ANNEX 2

New process for the homogenous loading of solid particles into a chamber

This invention relates to a new process for the homogenous loading of solid particles into a chamber.

This process relates more specifically to the filling of chemical or electrochemical, oil or petrochemical type reactors with solid particles in a divided state, that may be in the form of beads, grains, cylinders, pellets, sticks, or other shapes but all relatively small in size.

These particles may namely be molecular sieves or solid grains of catalyst, usually extruded, either irregular in shape or in the form of beads, or mono- or multilobar, whose dimensions vary, as applicable, from a few tenths of a millimeter to a few centimeters.

It is to this application in particular that we will refer in the remainder of this description, but the process as set forth in the invention naturally applies to the loading of any other type of particle in a chamber.

It is known that a fixed bed reactor has a better reaction yield when its catalytic mass is loaded in the most homogenous way possible. This homogeneity, which, for reasons of simplicity and efficiency, must be obtained during the loading phase of the catalyst, makes it possible to guarantee a uniform and constant contact between the various catalyst grains and the liquid reaction medium, without creating preferred paths for the latter.

Today's most commonly used loading methods consist in loading the reactor's fixed bed using a flexible tube, still called "sleeve" or "sock", from the term "sock loading", or using buckets filled with catalyst, whose contents are successively poured into the reactor through the hole of the upper part of the chamber to be loaded (called "man hole" or "filling hole").

These methods lead to charges loads done in a point-to-point manner in the reactor, usually favoring the creation of slopes and talus on the surface of the bed being loaded. The

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various directions of the grains and the segregation of the heavier ones as they roll along said slopes or talus naturally lead to heterogeneities that are harmful to the proper further operation of the reactor. Indeed, preferred paths, followed by the liquid reaction phase, then become apparent in the catalytic bed, because of the random presence of significant spaces between the catalyst grains thus loaded. Consequently, the contact of the liquid with the various catalyst grains, as well as the duration of said contact, decrease and lead to an incomplete chemical reaction that may lead to an obvious deactivation of the overall catalytic mass.

We have also known for some time that, to correct this problem and therefore increase the homogeneity of a catalytic bed that is to be loaded, we can use a loading process that is no longer point-to-point but rather distributed over the entire section of the chamber to be loaded, similar to rain. This distribution of solid particles using a rainlike effect is usually carried out using units placed above a catalyst grain feeding device, and comprised, for example, of a rotating cone, for a distribution of particles using a centrifuge effect, as described in the US patent A-3 804 273, or using static elements, onto which the catalyst grains fall and in whose direction air is sometimes blown sideways, as outlined in the US patent A-4 051 019. Other types of equipment have also been suggested in order to obtain an overall homogonous distribution over the entire surface of the bed to be loaded, for example in FR-A-2 319 427 and, more recently in DE-A1-198 35 699.

The applicant has patented a process and a device for the uniform distribution of a solid in divided form into a chamber, which are namely the object of EP-A-007 854 and EP-A-116 246 as well as EP-A-769 462.

Unfortunately, if all these loading processes, which are grouped under the name "dense loadings" have a tendency to increase the homogeneity of the catalytic mass, they also favor in considerable proportions a gain in the density of the load itself. This gain in density may be greater than 10 %, even 20 %, when a method of

dense loading is used instead of the method called "the sleeve".

The result is inevitably that the spaces between the catalyst grains, in which the reactor's reaction fluid must circulate, are smaller, which increases the difference in pressure between the input and the output of the load to be treated in the reactor, where said difference is called ΔP or loss of load of the reactor.

However, it turns out that in some cases and for some processes the industrial entrepreneur need only benefit from the improved homogeneity of the catalytic bed so obtained, without being subjected to the increase in the loss of load of the reactor.

In pursuing her/his work in this field, the applicant established that it is possible to obtain this result by distributing the particles in the chamber to be loaded over a liquid contained in said chamber and compatible with said particles, where the bed of particles is thus formed within said liquid.

The applicant has indeed noticed that, during traditional type dense loadings, meaning in a chamber that only contains a gaseous phase, the increase in the load density is most likely linked to the free fall velocity of the grains, and therefore to their impact energy when they arrive on the bed being formed, associated with a preferred angle of said grains in the catalytic bed. Therefore, it appears that by using a liquid as an intermediary to reduce said fall velocity, it is possible to resolve in a simple way, both the problem of the homogenous distribution of the grains and that of the increase in density.

