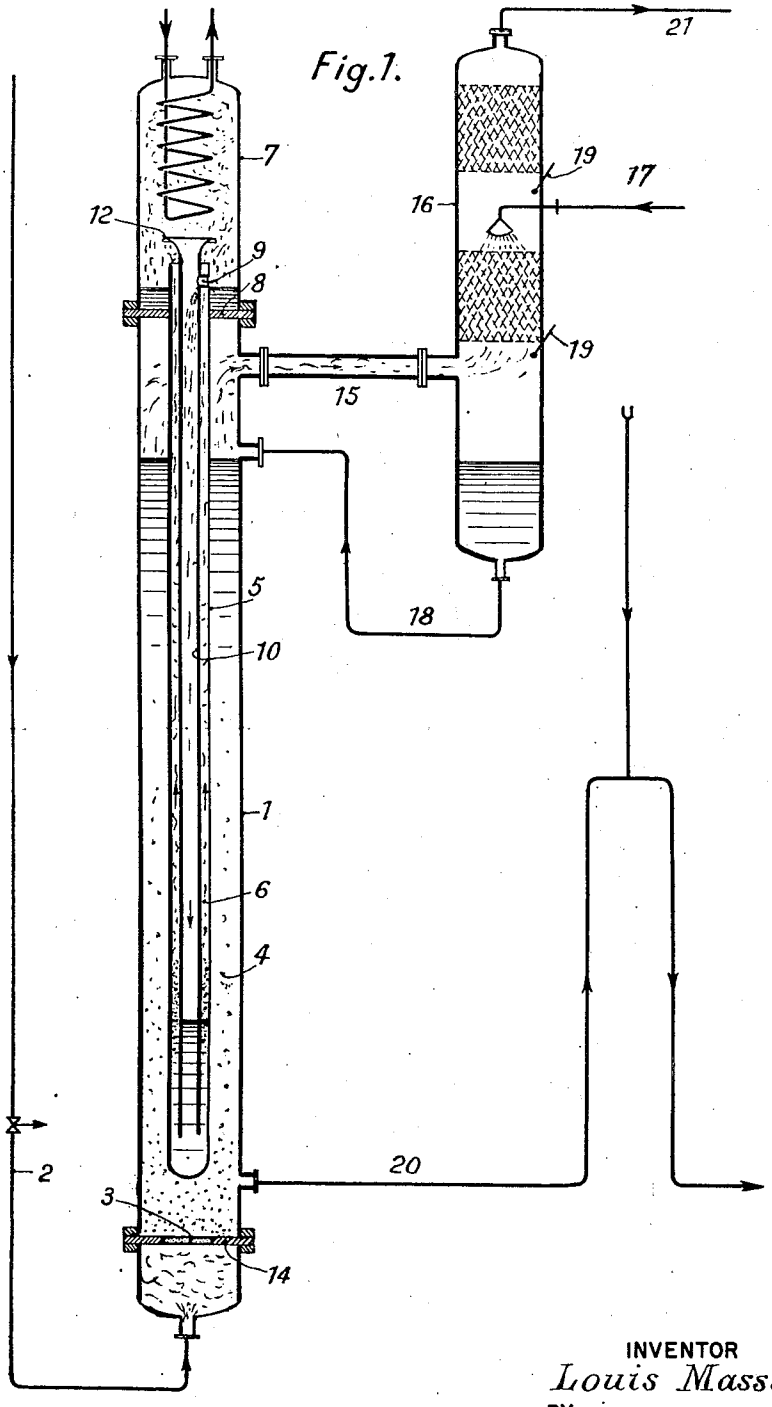
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APPARATUS FOR CARRYING OUT AN EXOTHERMIC REACTION AT SUBSTANTIALLY CONSTANT TEMPERATURE

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Fig. 1.



