F. MEYER & H. KERSTEIN.

REDUCTION OF CHLORIDS.

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1,173,012. Patented Feb. 22, 1916.

Fig. 1.

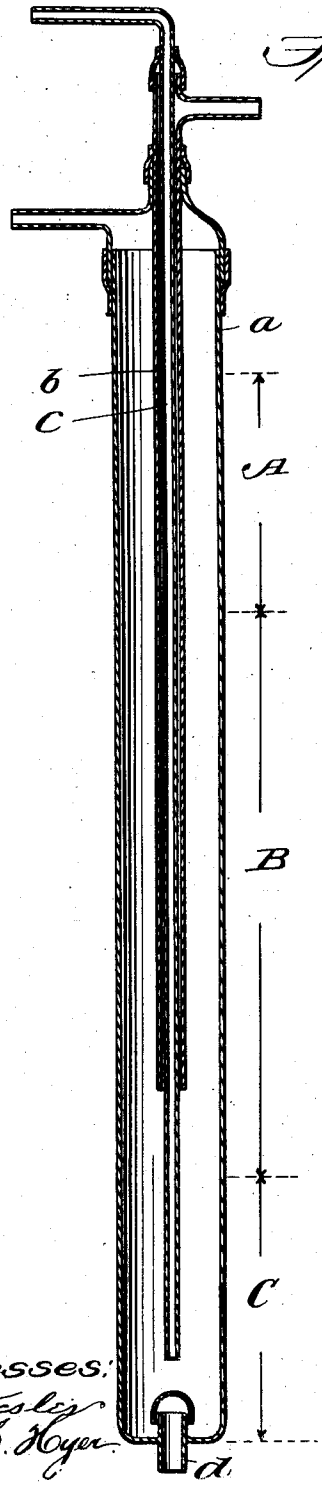
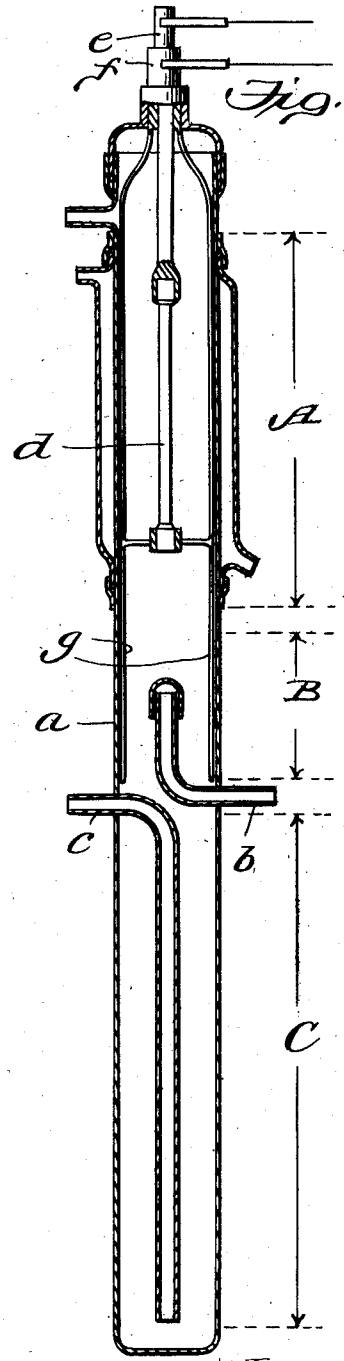


Fig. 2.



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REDUCTION OF CHLORIDS.

1,173,012. Specification of Letters Patent. Patented Feb. 22, 1916.

Application filed April 29, 1914. Serial No. 835,257.

To all whom it may concern:

Be it known that we, FRIEDRICH MEYER and HANS KERSTEIN, chemists, subjects of the German Emperor, both residing at Berlin, Germany, have invented certain new and useful Improvements Relating to the Reduction of Chlorids, of which the following is a specification.

