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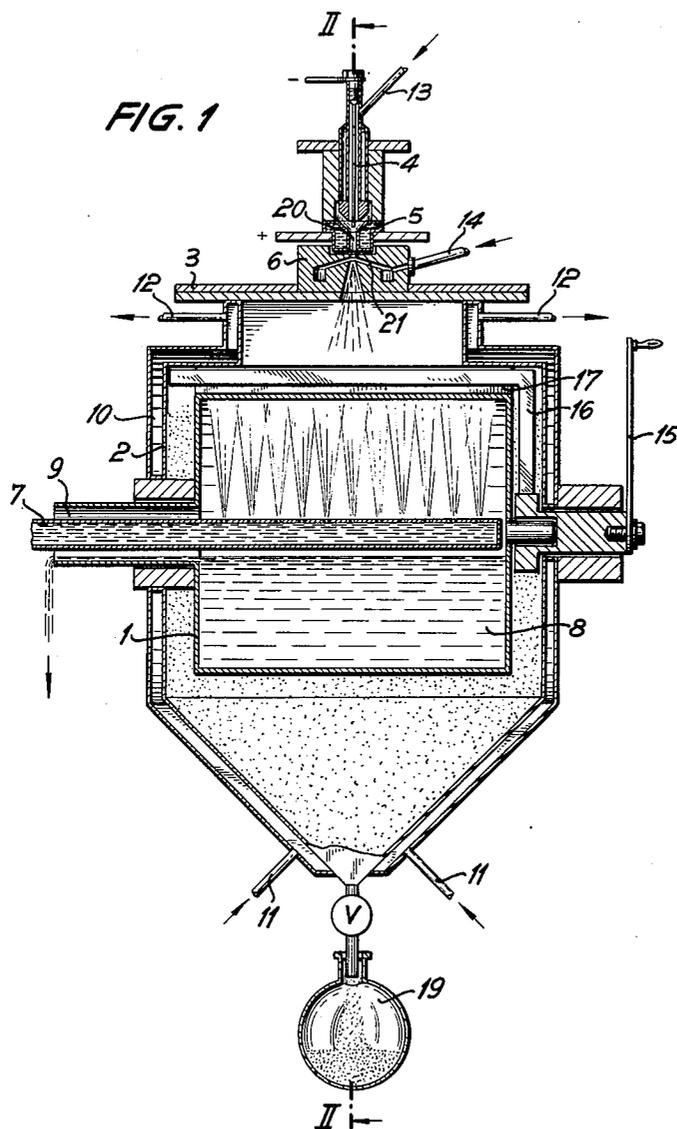
H. HARNISCH ETAL

3,211,520

PROCESS FOR THE MANUFACTURE OF LOW TITANIUM CHLORIDES

Filed July 19, 1961

3 Sheets-Sheet 1



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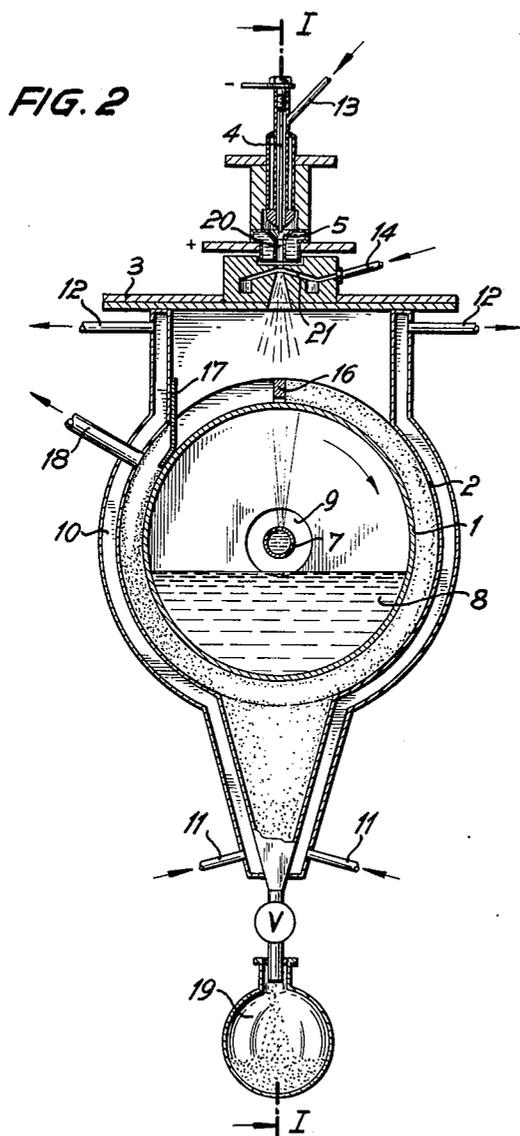
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PROCESS FOR THE MANUFACTURE OF LOW TITANIUM CHLORIDES