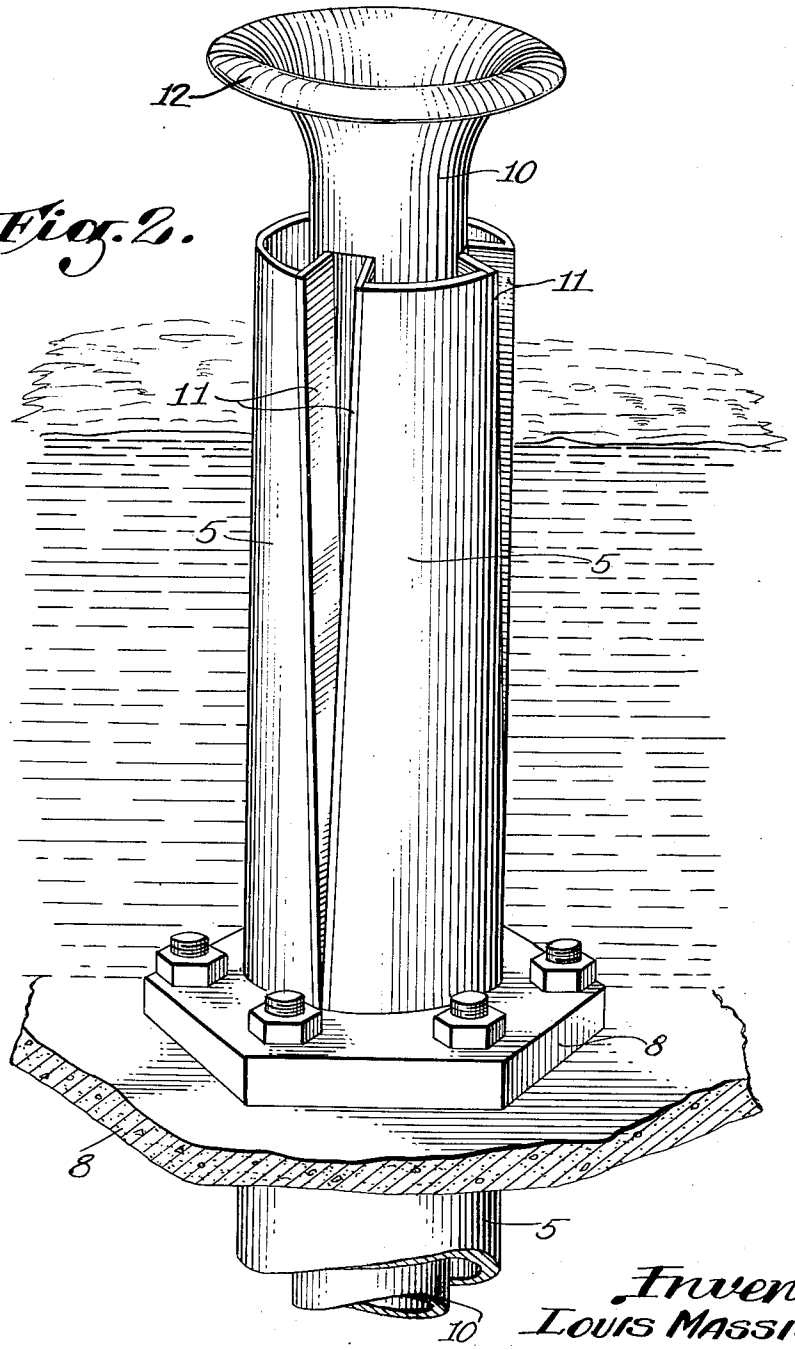
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Fig. 2.