Therefore, the object of this invention is a process for homogenous loading of solid particles into a chamber, characterized in that said chamber is filled, at least in part, with a liquid, and in that the flow of particles introduced in the chamber is divided, then distributed in a homogenous manner in a gaseous phase over the surface of said liquid, within which the particles move downward by means of gravity and come to settle while forming a fixed bed.

A first advantage of the process that is the object of the invention is therefore to obtain good homogeneity of the formed bed, without increasing the

density of the load. Indeed, in limiting the speed at which the grains fall into the liquid, it is possible to limit the energy of their impact, and thus favor the creation of sufficiently significant voids between the grains and, in the case of catalyst grains, a better contact and freer passage of the reaction liquid between said grains, without creating preferred paths, thus reducing by such the loss of load of the reactor.

A second advantage as set forth in the invention is the possibility of loading grains, namely catalysts, with a more fragile mechanical strength, for example extrudates in the form of cylinders whose length is several times greater than their diameter, for example a length that is greater than 5 millimeters or more, for a diameter of approximately 1 millimeter. Indeed, these extruded grains have a tendency to break when the dense loaded grains under gaseous atmosphere knock against each other, during their impact upon arriving on the catalytic bed. Indeed, the liquid phase used in the process as set forth in the invention limits said striking energy on the bed, which is the cause of grain breakage while also decreasing the phenomenon of attrition between the latter, thus reducing the quantity of catalyst fines or dust formed during the loading of the catalyst.

A third advantage of the process as set forth in the invention is linked to the decrease of the gaseous volume in the reactor due to the presence of the liquid in a quantity that is more or less significant. Said decrease may be a favorable element for implementing the loading process in the case where the particles, namely the catalyst, show a chemical reactivity with the loading gas, for example the air's oxygen. It can also be an important economic factor, because of the lesser quantity of gas that needs to be introduced into the reactor, when it involves a rare or inert gas, such as for example argon or nitrogen.

All types of liquids as well as their mixtures may therefore be used in implementing the process that is the object of the invention, provided that the catalyst grains that arrive at the upper level of the liquid may freely pass through said liquid up to the surface of the catalytic bed.

The man of the art will therefore choose a liquid or a mixture of liquids that are physically and chemically compatible with each other, as well as with the nature of the particles to be loaded, whose constitution and physico-chemical characteristics, such as for example density and viscosity, vary based on the parameters and precautions surrounding the loading. In the case of a chemical reactor and catalyst particles, the liquid being used may be the reaction liquid, a hydrocarbon such as an oil, water, or any other type of aqueous product. A liquid that evaporates rapidly, for example an alcohol, may also be used so as to evaporate at the end of the loading.

The distance needed for a solid particle, such as a grain of catalyst used to load reactors, to reach its speed limit in a liquid is in the range of a few centimeters, and it is therefore not necessary to have a large quantity of liquid over the surface of the catalytic bed. However, the height of the liquid in the reactor varies based on the quantity of loaded catalyst, this height must constantly be maintained greater than that of the bed throughout the loading, to make it possible to limit the fall velocity of the grains as proposed in this invention. The man of the art will calculate the quantity of liquid directly necessary for the loading, or will use known means to adjust said height based on the quantities of loaded catalyst. Preferably, the height of the liquid above the surface of the catalytic bad of particles will be greater than 10 cm.

The loading process that is the object of this invention makes it possible to use various types of gases in chemical reactors whose nature may vary based on the reactivity of the catalysts with said gases. Namely, the ambient air is generally used to load reactors, for example hydrotreatment reactors in the oil industry, and said air could be dried out or dehydrated to adapt it to the specific conditions needed to load certain types of catalysts.

Neutral or inert gases, such as for example argon or nitrogen, can be used to load specific catalysts

intended for specific processes, such as for example isomerization catalysts for light gasolines in an oil refinery.

