiling temperature or slightly therebelow in the presence of an about 20% aqueous solution of alkali hydroxide while stirring.

Once sufficiently inhibited, the catalyst is introduced through the loading tail pipes **21** on the vertical units **1**, **2**, **3**, **4**, and so on, at the rate of about 7 to 11% by weight of nickel as compared to the weight of furfuraldehyde to be hydrogenated.

Furfuraldehyde is then introduced into each of the units, hydrogen is forced in under a pressure which may range from about 2 to 20 kg./sq. cm. and the make-and-break switch **19** controlling the electromagnet coils is started in a manner that about one beat per second is obtained. Meanwhile, the vessels are heated to temperatures ranging from 80 to 130° C. by supplying steam through the pipes **11**.

The furfuryl alcohol formed is collected at the outlet of pipe **24**. The vertical units are supplied with furfuraldehyde continuously by means of the volumetric pump **23**. The percentage of furfuryl alcohol in the liquid rises gradually from No. 1 to the last one.

It takes several hours to perform the hydrogenation process. A check on said process can be had by shunting some of the liquid let out from the last unit into a pipe **26** past the optical device **27**. The refraction index must shift from 1.515 to 1.488.

Experiments have led to the following results:

The hydrogenation is completed within 6 hours by heating at 100° C. under a pressure of 5 kg./sq. cm., or at 120° C. under a pressure of 5 kg./sq. cm.

It is completed within 24 hours by heating at only 80° C. under a pressure of 20 kg./sq. cm.

It may be carried out under a pressure of 2 kg./sq. cm. but it will only start at 110° C. and takes 19 hours at 120° C.

The best yields obtained range from 90 to 92% by working under a pressure of 20 kg./sq. cm. at a temperature ranging from 80 to 90° C.

The most effective catalyst is obtained when the nickel-aluminum alloy from which the nickel powder is prepared contains 30% of nickel and 70% of aluminum, although it is also possible to use a 50–50% alloy. The amount of nickel to be used in the hydrogenation process may range from 7 to 11% by weight of the furfuraldehyde to be hydrogenated.

Where the reaction is to take at least 5 to 6 hours, it is advisable to add fresh powder in the course of the reaction. The powder used in the reaction is regenerated by heating it for a long time at a temperature ranging from 100 to 120° C. in an aqueous alkali solution; it may be reused indefinitely.

It is possible therefore to work at temperatures and under pressures which are considerably lower than heretofore, and this, in the presence of a catalyst which can be prepared easily and which can be re-used indefinitely following a quite simple regeneration process.

Examples showing how the reaction may be carried out are given hereinafter:

Example 1.—An inhibited nickel powder is prepared by admixing a solution of 19 kg. of sodium hydroxide in 75 litres of water with 15 kg. of an alloy powder containing 30% of nickel and 70% of aluminum, the solution being gently heated so that its temperature does not rise beyond 50° C. After the whole of the alloy powder has been added the mixture is heated for two hours at a temperature of 110° C. while stirring. The powder is allowed to settle, whereafter the liquid solution is decanted off. The nickel powder thus obtained is washed twice with lukewarm water and finally treated with a 1% aqueous acetic acid solution in order to remove the alkali. The nickel is then heated at a temperature of 100° C. in crude furfuraldehyde for at least half an hour while stirring, whereby on the one hand the aldehyde thus treated is purified while on the other hand the nickel is inhibited to such an extent that it will not remove the double bonds in the furfuryl alcohol molecule and consequently will become suitable for the hydrogenation of the aldehyde. In order to purify the powder from the impurities removed from the crude furfuraldehyde the said powder is regenerated by heating same for at least half an hour in soda lye.

Through the loading tail piece of each vertical unit there are poured in firstly 700 grs. of nickel powder (prepared from 2,333 grs. of alloy powder) and then 10 kgs. of furfuraldehyde. The proportion of nickel, therefore, is 7% by weight. Hydrogen is then forced into the units under a pressure of 20 kg./sq. cm. and the make-and-break switches assigned to the electromagnets of the vertical units are set into action in such a manner that about one beat per second is obtained. Steam is circulated through the jackets around the chambers so that the temperature of the liquid shall be kept at about 120° C.