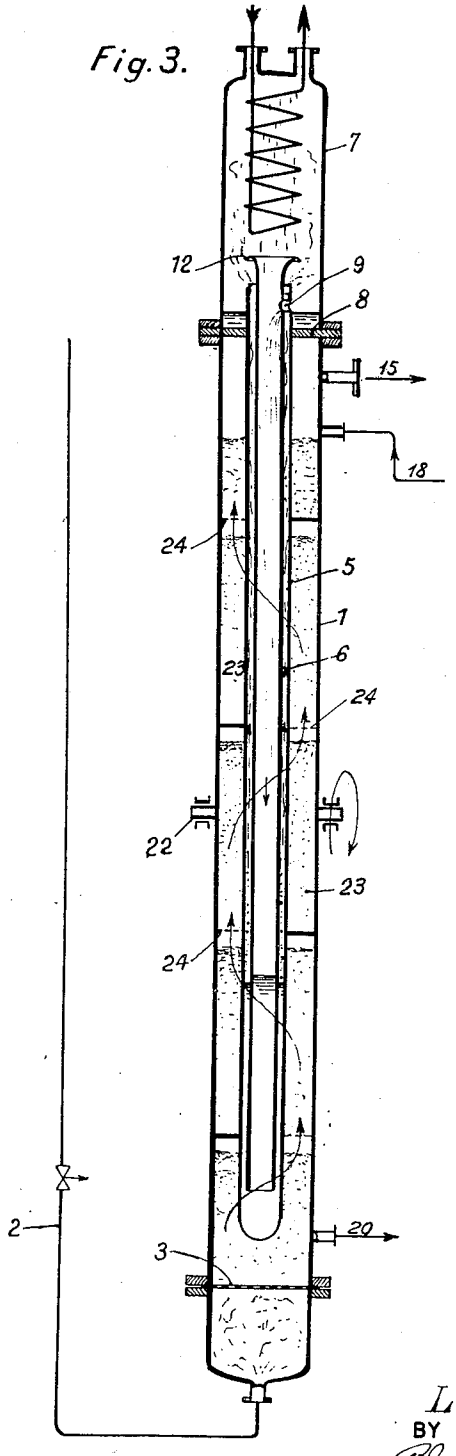
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Fig. 3.



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Fig. 5.

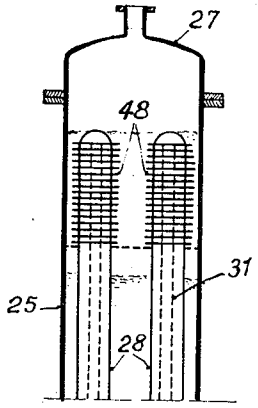


Fig. 4.

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Patented Jan. 9, 1951

2,537,472

UNITED STATES PATENT OFFICE

2,537,472

APPARATUS FOR CARRYING OUT AN EXOTHERMIC REACTION AT SUBSTANTIALLY CONSTANT TEMPERATURE

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Application December 15, 1945, Serial No. 635,385
In France August 16, 1944

Section 1, Public Law 690, August 8, 1946
Patent expires August 16, 1964

6 Claims. (Cl. 23—288)

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It is well known that exothermic reactions between gaseous fluids and liquids have been regulated heretofore according to methods and with means of various kinds among which it is possible to mention continuous operation in a boiler provided with stirring means and reaction in a column provided with surface contact means or with plates. It is also known that it is essential in all such methods to control the progress of the operation; it is necessary on one hand to reliably provide for constancy of temperature and on the other hand to achieve a complete absorption of the reacting gaseous fluid. This latter condition cannot be generally obtained by merely increasing the size of the apparatus used if the time of contact between the reacting materials is critical. This is the case for instance of chlorination when it is desired to avoid the production of super-chlorinated products. It is true that it is known to wash the gases produced by the product to be chlorinated but this is only a safety step and does not permit control of the operation.

A first object of the present invention consists in providing under rational and practical conditions for the regulating of exothermic reactions between gases and liquids.

In conformity with the invention the column, wherein the gases which have passed through the reaction chamber are washed, is used as a means for controlling the temperature.

This complementary part to be thus played by the washing column allows not only the exothermic reaction to be regulated, but also the size of this washing column to be reduced.

If in fact the hot zone of this regulating and washing column reaches the upper portion thereof, it is sufficient either to reduce the admission of gaseous fluid such as chlorine for instance or to allow the temperature of the reaction chamber to rise until a more complete absorption of the introduced gas is obtained.

In practice, the invention is executed by providing the washing column either with thermometers allowing manual adjustment or better still with thermostats which provide an automatic adjustment of the feed or of the temperature of reaction.

A second object of the invention consists in facilitating a reaction in a column substantially filled with a body of a reaction liquid. The use of such an apparatus is known and is suitable for laboratory purposes. On a larger scale, the

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liquid-filled column presents certain difficulties from the point of view of transfer of heat. If a tubular reactor is used, there arises a difficulty in uniformly distributing the gas throughout the cross-section of the reactor. Moreover in the presence of chlorine and hydrochloric acid or of any corrosive medium of the same kind, the parts of the apparatus in contact with the bath reacting materials should be coated with lead. Such a lead coating is very difficult to apply inside tubes having a substantial length.