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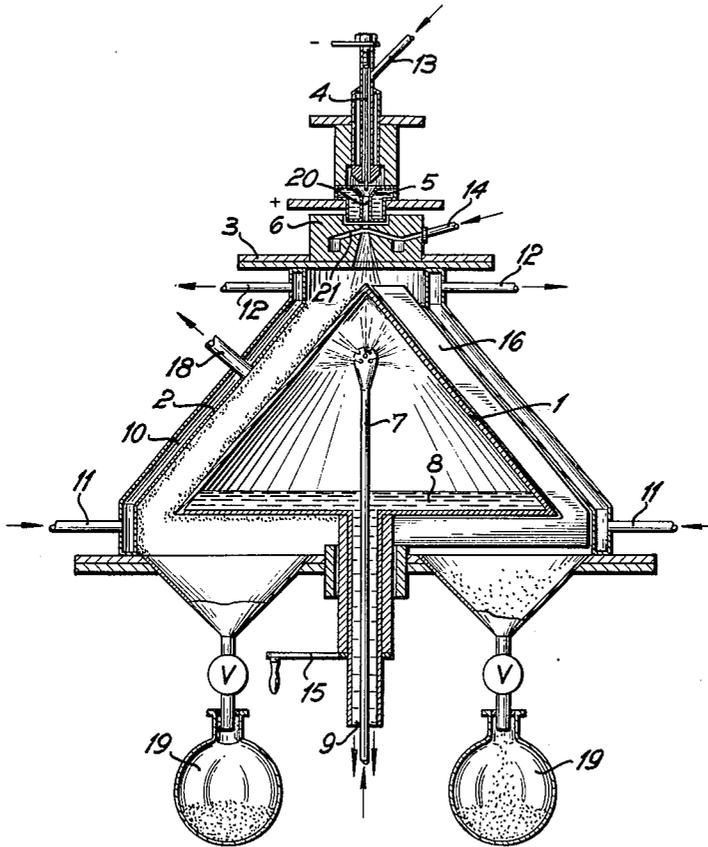
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3 Sheets-Sheet 3

FIG. 3



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PROCESS FOR THE MANUFACTURE OF LOW TITANIUM CHLORIDES

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9 Claims. (Cl. 23—87)

The present invention is concerned with a process for the continuous production of low titanium chlorides from titanium tetrachloride with the use of hydrogen as the reducing agent, and with an apparatus for carrying out said process.

It is known to make low titanium chlorides by reducing titanium tetrachloride in an alkali metal chloride melt by means of alkali metals or magnesium or by dispersing the alkali metal in an inert solvent and causing it to act in this form on the tetrachloride.

The aforesaid processes suffer from the disadvantage that the titanium dichloride or titanium trichloride formed is contaminated with the halide of the metal used for the reduction.

It has also been proposed to use metallic titanium as a reducing agent. In this case, sufficient amounts of metallic titanium must, however, be already available so that this process cannot be used for making an intermediate product for the manufacture of titanium.

The known processes using hydrogen as a reducing agent certainly enable pure subhalides to be obtained but they are all carried out discontinuously and generally yield only a few grams or at most a few kilograms of the desired product. In one of these processes, for example, a mixture of titanium tetrachloride and hydrogen is conducted through a red-hot tube and subsequently chilled rapidly on an indirectly cooled surface. The use of this process on an industrial scale is beset, however, with a number of difficulties: the hydrogen chloride formed in practice during the reduction at a temperature of 600° C. or more attacks the material of the vessel; furthermore the cooled surface used for chilling is covered with a layer of the reaction product which has a heat insulating action and, therefore, impedes the chilling of further reaction gases.