The first unit is fed slowly and uniformly, and once the hydrogenation process has become almost completed (which will occur after about three hours), the rate of flow is so adjusted that a liquid is obtained at the outlet of the plant the refraction index of which is 1.488. The nickel powder is separated from the liquid by decantation.

Whenever the plant is drained altogether in order to reclaim the excess nickel that may have settled therein, the liquid is decanted off and the powder is heated for 12 hours at boiling temperature in a 20% aqueous solution of sodium hydroxide. Thereafter it is washed twice with lukewarm water and finally once with a 1% aqueous solution of acetic acid, whereafter it is ready to serve in a new hydrogenation process.

Example 2.—An inhibited powder is prepared, and the units are loaded as described in Example 1. Hydrogen is forced in under a pressure of 20 kgs./sq. cm., the temperature of the liquid being kept however at 80° C.

Almost complete hydrogenation of the furfuraldehyde to furfuryl alcohol is obtained after about 24 hours instead of 3 hours.

The yield is as high as 90–92%.

Example 3.—Wet Raney's nickel powder previously used in the hydrogenation of animal fats, is introduced into the vertical units, the ratio being 10% of pure nickel to the weight of furfuraldehyde to be treated.

Hydrogen is forced in under a pressure of 2 kg./sq. cm. and the liquid is heated to 120° C. for 19 hours while stirring it with the stirring device.

Furfuryl alcohol is thus obtained (the yield being 88%)

which distils between 168 and 170° C. in normal pressure conditions once led over alumina. The refraction index of the alcohol thus obtained is 1.493.

Example 4.—The operation is carried out under a pressure of 2 kg./sq. cm. as described in Example 3, except the liquid is heated up slowly and progressively. It will be found that no hydrogenation occurs at a temperature of 100° C. The hydrogenation process will only begin at a temperature of 110° C. and proceeds only quite slowly at the said temperature. At 120° C. it will proceed normally as described in Example 3. The hydrogenation process will become comparatively rapid if the temperature be raised to 130–140° C.

Example 5.—A nickel powder prepared from 8 kg. of 50–50% nickel-aluminium alloy and subsequently inhibited as explained in Example 1 is charged into four of the vertical units in the proportion of 4 kg. of said nickel to 40 kg. of furfuraldehyde. Hydrogen is forced into the units under a pressure of 7 kg./sq. cm., whereafter the vessels are heated to 100° C.

At the end of the fourth hour there are added a further 200 gr. of nickel powder. At the end of the fifth hour a further amount of 200 gr. of nickel is added.

The conversion of furfuraldehyde to furfuryl alcohol is completed at the end of the sixth hour. The total weight of nickel used represents 11% of the weight of furfuraldehyde treated.

Example 6.—A 50–50% Ni-Al alloy powder is first heated as explained hereinbefore in Example 1 in a sodium hydroxide solution, after which the nickel powder thus obtained is used in the hydrogenation of vegetable oils.

The powder is reclaimed, from which an amount is taken in the wet state which corresponds to 4 kg. of pure nickel. The said amount is filled together with 40 kg. of furfuraldehyde into four of the vertical hydrogenation units.

Hydrogen is forced into said units under a pressure of 5 kg./sq. cm. The vessels are heated up to a temperature of 120° C. whereafter the stirrers are switched in. 200 grs. of fresh nickel are added at the end of the fourth hour and another 200 grs. at the end of the fifth hour. The hydrogenation is complete at the end of the sixth hour.

Example 7.—An inhibited nickel powder is prepared by incorporating 15 kg. of a powdered alloy which contains 28% of nickel, 66% of aluminum, 3% of chromium and 3% of copper to a solution of 40 kg. of sodium hydroxide in 150 litres of water which is mildly heated so that its temperature shall not exceed 50° C. The powder is washed twice with water, then once with a slightly acid solution and finally heated to a temperature of 100° C. in furfuraldehyde.