Applicant has eliminated these difficulties by providing cooling unit consisting of an outer tube having a closed end containing a vaporizable liquid and an inner tube within the outer tube for conducting the vaporizable liquid to the closed end of the outer tube. These cooling units are hereinafter referred to as cooling plugs. The heat absorbed from the reacting material produces inside the cooling plugs the boiling and evaporation of a suitable thermostatic liquid. Such plugs act therefore like vaporising tubes.

Certain characteristic features of the invention are illustrated in Figs. 1 and 2 of accompanying drawings which show respectively:

In Fig. 1, a diagram showing the application of the invention to the chlorination of a liquid such as gas oil.

In Fig. 2, a perspective view of the upper end of a cooling and vaporising plug.

In Figs. 3 to 5, further details of the apparatus.

Reverting to Fig. 1, the exothermic reaction in the example of chlorination of gas oil is executed in a cylindrical chamber 1. The chlorine admitted through a pipe 2 at the lower end of this chamber is injected therein through a number of porous plates 3 of which only one has been illustrated. The gas thus subdivided passes through the liquid 4 and produces by reacting with the latter an evolution of heat. The reaction should be executed at constant temperature, say 130° C. or thereabouts, and the heat is removed by a certain number of cooling plugs 5 of which only one has been illustrated in Fig. 1.

The heat absorbed produces inside the plug the boiling and vaporising of a thermostatic liquid such as toluene 6. The vapors produced are condensed in a reflux condenser shown diagrammatically at 7.

The condensed liquid and the liquid carried along by the gases fall back on an upper annular plate 8 and pass through openings 9 (Fig. 1) into

central tubes 10 which lead them back to the base of each of the plugs 5.

This transfer of liquid carried by the annular plate 8 towards the inside of the tube 10 forms one of the characteristic features of the invention.

A particular form of execution of this transfer is shown in Fig. 2.

The transfer is executed by means of a series of V-shaped overflow weirs 11, the number of which is three for instance, welded at 120° from one another, between the vaporising pipe 5 and the central collecting tube 10. These overflow weirs serve also as stays providing a rigid connection between the outer pipe 5 and the inner pipe 10.

The central collecting tubes preferably and with deflectors 12 which return downwardly the major part of the liquid carried along during vaporising.

The upper annular plate 8, the lower plate 14 carrying the porous plates 3 and the plugs 5 are preferably made of lead coated steel.

The plugs 5 are removable and are secured to the upper annular plate 8; they are held by stay plates not shown.

The hydrochloric vapors and the chlorine passing out of the reaction chamber 1 pass through the duct 15 into the small regulating column 16 inside which they are washed with gas oil entering from 17 and passing through the duct 18 into the reaction chamber 1.

Thermometers 19 located at various heights and of which two only have been illustrated, allow the control at each moment of the level of the hot zone. These thermometers may without departing from the scope of the present invention be replaced by thermostats acting on a cock or valve controlling the admission of gas oil at 17 or that of chlorine, or else said thermostats may regulate the condensation by regulating flow of the cooling fluid.

The chlorinated gas oil is removed through the duct 20 while the hydrochloric vapors are removed at 21 from the small regulating and washing column.

The foregoing description relates to apparatus for carrying out exothermic reactions between a liquid and a gas. Essentially the same apparatus may be used for carrying out reactions involving solid catalysts.

To facilitate the introduction of the catalyst, the apparatus is mounted to pivot about a horizontal axis which permits the apparatus to be rocked after it has been disconnected. After loading, the position corresponding to normal operation is resumed.

The catalyst mass is placed in the space between the cooling plugs and the body of the apparatus so as to form a single layer throughout the height of the apparatus or else a plurality of layers by means of intermediary grates if it is desired to avoid layers having too great a height.

The supporting grates may play the part of dampers or baffle plates for improving the contacting conditions between the fluid and the catalyst. It is sufficient to this end to provide perforations throughout only part of said grates.

Fig. 3, which corresponds to Fig. 1 with the same conventional simplification, shows the rocking axis 22 and the catalyst 23 heaped on the grates 24.

The rocking of the apparatus may be undesirable in the case of a brittle catalyst. Applicant has therefore disclosed a modification allowing the apparatus to be filled in its operative position, while retaining the possibility of rocking for emptying the exhausted catalyst.