In other processes, a mixture of titanium tetrachloride and hydrogen is conducted through an electric discharge device and subsequently cooled. These processes involve similar difficulties as regards chilling and the choice of the material for the vessel. Furthermore, it is difficult, as is known, to carry out electric discharges with any desired power and to design large apparatus.

It has also been proposed to conduct a mixture of hydrogen and titanium tetrachloride through a sodium chloride melt. This process suffers from the same disadvantages as the reduction of titanium tetrachloride with alkali metal or alkaline earth metals because the low halide is not present in a pure form but as a solid solution or complex compound in a melt.

According to another proposal, a mixture of hydrogen and titanium tetrachloride is reduced in an electric arc.

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This process, however, involves great difficulties as regards the material of the electrode sheathing and of the walls of the vessel.

Now we have found that the above disadvantages can be avoided by mixing hydrogen, which has been preheated to high temperatures, with titanium tetrachloride in a mixing device, for example a nozzle, which is kept at a relatively low temperature, whereby the titanium tetrachloride is reduced by the hydrogen, and chilling the resulting reaction mixture on a moving cooled surface which is continuously cleaned by a stationary cleaning device. In this manner, a mixture of low titanium halides of very good purity is obtained in a good yield. The temperature of the mixing nozzle ranges from the boiling point of titanium tetrachloride to below about 500° C., and is advantageously at 200° C.

The hydrogen must be preheated to a temperature above 1000° C., advantageously above 2500° C., to obtain economical yields. The hydrogen is advantageously heated electrically, for example in an electric arc, since it is very difficult to heat hydrogen indirectly in a heat exchanger to a temperature of 1000° C. and more owing to the permeability to hydrogen of the walls of the vessel. When the hydrogen is heated in an electric arc, such a high temperature is generally obtained that at least part of the hydrogen is present in the form of atoms. It is particularly advantageous to use an electric arc arrangement as described in German Utility Patent No. 1,781,880.

To obtain a good yield, the reactants are advantageously mixed in the gaseous phase as rapidly as possible. For this purpose, the heated hydrogen is conducted through a channel of annular cross-section and the titanium tetrachloride which has been converted into the gaseous state by heating to above the boiling point is introduced approximately vertically to the said channel through an annular slot provided in the channel. Advantageously, the titanium tetrachloride is evaporated under a certain pressure so that the titanium tetrachloride vapor is brought into contact with the preheated hydrogen at a relatively high speed. To increase the speed at which the titanium tetrachloride vapor issues, additional hydrogen gas may be admixed. Alternatively, the titanium tetrachloride or the mixture of titanium tetrachloride and hydrogen may be introduced tangentially into a channel of circular cross-section through which hot hydrogen flows. In any case, it is important to mix the two reactants as rapidly as possible.

The reaction gases are then conducted to a moved cooled surface in order to be chilled. The reaction product which has deposited on the moving cooled surface as a loose layer is removed therefrom by a cleaning device, such as a stationary knife or a brush, so that the reaction gases arriving at the said surface always strike a clean surface whereby, and especially also owing to the high thermal conductivity of the hydrogen used in excess, a very intense chilling is produced.

In the known processes, chilling is generally brought about by injecting cold liquids. When very hot gases are to be chilled, it is necessary to use a thermally stable liquid which does not react with the reaction products. It is, however, not possible to find such a liquid for the process of the invention since, on the one hand, stable liquids, particularly water, react with the reaction prod-

uct and, on the other hand, liquids that are inert with respect to the reaction product, such as organic liquids (benzene, toluene, decahydronaphthalene), are decomposed by the hot reaction gases, partially with separation of carbon, so that a pure reaction product cannot be obtained in this manner. It is, furthermore, very difficult to isolate as labile a substance as low titanium chloride from such chilling liquids.

Furthermore, an apparatus using a recycled chilling agent is more complicated than the apparatus of the invention which dispenses with all accessories necessary for such chilling cycle (pump, heat exchanger, storage container). Moreover in the chilling process, the heat content absorbed by the gases to be chilled is lost, whereas in the present process the energy may, under certain circumstances, be recovered, for example, in the form of hot water or steam.