All methods of dense loading implemented in the traditional way, meaning whose grain distribution device allows for a homogenous distribution of the grains all along the transversal section of the reactor or the chamber to be loaded, over the surface of a liquid, are likely to be used in accordance with the invention. In particular when the reactor must be loaded up to its upper part, one should use devices that can create a homogenous rain in the small gaseous space available over the liquid at the end of the loading. Advantageously, rotary devices that can spread out under the effect of the speed of rotation in the highest part of the reactor over at least half the transversal section of the latter will be put in place at the man hole or filling hole level arranged under a catalyst grain feeding sieve.

Preferably, we will use the device described in EP-A-769 462 or its equivalents. Indeed, this device includes a mobile axis, on which flexible deflector elements, each shaped like a vertical strap in resting position, are arranged at various levels and articulated so as to be able to lift up under the effect of the centrifugal force. Said flexible deflectors, which may for example be made of a rubbery matter and be animated with a slow rotation speed, generally less than 200 rotations per minute and preferably less than 150 rotations per minute, make it possible to limit the breaking of the catalyst grains that knock together when falling on the deflectors and the attrition phenomena that lead to the creation of catalyst fines. For some uses, the device may be put in place in a fixed manner level with the man hole, or lowered into the reactor and then be brought back up at the same time as the catalytic bed during the loading. Of course, other grain distribution devices can also be used such as those described above, whose distribution device is comprised of a rigid matter as described in EP 0 470 142 or FR-A-2 721 900.

Various types of solid particles can be loaded using the process that is the object of this invention such as beads, grains, cylinders, pellets, sticks, mono or multilobar shapes, or any other shapes whose various dimensions go from a few tenths of millimeters to a few centimeters. It could be catalyst grains, molecular sieve grains, contact mass grains for the needs of the chemical, oil or petrochemical industries. Other types of solid particles, with the dimensions indicated above and requiring a homogenous loading into a chamber, can of course be used.

The process as set forth in the invention allows for the loading of particles with a reactivity to the gaseous fluid, because of their short residence time in the latter, as the particles quickly end up in the liquid medium, which can be chosen to be chemically compatible with the nature of the particles. Liquid impregnations can also be made on said catalyst grains, prior to being loaded into the reactor, where said liquid can be of the same nature as that contained in the reactor, or simply chemically and physically compatible with it. Arrangements known to the man of the art, such as for example liquid flows in the form of sprays are then necessary upstream from the distribution, to break the grain aggregates and carry them through the distribution device using a rain effect.

The attached drawings represent a non restrictive manner of implementing the process as set forth in the invention and results of comparative examples that will be described hereafter.

About the drawings:

- Figure 1 is a schematic view of a chamber during loading using the process as set forth in the invention;

- Figure 2 is a schematic view of a chamber prior to loading;

- Figure 3 is a schematic view of the same chamber after loading;

-Figures 4, 5 and 6 are representations of photos of the surface of the catalytic bed after successive loadings of the same catalyst grains, using the process called

"sleeve" under gaseous atmosphere, after a loading under the same conditions as previously mentioned, but replacing the sleeve with a dense loading device and lastly following a loading in liquid, as set forth in the invention respectively.

Figure 1 represents a chamber 1, for example a chemical reactor, whose diameter and height may reach several meters, in which the catalytic bed 6, whose mass is supported in the reactor 1 by inert beads 7, is being loaded.

As set forth in the invention, a liquid 2, for example water, is arranged over said bed. Over said liquid, the gaseous phase can be comprised of various gases, namely air. The catalyst grains are continuously introduced into the upper part of the reactor, for example through a feeding sieve 3, then fall onto a distribution device so as to later obtain a homogenous distribution of said grains in the reactor 1.

The device represented and used in a preferred way, commercially called "Densicat", is described in detail in EP-A-0 769 462. Said device is comprised of rubber flexible deflectors, integral with several levels of a mobile axis, whose rotation speed is variable, to adjust the quality of the loading. The deflectors move further and further away from the mobile axis as the rotation speed of the latter increases, where said speed can reach more than a hundred rotations per minute. The grains of catalyst, after falling onto said rotation deflectors, are dispersed like rain in the gaseous phase over the entire transversal section of the reactor, above the surface of the liquid 5. The fall velocity of the grains passing through the liquid 2 is then slowed down, thus making it possible to reduce the grains' striking energy when the latter come into contact with the surface of the catalytic bed 6. Thanks to this decrease in energy, the grains can settle more softly and in a more homogenous manner on the catalytic bed, without grouping together, thus creating even spaces between them, reducing by as much the density of the loading.