This modification is illustrated in Fig. 4.

The reaction chamber essentially comprises a tubular member, cylindrical or not, 25, closed at its lower end by a plate 26 and at its upper end by a removable cover 27. The plate 26 is provided with openings in which it carries a series of plugs 28 closed at their upper ends 29 and open at their lower ends into a chamber 30. These plugs contain inner concentric tubes 31 opening through their upper end 32 inside the corresponding plug and secured at their lower end in openings in a plate 33 so as to communicate on the lower side of the latter with a chamber 34 connected through a pipe 35 with a reservoir 36. This reservoir, the diameter of which is smaller than that of the reaction chamber, contains at its upper end a water circulating condenser 37 and at its lower end a heat generating apparatus 38, illustrated diagrammatically each in the form of a coil. A thermostat 39 acts on the output of a pump 40 the duty of which is to recycle the thermostatic liquid through the pipes 41 and 42.

The catalytic space is bounded by the body or tubular member 25, the plate 26, the cover 27 and the plugs 28. The catalyst is heaped inside said space and forms either a single layer or else if necessary a plurality of layers on intermediary grates 43. The reacting vapors or liquids enter the catalytic chamber through the pipe 44 and pass out of the same through the duct 45. The reaction heat vaporises part of the thermostatic liquid contained in the plugs. This production of vapors produces a more or less intense circulation by reason of the airlift or sweeping phenomenon. The suspension thus produced is collected at 32 by the tubes 31 and is led to the reservoir 36 wherein the vapor produced is condensed on the worm 37: this condensate together with the liquid phase of the suspension falls back and is drawn into the pump 40 for recycling purposes. The rate of evaporation and consequently the intensity of superheating depends on the height of liquid in vaporising plugs 28: by varying the rate at which pump 40 withdraws liquid from the reservoir 36, it is possible to modify at will the supply of liquid and therefore the height thereof inside the plugs 28. If necessary, it is possible to produce inside said plugs a forced circulation of the thermostatic liquids.

It is possible to provide for a preliminary heating of the reacting fluid without any extra expense by using the reaction heat. It is sufficient to this end to provide at the upper end of the chamber a zone A, with or without catalyst in the vertical passage of which the plugs 28 are (or may not be) provided with fins 46 preferably transverse (Fig. 5). The reacting fluids enter cold at 44 and are heated through contact with the plugs 28, while the thermostatic fluid cools or condenses inside said zone. The height of the zone A is designed in a manner such that the product to be treated may be brought to a suitable temperature when it has reached the zone B or catalysing zone.

For starting, the apparatus being cold, it is necessary to first bring the catalytic mass to reaction temperature. To this end, the by-pass 46—47 is first opened and, the pump 40 being stopped, the thermostatic liquid is caused to boil through the action of the heat generating means 38: the vapors produced follow a path opposed to that described hereinabove and are led by the tubes 31 to the upper end of the plug 28 and con-

densed inside said plugs. The condensate returns through 42, 47, 46 to the reservoir 36.

If the thermostatic liquid does not require vaporisation for heating the reaction chamber, it is possible to use for the above purpose the normal circuit by making the liquid previously heated by the generator 38 circulate under the action of the pump 49.

It should be noted that the above disclosure as to the possibilities of heating for starting the exothermic reaction remains applicable to any reaction requiring a continuous input of heat. In this case, the heat required by the reaction is produced, not only for the starting but also throughout the duration of the reaction by the generator 38.

The arrangement described provides therefor the following advantages.

(*a*) It allows the execution of either endothermic or exothermic reactions;

(*b*) It allows the use as a catalytic chamber of the inter-tubular space as, by reason of the absence of any upper tube sheet the loading and unloading of the catalyst may be executed through any means known per se such as rocking, removal of the supporting grates etc.

(*c*) It allows heaping the catalyst throughout a height as considerable as may be desired by reason of the presence of the intermediary supporting grates; for a predetermined catalytic volume, the diameter may be reduced, which is important for apparatuses operating under pressure.

(*d*) It provides for the maintenance of a more nearly uniform temperature by reason of the use of the vaporising, condensation or forced circulation of a given fluid.