The present invention relates to the reduction of anhydrous chlorids, such as the chlorids of tin and titanium. The reduction of such compounds by means of gases, especially with hydrogen, is quite new as regards tin, but not new in general. As a rule the compounds, if they are volatile, are exposed to high temperatures in mixture with hydrogen, either by conducting them through a heated tube, or by causing the flame of an electric arc to burn in the gas-mixture. Very frequently these processes only lead to the next stage of reduction. For instance tetra-chlorid of tin yields dichlorid of tin, but never tin, tetrachlorid of titanium yields trichlorid of titanium, but the reduction never extends to the dichlorid or to metallic titanium. If the next stage of reduction is the metallic element, for instance in the hitherto unknown reduction of tin-dichlorid to tin, these processes give a bad yield.

We have discovered, that when applying the principle of reverse or counter-currents in a special manner, surprising results may be obtained in the reduction of such compounds. In the process hereafter described the reduction may be stopped at any desired stage of reduction, or it may be carried out within a very simple apparatus in such a manner, that it leads from the starting material to the element, for instance from tetrachlorid of tin to tin, from tetrachlorid of titanium to titanium, directly and continuously, while the whole quantity of the starting material is utilized.

In dealing with a compound, such as the dichlorid of tin, which has only one non-volatile reduction stage, it is sufficient to perform the reduction in a vertical tube, to introduce dichlorid and hydrogen simultaneously into the lower end of the tube, while taking care that the dichlorid, which owing to equilibrium has not been reduced, flows back by gravity into the reducing chamber, or in case the volatile body sublimates, that the unreduced portion is caused to fall back by mechanical means. Still more important is the use of the principle of reverse currents in the case of chlorids, whose reductions take place in several stages, and where the usual reduction only leads to the next stage of reduction. If in this case the principle of reverse currents is required to afford an advantage besides the usual better utilization of the reducing agent, and if it is desired to insure, that the reduction proceeds further than usual, it is necessary, that the product or products of reduction move toward the relatively pure reducing agent, that is the reducing agent, which is free from the starting material.

The accompanying diagrammatic drawing serves to elucidate the process in the case of the two chlorids of tin and of titanium, which have been repeatedly mentioned above.

Figure 1 indicates a vertical section of an apparatus suitable for the reduction of tin-chlorids and Fig. 2 a vertical section of an apparatus suitable for the reduction of titanium chlorids.

If it is desired to reduce dichlorid of tin to tin, which corresponds to one stage of reduction, we employ the apparatus shown by Fig. 1, but omitting the tube *b*. Hydrogen is introduced through the tube *c* and at the same time through the same tube dichlorid in a molten condition. The zone A and B is then heated to 250° C. (the melting point of the dichlorid) and zone C to a temperature between 600 and 1,000° C. The dichlorid evaporates in this zone (also below its boiling point) and is partially (viz: in accordance with the equilibrium corresponding to the temperature), reduced to tin, which collects at the lower end of the tube and flows off through *d*. The hydrochloric acid and the excess of hydrogen escape at the top of the tube. The dichlorid distilling off condenses in the zones B and A and flows back to C, where finally it is completely reduced to tin.

If the process is carried out in the same manner, except that through *c* tetrachlorid of tin instead of dichlorid is introduced simultaneously with the hydrogen, the reduction takes place through only one stage, in spite of the reverse current principle, and dichlorid may be drawn off at *d*, but in that

case the temperature of C must not be raised above 600° C. For the reduction of the tetrachlorid to tin the tube *b* must be also employed. In that case vapor of tin-tetrachlorid is admitted through *b* and pure hydrogen through *c*. Zone C is again heated to a temperature ranging between 600 and about 1000° C., zone B to a temperature of about 500 to 600° C. and zone A to 250° C. The reduction takes place so that at the lower extremity of *b* and in zone B dichlorid is formed, which condenses partly in zone B and partly in zone A and descends to C. There it is reduced to tin, which flows off through *d*. Any dichlorid that may have been volatilized, returns through zones B and A to C, while hydrochloric acid and excess of hydrogen escape from the apparatus at the top. The utility of the use of the reverse current principle in this form is apparent also from the second example, viz: its application to the reduction of titanic tetrachlorid.