The moving cooled surface must be disposed within a casing which is secluded from the outer atmosphere since the desired reaction products would react even with traces of oxygen or water vapor. The starting materials, titanium tetrachloride and hydrogen, must also be free from oxygen, nitrogen and other impurities, in order to obtain a pure reaction product. If the temperature of the cooled surface is too low, the separated reaction products absorb unreacted titanium tetrachloride. The temperature is, therefore, advantageously kept so high that such absorption is substantially avoided. In the manufacture of low titanium halides, it is, for example, sufficient to keep the cooling agent for the moving surface, for example water, at a temperature of about 50 to about 300° C., advantageously about 50 to about 100° C., in order to obtain a final product containing less than about 2% of titanium tetrachloride.

It is necessary to use the hydrogen in an excess amount over the stoichiometric amount resulting from the reaction equation. An excess amount of hydrogen of about 1.2 to about 20 times, preferably 10 to 15 times, the theoretical amount is advantageously used.

If the molar ratio of hydrogen to titanium tetrachloride is smaller than about 5, titanium trichloride is generally obtained almost exclusively, besides unreacted titanium tetrachloride. If a higher molar ratio is used, the titanium trichloride obtained contains increasing amounts of titanium dichloride.

The space-time yield exceeds 0.15 kg./l. h. and the reaction product is obtained in the form of a fine pyrophoric powder which oxidizes in air with glowing and emission of a white fog.

The reaction products which have been stripped off are collected under an inert gas in a receiver disposed beneath the housing of the cooling roller. The gases flowing off contain, in addition to unreacted titanium tetrachloride, reaction products in the form of dust, i.e. the gas flowing off contains a considerable portion of low titanium halides which are removed by dry gas purification. In the dry gas purification, it is necessary to maintain the walls of the apparatus used for the removal of the dust at temperatures which prevent a condensation of unreacted titanium tetrachloride. These temperatures depend on the partial pressure of the titanium tetrachloride in the apparatus and shall be about 5 to about 100° C. above the dew point of the titanium tetrachloride under the working conditions in a given case. The dust may be separated, for example, in a cyclone, impact crusher or quiescent vessel.

The unreacted titanium tetrachloride is separated from the dust-free exhaust gas in known manner by cooling and may be returned to the process. Cooling may be effected in, for example, two stages: first, in a liquid condensation stage operating at a temperature above the melting point of titanium tetrachloride (-23° C.) and then in a solid condensation stage operating at a temperature below the said melting point. The hydrogen used in excess then only contains hydrogen chloride, which

may be removed, for example, by absorption with the help of an appropriate device, so that the hydrogen can subsequently be dried and reused for the reduction.

The substances obtained by the process of the invention are very pure. For example, the reduction of titanium tetrachloride yields products which consist of more than 99.8% of titanium and chlorine. This is of particular importance when the process of the invention is carried out as a preliminary stage for the production of titanium metal.

Apparatus suitable for use in carrying out the process of the invention are illustrated diagrammatically and by way of example in the accompanying drawings.

Referring to the drawings: FIG. 1 is a side elevation of an apparatus in which the moving and cooled surface is, for example, cylindrical, the elevation being taken along line I—I of FIGURE 2;

FIGURE 2 is an elevation of the same apparatus taken along line II—II of FIGURE 1;

FIGURE 3 is a longitudinal elevational of an apparatus in which the moving and cooled surface is, for example, conical.

FIGURES 1 and 2 illustrate a technical mode of executing the reaction.

