UNITED STATES PATENT OFFICE.

HANS VON SCHÜTZ, OF WETZLAR, GERMANY.

PROCESS OF DETINNING TIN-PLATE BY MEANS OF CHLORIN.

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To all whom it may concern:

Be it known that I, HANS VON SCHÜTZ, merchant and metallurgist, citizen of Germany, subject of the King of Prussia and Emperor of Germany, residing at Philosophenweg 3, Wetzlar, in the Kingdom of Prussia and Empire of Germany, have invented certain new and useful Improvements in Processes for Detinning Tin-Plate by Means of Chlorin, of which the following is a full, clear, and exact description.

The treatment of tin plate material (tin plate waste and the like) with chlorin serves a double purpose, namely the obtaining of iron as free as possible from tin for the purpose of smelting, and a yield of tin, the latter in the form of the purest possible anhydrous stannic chlorid.

In the application of the process as known, it has not hitherto been possible to avoid grave defects which arose mainly owing to the fact that the moisture adhering more or less, and also imparted by the atmospheric air, to the material to be detinned, caused the formation of solid, *i. e.* hydrated stannic chlorid. The result of this is that in the apparatus crusts of basic tin tetrachlorid are deposited which attack the iron or cause the formation of ferric chlorid—which then enters as an impurity into the chloritic tin—and derange various pumping and ventilator mechanisms used in the process of chlorination, causing an abnormal increase in the power consumption of this machinery and indeed bringing the machines to a standstill after a short time of working and in addition narrowing or choking up the pipes. It is clear in short that this epresents a source of constant derangement in working and also the cause of large wear and tear. Finally the stannic chlorid crusts deposited in the apparatus are not utilizable for the market, and therefore represent a permanent loss of product. A series of further defects is inherent in the use of high chlorination pressure. The pressure required for forcing the chlorin into the material for de-tinning promotes a highly injurious,—because not uniform or not uniformly distributed—temperature of chlorination, and at the same time increases the difficulty of getting a perfect yield of liquid stannic chlorid. This is the case in a higher degree in proportion as the raw material is more powerfully compressed. The more powerful the compression the higher the pressure of the chlorin must be, and with the more desnity will the fluid be retained inside the material. Finally the tin plate cuttings, if after de-tinning they are subjected to special washing, so greedily absorb the washing liquid and retain it with such energy that railway trucks loaded with washed bundles show considerable leakage after running for hours. By this means not only is the rusting of the de-tinned cuttings—precisely the thing which it is desirable to avoid as far as possible—promoted, but injury is done to the trucks and other means used for transport by corrosion of the iron parts, decay of the wood, and the like, besides which the water retained increases the weight of the goods. All these defects are intended to be avoided by the present process and its methods of application.

The inventive idea is based in the first place on the avoidance of the use of all mechanical devices in the course of the chlorination process. Further, the raw material to be de-tinned is first of all completely dried before being chlorined. The chlorination process itself is carried out, not by forcing the chlorin into the substance under excessive pressure but by suction, a vacuum having been carefully produced beforehand in the raw material.

The present process is first of all characterized by the fact that the tin plate material placed in a closed chamber is deprived of all moisture, and is, before and during chlorination, cooled by the natural cooling action of gases expanding from the condensed or liquefied state.

After the removal of moisture and preliminary cooling of the material, the strongest possible vacuum is produced in the chlorination chamber. The chlorin is then vaporized from the liquid state, cold being thus developed, and is mixed in the gaseous state with cold air—which may likewise expand from the liquid state—and is let into the chlorination chamber, all pressure being avoided as far as possible. The chlorin and the air may suitably be introduced into the vacuum chamber through several nozzles distributed uniformly over the material in such a way that the mixture is immediately and uniformly distributed over the entire contents of the receptacle or chamber. The action of the chlorin on the tin therefore

takes place quite uniformly everywhere which results in a like uniform distribution of the heat of combustion. The growing heat of combustion is again counteracted by the coldness of the automatically circulating gas mixture. In proportion as the tin absorbs the chlorin there is an automatic further indraft of chlorin and air, the coldness of which continually cools the gradually warming mass. In this operation the mass of tin plate itself has a moderating effect. The chlorination is complete if the entering gases have finally destroyed the vacuum in the chlorination chamber and a condition of equilibrium has set in. It must however be observed that during the entire process no noticeable increase of pressure above the atmospheric occurs.

The gases passing through the material carry with them the liquid stannic chlorid in formation and in this way effectively assist its liberation. The avoidance of high pressure in admitting the chlorin is further aimed at obviating any excess of chlorin in the stannic chlorid, which would be highly detrimental to the later use of this product.