Each unit is filled first with 775 gr. of the powder (which is assumed to be anhydrous), i. e. 700 gr. of nickel and then with 10 kg. of furfuraldehyde. Hydrogen is let in under a pressure of 20 kg./sq. cm., the whole is heated to a temperature of 90° C. and the stirrers are switched on. The hydrogenation is completed within about 20 hours, the yield being about 90%.

The nickel powders used for the hydrogenation of furfuraldehyde may be, for instance, prepared as follows:

Preparation A.—In the preparation of an inhibited nickel powder a solution of 19 kg. of sodium hydroxide is started from which is heated to a temperature of 110° C. and to which is directly added powdered nickel aluminum alloy which contains 50% of nickel and 50% of aluminum. The powder is stirred for two hours in the solution which is kept at the said temperature. The powder thus obtained can be used as such in the reaction as described in Example 5.

Preparation B.—An inhibited nickel powder is prepared by heating to a temperature of 40° C. a solution of 54 kg. of potassium hydroxide in 75 litres of water, to which there are progressively added 15 kg. of a powdered alloy which contains 30% of nickel together with 70% of aluminum.

The temperature is then raised to 110° C. and the powder is stirred for two hours in the lye thus heated up. Thereafter, the powder is gathered and subjected at first twice to washing with lukewarm water, then once to an acid washing and heated for an hour with furfuraldehyde at a temperature of about 100° C., whereafter it is heated at a temperature of 110° C. in a 20% aqueous solution of potassium hydroxide.

After the powder has been washed twice with water and then in a slightly acid medium, it can be used as described in Example 1.

What I claim is:

1. A method of preparing furfuryl alcohol clear of tetrahydrofurfuryl alcohol by hydrogenating furfuraldehyde, which consists in heating a powdered alloy consisting mainly of nickel and aluminum in which the percentage of nickel ranges from 25 to 50% for at least sixty minutes and at a temperature ranging from 100 to 120° C., in an aqueous solution of an alkali, heating the powder thus obtained for at least half an hour in raw furfuraldehyde to provide a pre-inhibited nickel powder, mixing the powder thus treated with furfuraldehyde in a proportion ranging from 7 to 11% by weight of nickel to the weight of aldehyde and stirring the mixture for several hours in the presence of hydrogen under a pressure ranging from 2 to 20 kg./sq. cm. at a temperature ranging from 80 to 130° C.

2. A method of preparing furfuryl alcohol clear of tetrahydrofurfuryl alcohol by hydrogenating furfuraldehyde, which consists in heating a powdered allow consisting mainly of nickel and aluminum in which the percentage of nickel ranges from 25 to 50% for a least sixty minutes, and at a temperature ranging from 100 to 120° C. in an aqueous solution of an alkali, using the powder thus obtained in the hydrogenation of fats to provide a pre-inhibited nickel powder, mixing the powder thus treated with furfuralydehyde in a portion ranging from 7 to 11% by weight of nickel to the weight of aldehyde, and stirring the mixture for several hours in the presence of hydrogen under a pressure ranging from 2 to 20 kg./sq.cm. at a temperature ranging from 80 to 130° C.

3. A method of preparing furfuryl alcohol clear of tetrahydrofurfuryl alcohol by hydrogenating furfuraldehyde, which consists in subjecting a nickel powder used in a previous hydrogenation process to a regeneration process by keeping it for several hours at boiling temperature in the presence of an about 20% aqueous solution of alkali hydroxide while stirring, thus providing a pre-inhibited nickel powder, mixing the powder thus treated with furfuraldehyde in a proportion ranging from 7 to 11% by weight of nickel to the weight of aldehyde, and stirring the mixture for several hours in the presence of hydrogen under a pressure ranging from 2 to 20 kg./sq. cm. at a temperature ranging from 80 to 130° C.