It is important to make sure that, during the loading, the height of the liquid over the catalytic bed remains at least at its

minimum level, and it will be adjusted by any means known if necessary.

The liquid phase introduced into the reactor before the loading can have any height, but is should preferably be greater than ten centimeters, which corresponds to the minimum level 8 indicated in figure 2.

At the end of the loading, the liquid reaches its highest level 9, indicated in figure 3. The previously described device comprised of deflectors makes it possible, through its small overall dimensions, to be operational even if the maximum level of liquid 9 is very close to the upper extremity of the reactor.

In figure 4, we see the aspect of the catalytic bed surface, following loading with a feeding sleeve, which makes it possible to distribute the catalyst grains over the surface of the bed, at best in a point-to-point manner and using human means. The spaces between the grains are distributed randomly and the grains are not packed down, offering numerous and important preferred paths for the reaction liquid, that lead to an incomplete chemical reaction. The loading is not homogenous and not dense.

On the other hand, in figure 5, the catalyst grains are very much grouped together and take up the maximum available space therefore the voids between the particles are very small. The dense loading carried out for this test made it possible to load the reactor in a homogenous and dense manner, meaning with a maximum of catalyst grains in the reaction liquid, but leaving very few spaces for the free circulation of the liquid which leads to strong losses of charges inside the reactor.

In figure 6, we see the aspect of the surface of the catalytic bed after loading of the same catalyst as that used for the two previous loadings, but now carried out using the process as set forth in the invention, meaning in a liquid. The grains are distributed in a homogenous manner and on the whole even spaces are distributed around the grains. Therefore, on the whole the molecules that make up the reaction liquid have the same probability of meeting the same quantity of catalyst grains, without being deviated by the presence of preferred paths. This results in an even and sufficient flow, made easier by a presence that is also

homogenous of spaces evenly distributed around the grains, making it possible to optimize the desired chemical reaction. The loading is homogenous and dense.

The examples provided below are intended to illustrate the invention and not limit it in any way.

Example 1

Three series of tests were carried out in a laboratory using the same catalyst, over a transparent column, whose dimensions are as follow:

- diameter 440 mm,
- height 1000 mm.

The catalyst used for the tests is comprised mainly of alumina and presents itself in the form of dry extrudates whose average dimensions are as follows:

- length: 5 mm,
- diameter: 3 mm.

Test 1

The catalyst is loaded in the traditional way, meaning in a gaseous phase (air), using a sleeve comprised of a flexible tube with a diameter of 10 cm.

Test 2

The same batch of catalyst is loaded in the air using the distribution device with a Densicat type rain effect (dense loading), meaning including flexible rubber deflectors, integral with several levels of an axis animated by a variable speed rotation movement.

Test 3

Prior to loading, we added a volume of water whose height is 100 mm in the column.

The same batch of catalyst is loaded into this liquid with a distribution device that is identical to the one used in Test 2, meaning favoring a dense load, as set forth in the invention.

The results obtained are summarized in Table 1 below.

Table 1

	Test 1	Test 2	Test 3
Loading Method	Sleeve	Dense Loading	Liquid
Loading medium	Air	Air	Water
Height of Water	0	0	100 mm
Quantity of loaded catalyst	46,39 kg	46,39 kg	46,39 kg
Density of the catalytic bed (t/m^3)	0,78	0,90	0,77
State of the catalytic bed	See Figure 4	See figure 5	See figure 6

We see that the density of the catalytic mass obtained, with a dense type loading method in air (Test 2), is greater on the whole by 15 % than that obtained by loading with a sleeve in air (Test 1).

Loading in a liquid (Test 3), carried out using the same device as that used for the dense loading (Test 2), but in a liquid, as set forth in the invention, makes it possible to significantly reduce the density whose value is considerably closer to the value recorded with a sleeve loading. Therefore, when using the process as set forth in the invention, we obtain a dense type loading in which the presence of the liquid makes it possible to significantly reduce the increase in density of the catalytic mass inherent to this type of loading.