The stannic chlorid formed is itself drawn off from time to time in a suitable way.

Only after completion of the entire chlorination process is there a short contact of the chlorin with mechanical devices, the last residues of it being sucked out of the chlorination chamber by means of a pump and conveyed into a second chamber, where these chlorin residues are deposited in some suitable way, for instance in water.

A gentle raising of the de-tinned material to a dull glow by heating finally effects its rapid and complete liberation from the very last chemical residues, and at the same time results in the coating of the de-tinned stuff with an oxid layer serving as a rust protector.

As receptacles in which to carry out the chlorination, chambers in the style of coke furnaces are contemplated, in which the material to be detinned is placed in bundles, or better still, in a block filling up the entire chamber. In using such blocks the final work will consist in cutting them into suitable pieces immediately after heating. The adoption of these large blocks has for its object to give the material a uniformly solid form without any spaces, by means of a single mechanical operation, thus allowing of rapid charge and uniform chlorination without special intermediate receptacles being required.

The process thus described may then be subjected to two further modifications:— one of which consists in the special method of drying the tin plate-goods prior to subjecting them to the chlorin process and the second improvement deals with the removal of the last remnants of the tin tetrachlorid still adhering to the de-tinned tin plate, by means of a special washing process. The novelty of the drying process lies in the fact that the drying of the tin plate takes place in the chlorination chamber itself. The chamber is for this purpose subjected to heating, direct or indirect; the latter may be from without, or by means of heating coils arranged in the chamber, or finally the drying may be effected by forcing hot air, waste gases, and the like, through the tin plate material to be treated. In this way the material for chlorin treatment is sufficiently prepared and effectively dried; after this the de-tinning process proper takes place in the way before described, whereupon now, for the purpose of completely removing the last residues of the tin tetrachlorid still adhering to the de-tinned plate, the latter is subjected to a special washing process in the chlorination chamber itself. This washing process is carried out in the chlorination chamber by submerging the de-tinned material in water once or more, or by treating the tin plate bundles for a certain length of time by means of a current of water flowing through. A further advantage in this washing process to be carried out in the chlorination chamber lies in the fact that the latter chamber is itself cleaned by the washing process. Again in the same chlorination chamber there finally takes place the drying of the de-tinned and washed material inasmuch as the chamber is subjected to direct or indirect heating, or hot air, waste gases, and the like, are forced through the washed material similarly as in the above described preliminary drying process. Another advantage of the subsequent drying of the de-tinned and washed material in the chlorin chamber itself, consists therein that by this means the chamber is itself also dried and is ready for charging again immediately after emptying. After washing and drying the further treatment of the completely de-tinned plate takes place, whereby these plates are compressed into the large blocks described.

What I claim is:

1. The process which consists in subjecting tin-bearing material to the action of chlorin gas, the gas being below normal temperatures.

2. The process which consists in placing the tin-bearing material in a closed chamber, producing a vacuum therein and allowing chlorin gas to expand from the condensed or liquefied state into such chamber.

3. The process which consists in completely drying tin-bearing material and then subjecting it to the action of chlorin gas, the gas being below normal temperatures.

4. The process which consists in subjecting tin-bearing material to the action of

chlorin cooled below normal temperature to remove the tin, and then heating the tin material.

5. The process which consists in placing tin-bearing material in a closed chamber, subjecting the material in said chamber to heat to dry the same, and then subjecting the material in said chamber to the action of chlorin cooled below normal temperature.

6. The process which consists in placing tin-bearing material in a closed chamber, subjecting the material in said chamber to heat to dry the same, then subjecting the material in said chamber to the action of chlorin cooled below normal temperature, and removing the tin tetrachlorid from said chamber.

7. The process which consists in placing tin-bearing material in a closed chamber, subjecting the material in said chamber to heat to dry the same, then subjecting the material in said chamber to the action of chlorin cooled below normal temperature, then washing the material to remove the tin tetrachlorid, and subsequently drying the same.

8. The process of treating tin-bearing material which consists in washing, drying and cooling such material and then subjecting it in a closed chamber to the action of chlorin gas cooled below normal temperature.

9. The process which consists in placing a tin-bearing material in a closed chamber, producing a vacuum therein, and allowing chlorin gas to expand into such chamber.

In witness whereof, I subscribe my signature, in presence of two witnesses.

HANS VON SCHÜTZ.

Witnesses:
JEAN GRUND,
CARL GRUND.