Hydrogen is introduced into the burner at 13 and preheated on its passage through an electric arc between cathode 4 and anode 5. In mixing nozzle 6, the preheated hydrogen, which is partially split into atoms, is admixed with gaseous titanium tetrachloride introduced through feed pipe 14. The burner and the mixing nozzle 6 are disposed in a recess of cover 3. The reaction products and the unreacted starting material strike the moved cooled roller 1. Through perforated pipe 7, which is disposed in the roller axis, a cooling agent, for example water or oil, of a temperature of about 50 to about 300° C. is sprayed from the inside against that segment of roller 1 which is nearest to the burner. The lower part of roller 1 is filled with the cooling agent coming from the upper part of roller 1. The excess of cooling agent leaves roller 1 at 9 through an open cylinder. Cooling roller 1 is surrounded with casing 2 provided with cooling jacket 10. The solid reaction products adhering to the surface of roller 1 and the inside wall of casing 2 are removed by knife 17 secured to the casing and by a rotatable knife 16. The latter can be operated by crank 15 or another mechanical drive disposed at that place. The reaction products fall into receiver 19. The exhaust gas leaves the apparatus through outlet 18 (FIG. 2) to be conducted through another separator, for example a cyclone or impact crusher.

Another mode of executing the process of the invention can be realized with the apparatus shown in FIG. 3 in which the reaction products are chilled and separated on a rotating cone. The other parts of apparatus are analogous to those shown in FIGURE 1 and need not be explained here.

The following remarks are made with regard to the execution of the process of the invention for the continuous production of low titanium chlorides with the use of hydrogen preheated to above 1000° C. in an electric arc arrangement.

The aforesaid hydrogen, which is used in an amount about 1.2 to about 20 times, advantageously 10 to 15 times, in excess of the theoretical amount, is rapidly mixed intimately in the gaseous phase with a higher titanium chloride, with the help of a mixing device, such as a nozzle, which is kept at a low temperature. The reaction products are chilled, with the exclusion of the atmosphere, on a moving cooled surface from which the reaction products depositing thereon are continuously removed by a cleaning device and the reaction products are then collected under an inert gas in a receiver.

The hydrogen is advantageously heated by means of an electric arc arrangement to a temperature advantageously above 2500° C.

The process may also be carried out in a manner such that additional hydrogen is added to the titanium tetrachloride before the latter enters the mixing device.

In another form of the process of the invention, the heated hydrogen is conducted through a channel 20 of, for example, circular cross-section and the titanium tetrachloride or the mixture of titanium tetrachloride and hydrogen is brought into contact with the hydrogen about vertically to the direction of flow of the hydrogen through an annular slot 21 which opens into channel 20 or it may be introduced tangentially into channel 20.

It is also advantageous to maintain the moving cooling surface at a temperature within the range of about 50 to about 300° C., preferably 50 to 100° C., and to use the preheated hydrogen advantageously in an amount 10 to 15 times in excess of the theoretically required amount.

In order to render the process of the invention still more economical, titanium tetrachloride and hydrogen may be separated from the exhaust gases which have been freed in known manner from hydrogen chloride and reaction product present in the form of dust, and returned to the reaction process after they have been separated from each other in known manner.

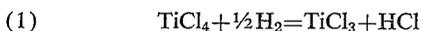
The manufacture of low titanium chlorides with the use of hydrogen as a reducing agent is advantageously carried out in an apparatus in which, according to FIGURES 1 and 2, an electric arc arrangement with mixing nozzle, advantageously of the type described in German Utility Patent 1,781,880, is mounted on a recess of cover 3 of closed casing 2 which is provided with cooling jacket 10 and gas outlet 18, the cooling jacket being provided with short feed pipes 11 and short discharge pipes 12. In casing 2 is disposed the cooling surface 1, which has the shape of a rotating hollow cylinder, into the interior of which there is introduced feed pipe 7 which is provided with holes or nozzles for the introduction of cooling agent 8 which can flow off through pipe 9. Knife 17 rigidly connected to casing 2 and knife 16 which can be turned by crank 15 or another device are disposed in a manner such that the reaction product depositing on the cooling surface is stripped off in order to be collected in receiver 19.

In another form of constructing the apparatus of the invention, cooling surface 1 has the shape of a cone whose apex faces the atomized jet (see FIG. 3).

The following examples serve to illustrate the present invention but they are not intended to limit it thereto, the parts being by weight.