When checking figures 4, 5 and 6, which are representations of photos of the surface of the catalytic bed obtained in each of the above loading tests, we see that the loading process as set forth in the invention, while reducing the density of the

catalytic mass to a value close to that obtained with the sleeve, it is also possible to obtain a mostly homogenous distribution of the grains, as only the dense type loadings in air can do currently, which, in counterpart, led to a significant increase in the density of the load.

Therefore, the process as set forth in the invention provides a solution to the problem caused when obtaining a homogenous distribution that usually results from a dense type loading, but whose density of the loaded mass here is for the most part identical to the density recorded with a sleeve type distribution.

Example 2

The above-mentioned tests are done over, but, in Test 3, the liquid has been replaced with an aqueous ethylene-glycol solution with a viscosity that is 17 to 18 times higher than that of water, to study the influence of the viscosity of the liquid being used.

The results obtained are shown in Table 2 below.

Table 2

	1	2	3
Method of loading	Sleeve	Dense loading	Liquid
Loading medium	Air	Air	Water + ethylene-glycol
Height of the liquid	0	0	100 mm
Quantity of loaded catalyst	45, 27 kg	45,27 kg	45,27 kg
Density of the catalytic bed (t/m^3)	0,78	0,90	0,79

We see that a greater liquid viscosity has no affect on the results obtained and that the process as set forth in the invention does not

depend on the viscosity of the liquid used for loading the catalyst grains.

CLAIMS

1. Process for the homogenous loading of solid particles into a chamber (1), characterized in that said chamber (1) is filled at least in part with a liquid (2), and in that the flow of particles (3) introduced into the chamber (1) is divided, then dispersed in a homogenous manner in a gaseous phase (4) over the surface (5) of the liquid, within which the particles move downward by means of gravity to settle and form a fixed bed.

2. Process as set forth in claim 1, characterized in that the liquid phase (2) is comprised of a liquid or a mixture of liquids physically and chemically compatible with the chemical nature of the solid particles.

3. Process as set forth in any one of claims 1 through 2, characterized in that, throughout the loading, the height of the liquid (2) through which the solid particles pass, over the bed of particles being created, is greater than 10 cm.

4. Process as set forth in any one of claims 1 through 3, characterized in that the gaseous phase is comprised of a gas or a mixture of gases physically and chemically compatible with the chemical nature of the solid particles.

5. Process as set forth in any one of claims 1 through 4, characterized in that the flow of particles (3) introduced into the chamber (1) is divided, then distributed in a homogenous manner, using a device (4) that makes possible a rainlike distribution of said particles over the entire transversal section of the chamber (1).

6. Process as set forth in claim 5, characterized in that the distribution device (4) is comprised of flexible deflectors integral with several levels of an axis animated with a rotary movement.

7. Process as set forth in claims 5 and 6, characterized in that the deflectors are articulated on the mobile axis so as to be able to move upward under the effect of the centrifugal force.

8. Process as set forth in any one of claims 5 through 7, characterized in that the rotation speed of the mobile axis is less than 200 rotations per minute and preferably less than 150 rotations per minute.

9. Process as set forth in any one of claims 5 through 8, characterized in that each of the deflectors is comprised of a flexible strap.

10. Process as set forth in any one of claims 5 through 8, characterized in that the particle distribution device is comprised of a rigid matter.

11. Process as set forth in any one of claims 1 through 10, characterized in that the liquid phase (2) is the reaction liquid of a chemical reactor.

12. Process as set forth in any one of claims 1 through 11, characterized in that the liquid phase (2) is a hydrocarbon, an aqueous phase, an alcohol or their derivatives.

13. Process as set forth in any one of claims 1 through 12, characterized in that the gaseous phase is air.

14. Process as set forth in any one of claims 1 through 12, characterized in that the gaseous phase is a neutral or inert gas.

15. Process as set forth in claim 14, characterized in that the neutral or inert gas is argon or nitrogen.

16. Process as set forth in any one of claims 1 through 15, characterized in that the gas used is dried or dehydrated.

17. Process as set forth in claims 1 through 17, characterized in that the solid particles have dimensions that range between a few tenths of a millimeter and a few centimeters.

18. Process as set forth in claim 17, characterized in that the solid particles are saturated with a liquid prior to being loaded.

19. Process as set forth in claims 1 through 18, characterized in that the chamber (1) is a chemical reactor, whereas the particles (3) are grains of catalyst.