

UNITED STATES PATENT OFFICE

2,031,179

METHOD OF EVAPORATING AQUEOUS
HYDROCHLORIC ACID

Klaus Raschig, Ludwigshafen-on-the-Rhine, Germany, assignor to Dr. F. Raschig G. m. b. H.,
Ludwigshafen-on-the-Rhine, Germany

No Drawing. Application November 22, 1934,
Serial No. 754,280. In Germany November 27,
1933

9 Claims. (Cl. 23—154)

The present invention relates to the evaporation of aqueous hydrochloric acid for the purpose of purification, distillation, working up and similar processes which are to be carried out in an ordinary evaporating vessel made of a technically usual material.

As is known aqueous hydrochloric acid, especially at higher temperatures, attacks the metals usually employed in the construction of apparatus such for example as iron, copper and the like, extraordinarily strongly so that it was not possible hitherto to evaporate aqueous hydrochloric acid from evaporating vessels which are made of such metals.

It has therefore been proposed to make evaporation vessels for aqueous hydrochloric acid from metals which are resistant against boiling hydrochloric acid and for this tungsten, tantalum, antimony alloys and the like have been used. Apparatus made from such materials are very expensive, however, on the one hand because of the high price of the metals mentioned and on the other hand on account of the difficulty in working them, which is to be ascribed to their very high melting point and to their great brittleness. Apparatus of tungsten, tantalum and so forth are therefore used in practice only to a limited extent, and the object of the present invention is to make possible the evaporation of aqueous hydrochloric acid in evaporation vessels made of relatively cheap and easily workable metals.

In order to overcome the difficulties which the evaporation of aqueous hydrochloric acid presents, it has also been proposed to carry out the evaporation in apparatus made of iron by introducing aqueous hydrochloric acid in a state of very fine sub-division into a stream of superheated hydrochloric acid vapour for example by means of atomizing nozzles and the like. Normal evaporating apparatus in which the heat supplied is transferred directly to the material to be evaporated, cannot be used, however, for carrying out this process, but rather, special apparatus is necessary in which instead of direct heating for example with steam, large heat transfer surfaces heated by fire gases are employed. Moreover special fans are required for moving the superheated hydrochloric acid vapour. Apart from these disadvantages, the use of direct firing which is required for heating the heat transfer surfaces, demands constant supervision of the apparatus by a special staff which renders the process expensive. Moreover direct firing cannot neces-

sarily be carried out in every factory on account of the danger of fire associated with it.

By reason of the foregoing remarks it is to be seen that an apparatus suitable for evaporating aqueous hydrochloric acid must fulfil the following conditions: it must on the one hand be made of a technically easily accessible and workable metal and it must moreover be of normal kind of construction and so must be capable of being heated with steam.

In a very surprising manner it has been found that copper, of which it is known that it does not resist attack by aqueous hydrochloric acid, can be employed in a most satisfactory manner as a material for evaporating vessels for hydrochloric acid, if the evaporation of the aqueous hydrochloric acid from such reaction vessels is carried out in the presence of phosphoric acid.

In this connection it has been found that even a small addition of phosphoric acid to the aqueous hydrochloric acid considerably reduces the attack of boiling hydrochloric acid. On the other hand copper itself in the presence of highly concentrated phosphoric acid at boiling temperature is not perceptibly attacked by hydrochloric acid. The cause of this protective action exerted by the phosphoric acid is not known. Possibly it may be associated with the occurrence of a black coating firmly adhering to the copper wall which forms after a short period of operation.

It has previously been proposed to mix aqueous hydrochloric acid with an auxiliary liquid such as sulphuric acid, calcium chloride, magnesium chloride or zinc chloride solutions and the like and to evaporate it out of these solutions. In this process however, copper was not used as a material for the apparatus which is to be explained by the fact that none of these liquids is capable of preventing the attack of aqueous hydrochloric acid on copper.