The reduction of titanium tetrachlorid to trichlorid succeeds quantitatively when the process given by St. Claire-Deville, or the so-called Deville tube, is employed. Its effect is based upon the quick chilling of the product of the reacting mixture previously highly heated. The most favorable construction, especially for the present case, consists of two concentric tubes with the reaction compound therebetween, the one tube being maintained at a high temperature of about 900° to 1000° C., and the other tube being cooled down to a low temperature. Hydrogen, without being itself consumed, acts upon two molecules of trichlorid under formation of one molecule of dichlorid and one molecule of tetrachlorid. The reaction that takes place is as follows:

$$2TiCl_3 + H_2 = 2TiCl_2 + 2HCl$$
$$2TiCl_3 + 2HCl = 2TiCl_4 + H_2$$
$$\overline{4TiCl_3 = 2TiCl_2 + 2TiCl_4}$$

Analogous is the action of hydrogen upon the dichlorid as follows:

$$TiCl_2 + H_2 = Ti + 2HCl$$
$$TiCl_2 + 2HCl = TiCl_4 + H_2$$
$$\overline{2TiCl_2 = Ti + TiCl_4}$$

The whole reduction of titanium tetrachlorid into titanium takes place according to the equation as follows:

$$4TiCl_4 + XH_2 = Ti + 3TiCl_4 + 4HCl + (X-2)H_2$$

with a yield of but 25%. If, however, the reduction is performed by the above described process, the conversion may be effected with a quantitative yield. The apparatus used for this purpose is illustrated by Fig. 2. Titanic tetrachlorid in the form of vapor is introduced into the apparatus through tube *b* and pure hydrogen through tube *c*. If it is desired to reduce only to dichlorid, zone C is kept at a temperature below 700° C., for reducing down to metallic titanium, a temperature of 800 to 900° C. is employed. Zone B must be kept at about 500° C., zone A is formed by what is known as a Deville tube. In this connection it should be observed, that *d* indicates an internal heating device, for instance a carbon rod rendered incandescent by electrical means. *g* are the lower leading-in wires for the heating body, which simultaneously serve as scrapers, for detaching from the cold wall of the tube *a* the trichlorid settling on the same, so that it drops down to C by gravity. Current is supplied to the apparatus at *e* and *f* through a revoluble cap mounted on the tube *a*. The scrapers *g* extend into the zone B having a temperature of 500° C.

In zone A complete conversion of the tetrachlorid into trichlorid takes place. The trichlorid drops through B to C, where it is converted into titanium or titanium chlorid and tetrachlorid. The latter will, however, not escape, but will be re-converted at B into trichlorid. A partial sublimation of dichlorid also takes place, which is held back in zone B and caused to descend to C by the scrapers. Finally the lower part of C will be filled with titanium, while only hydrochloric acid and excess of hydrogen escape at the top, without any waste of titanium chlorid taking place. The process is applicable to all chlorids, where the starting material is a substance capable of being evaporated or sublimated, or where it yields such a substance as an intermediate product in the reaction.

The present process seems to be specially valuable for utilizing the tetrachlorid of tin obtained in the removal of tin from tinplate, and for obtaining certain metals, which otherwise are difficult to obtain in a pure condition, such as the titanium. The gaseous reducing agent may be, for instance a mixture of carbonic oxid and aqueous vapor, instead of hydrogen, and the reduction may take place with the aid of pressure.

What we claim is:—

1. The process for the reduction by means of reducing gases of anhydrous chlorids yielding volatile intermediate products during the reduction, which consists in performing the reduction by using the principle of reverse currents, in such a manner, that in case there exist several stages of reduction, the products of the reduction are caused to move toward the pure reducing material, free from the starting material, substantially as described.

2. The process for reducing anhydrous volatile chlorids by means of reducing gases, which consists in effecting the reduc-

tion by using the principle of reverse currents in such a manner, that the products of the reduction travel toward the pure reducing material free from starting material, substantially as described.

3. The process of manufacturing tin, consisting in reducing dichlorid of tin in such manner that the product of reduction is caused to move toward the reducing material, the dichlorid, which, owing to the equilibrium has not been reduced, flowing back by gravity, substantially as described.

In testimony whereof we have hereunto set our hands in presence of two subscribing witnesses.

DR. FRIEDRICH MEYER.
HANS KERSTEIN.

Witnesses:
HENRY HASPER,
WOLDEMAR HAUPT.