4. A process for the preparation of furfuryl alcohol clear of tetrahydrofurfuryl alcohol by hydrogenating furfuraldehyde, which consists in heating a powdered alloy consisting mainly of nickel and aluminum in which the percentage of nickel ranges from 25 to 50% for at least sixty minutes and at a temperature ranging from 100 to 120° C., in an aqueous solution of an alkali, heating the powder thus obtained for at least half an hour in raw furfuraldehyde to provide a pre-inhibited nickel powder, introducing the powder thus treated in communicating enclosed spaces arranged in series, the nickel rate ranging from 7 to 11% by weight of the initial weight of aldehyde to be treated, circulating a flow of furfuraldehyde in the liquid phase at a temperature of 80 to 130° C. through the said series of enclosed spaces, at a rate slow enough to maintain the circulating liquid phase during several hours inside said series of enclosed spaces, feeding the same simultaneously with hydrogen under a

pressure of 2 to 20 kg./sq. cm., continuously agitating in said enclosed spaces the furfuraldehyde in mixture with the pre-inhibited nickel powder contained therein, whereby the quantities of furfuraldehyde present in said successive enclosed spaces are hydrogenated to furfuryl alcohol in progressively increasing amounts from the first to the last enclosed space of the series whereas the furfuraldehyde is in contact with a nickel powder of progressively increasing activity, and tapping furfuryl alcohol from the last enclosed space of the series.

5. A process for the preparation of furfuryl alcohol clear of tetrahydrofurfuryl alcohol by hydrogenating furfuraldehyde, which consists in heating a powdered alloy consisting mainly of nickel and aluminum in which the percentage of nickel ranges from 25 to 50% for at least sixty minutes, and at a temperature ranging from 100 to 120° C. in an aqueous solution of an alkali, using the powder thus obtained in the hydrogenation of fats to provide a pre-inhibited nickel powder, introducing the powder thus treated in communicating enclosed spaces arranged in series, the nickel rate ranging from 7 to 11% by weight of the intial weight of alhehyde to be treated, circulating a flow of furfuraldehyde in the liquid phase at a temperature of 80 to 130° C. through the said series of enclosed spaces, at a rate slow enough to maintain the circulating liquid phase during several hours inside said series of enclosed spaces, feeding the same simultaneously with hydrogen under a pressure of 2 to 20 kg./sq. cm. continuously agitating in said enclosed spaces the furfuraldehyde in mixture with pre-inhibited nickel powder contained therein, whereby the quantities of furfuraldehyde present in said successive enclosed spaces are hydrogenated to furfuryl alcohol in progressively increasing amounts from the first to the last enclosed space of the series whereas the furfuraldehyde is in contact with a nickel powder of progressively increasing activity, and tapping furfuryl alcohol from the last enclosed space of the series.

6. A process for the preparation of furfuryl alcohol clear of tetrahydrofurfuryl alcohol by hydrogenating furfuraldehyde, which consists in subjecting a nickel powder used in a previous hydrogenation process to a regeneration process by keeping it for several hours at boiling

temperature in the presence of an about 20% aqueous solution of alkali hydroxide while stirring, thus providing a pre-inhibited nickel powder, introducing the powder thus treated in communicating enclosed spaces arranged in series, the nickel rate ranging from 7 to 11% by weight of the initial weight of aldehyde to be treated, circulating a flow of furfuraldehyde in the liquid phase at a temperature of 80 to 130° C. through the said series of enclosed spaces, at a rate slow enough to maintain the circulating liquid phase during several hours inside said series of enclosed spaces, feeding the same simultaneously with hydrogen under a pressure of 2 to 20 kg./sq. cm. continuously agitating in said enclosed spaces the furfuraldehyde in mixture with the pre-inhibited nickel powder contained therein, whereby the quantities of furfuraldehyde present in said successive enclosed spaces are hydrogenated to furfuryl alcohol in progressively increasing amounts from the first to the last enclosed space of the series whereas the furfuraldehyde is in contact with a nickel powder of progressively increasing activity, and tapping furfuryl alcohol from the last enclosed space of the series.

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