By reason of the entirely unexpected fact that copper in the presence of concentrated phosphoric acid behaves quite differently with respect to aqueous hydrochloric acid from the way it behaves in the absence of phosphoric acid, it is now possible to manufacture evaporating apparatus for aqueous hydrochloric acid solutions from an easily accessible and conveniently workable material. In particular it is now possible to construct such apparatus in the form usual for evaporation plant and so to employ the usual kind of heating such for example as steam heating, by means of normal heating tubes or heating coils. In this connection also the good heat conductivity of copper acts favourably. It is

obviously also possible to employ other kinds of heating such for example as electrical heating or the like.

Since, when using large evaporating apparatus, sometimes on account of insufficient heating, a condensation of aqueous hydrochloric acid may take place in the upper parts of the apparatus which are not covered by liquid and this might very easily lead to a corrosion of the parts of the apparatus consisting of copper which are not subject to the protecting action of the phosphoric acid, it is recommended when using large evaporating apparatus that those parts of the apparatus which are not washed over by the phosphoric acid should be heated by means of additional heating to such a temperature that no condensation of aqueous hydrochloric acid can take place. Hydrochloric acid vapour does not indeed perceptibly attack copper. The heating is advantageously effected by heating the upper part of the evaporating apparatus by means of steam tubes welded upon or fitted on, which tubes are well heat insulated on the outside. Preferably a temperature is maintained which lies above the temperature of condensation of the hydrochloric acid, that is, at normal pressure, above 110° C.

In case it is desired to evaporate aqueous hydrochloric acid which contains small quantities of sulphuric acid, in an apparatus consisting of copper, it is recommended to add to the phosphoric acid salts of metals soluble in excess phosphoric acid which with the sulphuric acid form deposits difficultly soluble or insoluble in phosphoric acid. By the precipitation of the sulphuric acid the concentration of the latter in the evaporating apparatus and consequent corroding actions are avoided. In particular soluble alkaline earth metal salts such for example as barium or calcium chloride and the like are suitable for precipitating the sulphuric acid.

Since the precipitated alkaline earth metal sulphate forms a suspension in the phosphoric acid which suspension together with the copper chloride resulting from a certain not entirely avoidable corrosion of the apparatus, and likewise forming a suspension in the phosphoric acid, and other impurities contained in the hydrochloric acid, would gradually render the phosphoric acid unsuitable for carrying out the process, it is recommended to remove the deposit formed in the phosphoric acid in a suitable manner, for example by filtration or centrifuging, and this can be effected periodically or also continuously during the operation, by continuous removal of a small quantity of phosphoric acid which is returned after having been cleansed.

The evaporation can be carried out in various ways. For example the process may be a discontinuous one, in which a mixture of phosphoric acid and hydrochloric acid is first introduced into the still of the evaporating apparatus and then subjected to evaporation. Preferably, however, a continuous method is employed in which concentrated phosphoric acid, which may if desired contain some barium chloride, is introduced into the evaporating vessel, this is then heated and then with continued vigorous heating the aqueous hydrochloric acid, preferably prewarmed, is caused to flow into the hot phosphoric acid. The concentration of the phosphoric acid employed can be suitably selected within wide limits, with corresponding regulation of the heating and corresponding regulation of the quantity of hydrochloric acid flowing in, for the final concentration adjusts itself automatically in the

course of the evaporation in dependence on the heating temperature employed.

In the following the manner of carrying out the new process and the apparatus employed will be explained with reference to one embodiment by way of example and it is expressly to be observed that the present invention is not limited to the proportions and dimensions, temperatures and the like mentioned, but that modifications such as would occur to anyone skilled in the art may of course be made.