(*e*) It allows an adjustment of the heat transfer rate and therefor to a certain extent of the reaction temperature in a particularly simple manner consisting in the adjustment of the speed of circulation of the cooling or heating fluid.

(*f*) It allows recovering in situ whenever desired the reaction heat with a view to the preliminary heating of the charge.

(*g*) The mounting of the apparatus is made in a particularly easy manner by reason of the omission of the upper tube sheet; the tubes are free and may extend without any impairment of the solidity of the apparatus.

(*h*) By reason of the simplified construction of the apparatus, it is possible without any difficulty to use the thermostatic fluid under a high pressure. The same thermostatic liquid may be suitable throughout a comparatively wide range of temperature by making its pressure vary inside the chamber by control of flow of water inside the condenser 37. This pressure will be adjusted advantageously by acting on the throughput of water by means of a manostat 48 through the agency of an automatic valve 49.

According to another further characteristic feature of the invention, the small column 16 serving for washing the gases and for regulating the reaction, may also serve for introducing the catalyst into the reacting medium.

When the catalyst used is not soluble or is difficult to dissolve in the reacting substances and if for instance it is desired to proceed with a chlorination in presence of ferric chloride, difficulties will be met with when it is attempted to distribute in a homogeneous manner the catalyst in the hydrocarbon to be chlorinated.

It will be then advantageous to provide the small column 16 with iron shavings or turnings. Whereas iron is not attacked by hydrochloric acid in an anhydrous medium, it will be noted that there forms in the presence of hydrocarbons and of the small amounts of chlorine passing into the column, a compound substance which is carried along by the product to be chlorinated inside the reaction chamber.

It is moreover possible to adjust the introduction of the catalyst by using two small columns of which one will serve for regulating and washing purposes, while the other serves for the introduction of the catalyst and is alone filled with iron shavings. Only a fraction of the products passing out of the reaction chamber is caused to pass through the latter small column so as to limit, if required, the attack on the iron shavings.

What I claim is:

1. Apparatus for carrying out an exothermic reaction at substantially constant temperature comprising in combination, a vertical elongated casing; a partition dividing said casing into a reaction chamber adapted to contain a reaction mixture and a relatively small condensing chamber near the top of said casing; at least one pair of concentric tubes mounted in said casing, communicating at one of their ends with said condensing chamber, and extending downwardly through said partition into said reaction chamber; the outer of said tubes having a closed lower end within said reaction chamber and cooperating with the inner tube to define an annular space adapted to contain a cooling liquid in heat exchange relation with said reaction mixture within said reaction chamber, whereby the heat of reaction of said reaction mixture vaporizes said cooling liquid to cause vapors thereof to pass through said annular space into said condensing chamber, a refrigerated condensing unit mounted in said condensing chamber to condense vapors of said cooling liquid entering said condensing chamber, and at least one conduit interconnecting the exterior of said outer tube and the interior of said inner tube for conducting condensed cooling liquid from said condensing chamber to said inner tube and thence to the bottom of said outer tube within said reaction chamber.

2. Apparatus according to claim 1 and wherein said condensing unit is aligned with said inner tube and the upper end of said inner tube is flared outwardly beyond the periphery of said outer tube to collect condensate dropping from said condensing unit and prevent it from entering said annular space.

3. Apparatus according to claim 1 and wherein said conduit consists of a pair of members extending between said inner and outer tube and forming a V-shaped opening providing a weir to regulate flow of condensate from said condensing chamber into said inner tube.

4. Apparatus according to claim 1 including two or more of said conduits equally spaced around said tube, said conduits providing means whereby said inner tube is supported on said outer tube.

5. Apparatus according to claim 1 and wherein said casing is mounted near its center on pivots to permit rocking of said casing about a horizontal axis.

6. Apparatus according to claim 1 and wherein said reaction chamber is provided with a series of vertically spaced grates for supporting layers of catalysts.

LOUIS MASSIOT.

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Certificate of Correction

Patent No. 2,537,472 January 9, 1951

LOUIS MASSIOT

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 26, after the word "chlorine" insert , *if present*,; column 4, line 36, for "airlift or sweeping" read "*airlift*" or "*sweeping*";

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 26th day of June, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.