Example 1

4750 parts titanium tetrachloride were evaporated, the liquid titanium tetrachloride flowing into the evaporator at an average rate of 9.5 kg./h., and then reacted in the gaseous state according to the following Equation 1



with 2.25 cubic meters (measured at N.T.P.) of hydrogen heated in the electric arc. According to Equation 1, this corresponded to an excess of hydrogen of 8 times the theoretical amount. The rate of flow of the hydrogen was 4.5 cubic meters/h. (measured at N.T.P.). The mixing nozzle was kept at 150° C., by cooling with air. The amount of energy supplied to the electric arc for heating the hydrogen amounted to 22 kwh. (135 amperes, 325 volts). 2320 parts of pure titanium trichloride were obtained. Yield: 60%, calculated on the titanium tetrachloride used as the starting material.

Example 2

3340 parts titanium tetrachloride were evaporated, the liquid substance flowing into the evaporator at a rate of 6.68 kg./h., and then reacted with 2.25 cubic meters (measured at N.T.P.) of hydrogen heated in the electric

arc. According to Equation 1, this corresponded to an excess of hydrogen of 11.4 times the theoretical amount. The rate of flow of the hydrogen amounted to 4.5 cubic meters/h. (measured at N.T.P.). The amount of energy supplied to the electric arc for heating the hydrogen amounted to 25 kwh. (145 amperes, 345 volts). A mixture of 1810 parts of low titanium halides was obtained (6% titanium dichloride+94% titanium trichloride). Yield: 67.5%.

Example 3

5900 parts titanium tetrachloride flowed at a rate of 5.9 kg./h. into the evaporator and were reacted in the gaseous state with 4.5 cubic meters (measured at N.T.P.) of hydrogen. The rate of flow of the hydrogen amounted to 4.5 cubic meters/h. (measured at N.T.P.). According to Equation 1 this corresponded to an excess of hydrogen of 13 times the theoretical amount. The amount of energy supplied to the electric arc for heating the hydrogen amounted to 48 kwh. (150 amperes, 320 volts). A mixture of 3020 parts of low titanium halides was obtained (7% titanium dichloride+93% titanium trichloride). Yield: 64.5%.

We claim:

1. A process for continuously manufacturing hydrogen free, low titanium chlorides by reducing titanium tetrachloride with hydrogen comprising separately preheating hydrogen to a temperature above 1000° C. to split the hydrogen at least partially into atoms, supplying a stream of the preheated hydrogen continuously to a nozzle in a stoichiometric excess amount, continuously supplying a substance selected from the group consisting of vaporous titanium tetrachloride and a mixture of vaporous titanium tetrachloride and hydrogen to said nozzle substantially perpendicularly to the stream of hydrogen, maintaining the nozzle at a temperature between the boiling point of titanium tetrachloride and about 500° C., mixing the hydrogen and the substance selected from the group consisting of vaporous titanium tetrachloride and a mixture of vaporous titanium tetrachloride and hydrogen rapidly and intimately in the nozzle, discharging the resulting reaction products from said nozzle onto a moving, cooled surface to continuously chill the reaction products and continuously collecting the chilled reaction products from the cooled surface while maintaining an inert gas atmosphere in the collecting area.

2. A process as claimed in claim 1, wherein the hydrogen is preheated in an electric arc zone.

3. A process as claimed in claim 1, wherein the hydrogen is preheated to a temperature above 2500° C.

4. A process as claimed in claim 1, wherein at least one substance selected from the group consisting of titanium tetrachloride and a mixture of titanium tetrachloride and hydrogen is added tangentially to the preheated hydrogen stream.

5. A process as claimed in claim 1, wherein the moving cooling surface is maintained at a temperature within the range of about 50° to about 300° C.

6. A process as claimed in claim 1, wherein the moving cooling surface is maintained at a temperature within the range of about 50° to about 100° C.

7. A process as claimed in claim 1, wherein the preheated hydrogen is used in an excess of 10 to 15 times the stoichiometric amount.

8. A process as claimed in claim 1, wherein the exhaust gas is freed from hydrogen chloride and reaction products present in the form of dust, the titanium tetrachloride is separated from the hydrogen and the titanium tetrachloride and the hydrogen are returned to the reaction process.

9. The process of claim 1, wherein the TiCl_4 is first admixed with hydrogen before being supplied to the nozzle, and then reduced in said nozzle by the preheated hydrogen.

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