In the embodiment to be described the actual evaporation chamber consists of a horizontal cylindrical vessel of copper having a length of about 3.5 metres and a diameter of about 1.4 metres. The bottom of the vessel is provided with steam tubes which have an external diameter of about 50 mm. and a length of about 80 metres. On the outside it is provided with good heat insulation. The upper parts of the evaporating chamber which are not covered or washed over by the liquid are provided on the outside with iron steam tubes which with a view to reasonable transfer of heat lie directly on the copper wall. As has already been explained they are intended to heat the upper part of the boiler in such manner that the condensation of hydrochloric acid vapour is prevented. The upper part of the evaporating vessel together with the heating tubes are likewise heat insulated. The evaporating vessel is half filled with phosphoric acid of about 80% to which are added about 0.5 to 2% of barium chloride. Since during the operation the strength of the acid is adjustable by variation of the quantity of heating steam or the quantity of hydrochloric acid flowing in as may be desired, it is also possible to start with a weaker or stronger acid. The contents of the boiler are then heated to about 150° centigrade after which with further heating about 1000 kilos of 17% hydrochloric acid are allowed to flow hourly into the phosphoric acid preferably distributed at different places. After attaining the condition of equilibrium the vapours drawn off show the same composition as the hydrochloric acid added. During the evaporation about 50 litres of phosphoric acid are continuously drawn out of the evaporator hourly by means of a small pump and forced through a filter consisting of fine copper wire mesh which separates the impurities contained in the phosphoric acid. The filtered phosphoric acid flows back continuously to the evaporator. With the quantity of phosphoric acid given the evaporation of aqueous hydrochloric acid can be carried out in a continuous manner for a very long time without any renewal of the phosphoric acid being necessary.

What I claim is:

1. A method evaporating aqueous hydrochloric acid consisting in carrying out the evaporation in an apparatus made of copper in the presence of phosphoric acid.

2. A method of evaporating aqueous hydrochloric acid consisting in carrying out the evaporation in an apparatus made of copper in the presence of phosphoric acid of over 60%.

3. A method of evaporating aqueous hydrochloric acid consisting in carrying out the evaporation in an apparatus made of copper in the presence of phosphoric acid the parts of the apparatus not touched by the phosphoric acid being heated to a temperature lying above the temperature of condensation for aqueous hydrochloric acid.

4. A method of evaporating aqueous hydrochloric acid containing sulfuric and as an im-

purity consisting in carrying out the evaporation in an apparatus made of copper in the presence of phosphoric acid to which salts of metals are added which are soluble in excess phosphoric acid and which form with sulphuric acid salts difficultly soluble in phosphoric acid.

5 5. A method of evaporating aqueous hydrochloric acid containing sulfuric acid as an impurity consisting in carrying out the evaporation in an apparatus made of copper in the presence of phosphoric acid to which alkaline earth metal salts which are soluble in excess phosphoric acid are added.

10 6. A method of evaporating aqueous hydrochloric acid containing sulfuric acid as an impurity consisting in carrying out the evaporation in an apparatus made of copper in the presence of phosphoric acid to which alkaline earth metal chlorides are added.

15 7. A method of evaporating aqueous hydrochloric acid consisting in carrying out the evaporation in a continuous process in an apparatus made of copper in the presence of phosphoric acid.

8. A method of evaporating aqueous hydrochloric acid containing sulfuric acid as an impurity consisting in carrying out the evaporation in an apparatus made of copper in the presence of phosphoric acid to which are added salts of metals which are soluble in excess phosphoric acid and which with sulphuric acid form salts which are difficultly soluble in phosphoric acid the deposits which form and which are difficultly soluble in phosphoric acid being removed by filtration.

9. A method of evaporating aqueous hydrochloric acid containing sulfuric acid as an impurity consisting in carrying out the evaporation in an apparatus made of copper in the presence of phosphoric acid to which are added salts of metals which are soluble in excess phosphoric acid and which with sulphuric acid form salts which are difficultly soluble in phosphoric acid, the deposits which form and which are difficultly soluble in phosphoric acid being continuously removed by filtration.

KLAUS RASCHIG.

CERTIFICATE OF CORRECTION.

Patent No. 2,031,179.

February 18, 1936.

KLAUS RASCHIG.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 59, claim 1, after the word "method" insert of; and line 75, claim 4, for "and" read acid; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day June, A. D. 1936.

Seal)

Leslie Frazer
Acting Commissioner of Patents.